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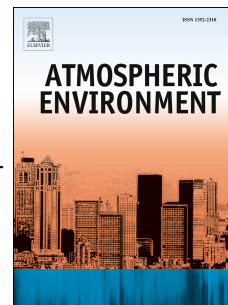
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Spatial and temporal distribution of current-use pesticides in ambient air of Provence-Alpes-Côte-d'Azur Region and Corsica, France

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1 **Spatial and temporal distribution of Current-Use Pesticides in ambient air of Provence-**
2 **Alpes-Côte-d'Azur Region and Corsica, France**

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19

20 Abstract

21 A total of 59 current-use pesticides were monitored in ambient air samples collected from
22 February 2012 to December 2017, at two rural and six urban sites in Provence-Alpes-Côte-
23 d'Azur Region and Corsica, France. 45 of searched active substances were detected at least in
24 one sample, at frequencies ranging from 0.1 to 98.6%. Among the most frequently detected
25 pesticides, we found the herbicide Pendimethalin (64.6%), the fungicide Tebuconazole
26 (65.9%), and the insecticides Chlorpyrifos (71.5%) and Lindane (98.6%). A wide range of
27 atmospheric concentrations was measured from few pg m^{-3} to several hundreds of ng m^{-3} ,
28 with a maximum concentration of 407.79 ng m^{-3} for Chlorpyrifos (Cavaillon, May 2012). 17
29 active substances exceeded an atmospheric concentration of 1 ng m^{-3} for at least one sample,
30 including Folpet (147 times/162 detections), Chlorpyrifos (56/520), and Pendimethalin
31 (29/464). The spatial distribution shows that pesticides were detected both in the eight rural
32 and urban sampling sites, suggesting an atmospheric transport from agricultural areas to
33 cities. Classifying the 8 sampling sites according to samples composition, two types of site
34 were observed, those (Aléria, Arles, Avignon, Port-de-Bouc, and Toulon) where a majority of
35 fungicides are found and those (Cannes, Cavaillon, and Nice) where insecticides are
36 dominant. Long-term (6 years) monitoring shows a seasonally trend for each pesticide,
37 depending on pest pressure. Inter-annual variation suggests a downward trend which is
38 consistent with the regional sales data.

39

40 Keywords

41 Pesticides; Atmosphere; Monitoring; Transport

42

43 Highlights

- 44 • 45 active substances were detected at frequencies ranging from 0.1 to 98.6%.
- 45 • Active substances were detected both in rural and urban sampling sites.
- 46 • The insecticide Chlorpyrifos has reached a concentration exceeding 400 ng m^{-3} .
- 47 • Pesticides can be transported from rural to urban areas at local scale.
- 48 • A downward trend was observed for most pesticides.

49

50

51 **1. Introduction**

52 Ubiquitous in today's farming culture, pesticides are used to protect the crops against weeds
53 (herbicides), fungi (fungicides), or insects (insecticides), and to ensure a regularity in
54 agricultural production necessary for people's diet. Not surprisingly, the current agricultural
55 practice is considered as the main source of atmospheric pesticide pollution (Samsonov et al.,
56 1998; Lichiheb et al., 2015), even if other important sources of pesticide pollution include
57 production, industrial, and urban applications.

58 In 2016, according to the most recent statistics on agriculture, forestry, and fisheries for
59 European Union (Eurostat, 2018), the total quantity of pesticide sales in Europe amounted to
60 close to 360,000 tons with a major use of fungicides and bactericides (44%) and herbicides
61 (32%). Looking at the individual EU Member States, France ranks at the second pesticide
62 consumer, with 20.2% of the total agricultural yield (i.e., around 72,000 tons of active
63 substances). France has a wide variety of agricultural crops (cereals, sugar beets, oleaginous,
64 potatoes, and perennial crops such as vineyards and orchards). With about 27 million hectares
65 of Utilized Agricultural Land (30% of the total surface area), i.e., around 2.7 kilograms of
66 active substances sold per hectare, France is one of the first countries to export foodstuffs
67 (Agreste, 2010).

68 Despite a protective role (mosquito control, allergenic plants, mycotoxins for example), the
69 use of pesticides is currently a real health issue. Several reports highlighted a worrying
70 situation for pesticide exposure in terms of public health (Inserm, 2013) and environmental
71 hazards (EFSA, 2013). Toxicity of pesticides and their health hazards have been the subject of
72 many studies. All these studies demonstrated that pesticides pose adverse health effects, from
73 skin and eye irritation to asthma and bronchial diseases (Canal-Raffin et al., 2007, 2008),
74 decrease of fertility (Al-Thani et al., 2003; Clementi et al., 2008; Petrelli and Mantovani,
75 2002), birth defects and fetal death (Clementi et al., 2007; Redigor et al., 2004), Parkinson
76 disease (Hatcher et al., 2008; Le Couteur et al., 1999), neurotoxicity (Axelrad et al., 2002;
77 Raffaele et al., 2010), and finally to very severe illnesses such as lung, prostate and breast
78 cancer (de Brito Sa Stoppelli and Crestana, 2005; Lee et al., 2006; Van Maele-Fabry and
79 Willems, 2003).

80 On the other hand, the main environmental concern lies in the fact that most pesticides are
81 persistent particularly in the atmosphere (Socorro et al., 2015, 2016; Mattei et al., 2018 and
82 reference therein). Hence, the atmosphere is an important spread vector at local, regional, and
83 global scales. As proof, a wide variety of pesticides was found in the atmosphere, including

84 remote areas where they are not spread (Arctic, Antarctic, mountain peaks, etc.) (Ruggirello et
85 al., 2010).

86 Nevertheless, there is currently no regulatory threshold for the content of pesticides in the
87 atmosphere and no obligation to monitor them. However, atmospheric pesticide
88 contamination was observed in urban and rural areas with concentration levels from some
89 picograms per cubic meter (pg m^{-3}) to several nanograms per cubic meter (ng m^{-3}) (Coscollà
90 et al., 2013, 2014; Estellano et al., 2015; Zivan et al., 2016, 2017). This contamination can be
91 due to spray drift during pesticide applications (about 15 to 40%; Sinfort et al., 2009; Yates et
92 al., 2015; Zivan et al., 2016, 2017), post-application volatilization from treated plants (Zivan
93 et al., 2016, 2017), soil (White et al., 2006), or aquatic surfaces (Luo et al., 2012) (about 0.1
94 to several dozen %; Lichiheb et al., 2015), and wind erosion (Glotfelty et al., 1989).

95 The aim of this work is to establish a diagnostic of pesticides concentrations in the air of two
96 French regions, Provence-Alpes-Côte d'Azur (PACA) and Corsica, in different contexts of
97 sources (non-agricultural and various agricultural sectors: field crops, orchards, vegetable
98 crops, vineyards, etc.). For six years (2012-2017), 59 active substances were monitored in 6
99 urban sites (Arles, Avignon, Cannes, Port-de-Bouc, Nice, and Toulon) and 2 rural sites
100 (Aléria and Cavaillon). The compounds under study were selected based on their regional
101 sales quantity, their toxicity, and their atmospheric lifetime. They included authorized, banned
102 or relatively recent banned classes of herbicides, fungicides, and insecticides (Table 1).
103 Spatial and temporal distributions of detection frequencies and atmospheric concentrations
104 were analyzed according to sampling sites.

105

106 **2. Material and methods**

107 **2.1. Chemicals**

108 Pesticide standards were purchased from Sigma-Aldrich (PESTANAL, analytical standard)
109 and their purity was guaranteed at least 95%. The main physicochemical properties, the
110 agricultural uses and the legal situation of pesticides studies are summarized in Table 1.
111 Acetonitrile (ACN) was purchased from Fisher Scientific (Optima LC/MS Grade, 99.99%).
112 Dichloromethane (DCM) and acetone were purchased from Sigma-Aldrich (Chromasolv for
113 HPLC, $\geq 99.8\%$). The Ultra-High Quality water (UHQ water, $18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C) was
114 obtained from a MilliQ water purification system (Direct 8 MilliQ, Merck Millipore).

115 Triphenyl phosphate (TPP; $\geq 99\%$) and anthracene-d10 ($\geq 98\%$) were used as internal
 116 standards and were purchased from Sigma-Aldrich.

117

118 2.2. Sampling and site characterization

119 A total of 59 active substances were monitored during sampling campaigns (2012-2017),
 120 including 25 herbicides (H), 19 fungicides (F), 14 insecticides (I), and 1 synergist (i.e.,
 121 Piperonyl butoxide (PBO) which will be considered as insecticide thereafter). According to
 122 the octanol-air partition coefficient model (Bidleman and Harner, 2000), the estimated
 123 distribution of the active substances between gas and particulate phases (Table S1) showed a
 124 large distribution among the compounds under study ranging from less than 1% sorbed to
 125 atmospheric particulates (Dimethenamid-P, H) to almost 100% (Fenhexamid, F).

126 Sampling was undertaken at eight sites located throughout the Provence-Alpes-Côte-d'Azur
 127 (PACA) region and Corsica, France (Figure S1). The description of sampling sites and the
 128 sampling periods are summarized in Table 2. All the samplings of the urban sites were
 129 implemented in their city center. As regards the two rural sites, Cavaillon (hamlet of Les
 130 Vignères) is located in an intensive arboriculture area, whereas Aléria (hamlet of Tepepe
 131 Rosse) is located near fields of cereals (corn, barley), vineyards and orchards (clementine).

132 Table 2: Sampling sites description

Sampling site (French department)	Latitude	Longitude	Altitude	Typology	Description ^a	Sampling period	Total sample number
Aléria (Haute-Corse)	42.10218 N	9.47368 E	29 m	Rural	Scrub and/or herbaceous vegetation associations (67%), Complex cultivation patterns (11%), Vineyards (8%)	11 Apr. 2016 04 Oct. 2017	36
Arles (Bouches-du-Rhône)	43.67514 N	4.62923 E	15 m	Urban	Rice fields (45%), Complex cultivation patterns (16%), Non-irrigated arable land (14%), Pastures, meadows, and other permanent grasslands under agricultural use (10%)	13 Feb. 2012 12 Dec. 2013	46
Avignon (Vaucluse)	43.93708 N	4.82496 E	21 m	Urban	Complex cultivation patterns (33%), Vineyards (30%), Fruit trees and berry plantations (14%) Urban fabric (10%)	13 Feb. 2012 15 Dec. 2017	152
Cannes (Alpes-Maritimes)	43.56253 N	7.00672 E	79 m	Urban	Urban fabric (46%), Forests (34%), Scrub and/or herbaceous vegetation associations (10%)	18 Feb. 2012 12 Dec. 2013	35
Cavaillon (Vaucluse)	43.88128 N	5.00611 E	60 m	Rural	Complex cultivation patterns (52%), Fruit trees and berry plantations (18%), Urban fabric (11%)	13 Feb. 2012 15 Dec. 2017	142
Nice	43.70207	7.28539 E	0 m	Urban	Urban fabric (47%), Forests (24%), Scrub and/or	02 Apr. 2014	100

(Alpes-Maritimes)	N				herbaceous vegetation associations (16%)	15 Dec. 2017	
Port-de-Bouc (Bouches-du-Rhône)	43.40195 N	4.98197 E	1 m	Urban	Scrub and/or herbaceous vegetation associations (51%), Urban fabric (27%), Forests (11%)	15 Jan. 2014 15 Dec. 2017	101
Toulon (Var)	43.12681 N	5.92142 E	7 m	Urban	Forests (41%), Urban fabric (25%), Scrub and/or herbaceous vegetation associations (14%), Vineyards (8%), Complex cultivation patterns (8%)	13 Feb. 2012 16 Dec. 2016	114

133 ^a Corine Land Cover nomenclature (zone of 10 km radius around the sampling site)

134

135 The sampling was carried out according to the AFNOR standard XP X43-058 (AFNOR,
136 2007a) using a high-volume sampler (Digitel Aerosol Sampler DHA-80) equipped with a
137 Total Suspended Particulates (TSP) inlet. Samplings were done two meters above ground-
138 level. Particulate and gaseous samples were collected simultaneously on 150 mm diameter
139 ashless quartz microfibre filter (ALBET LabScience) for particulate pesticides followed by a
140 combination of two polyurethane foams (PUF; Tisch Environmental, Inc.) and 20 g of
141 Amberlite XAD-2 resin (Supelco) for gaseous pesticides. Prior to use, filters, PUF, and resin
142 were subject to clean-up by warming at 900°C and with DCM and acetone, respectively. The
143 sampling flow was 10 m³ h⁻¹ for 48 h, giving a total volume of filtered air around 480 m³.

144 A total of approximately 24 samples per site and per year were collected, for a total of 726
145 samples. The sampling frequency was higher during spring and summer (April to September)
146 corresponding to application periods. Once collected, samples were stored and protected from
147 light at -18°C until their analysis.

148 Moreover, in order to estimate the sampling matrixes contamination induced by sample
149 handling and storage, field air blanks were regularly carried out at each site. They consist of
150 filter, PUFs, and resin that were briefly placed in the high-volume sampler then stored and
151 analyzed according to the same protocol than the other samples. No contamination was
152 detected.

153

154 2.3. Sample extraction and analysis

155 According to the AFNOR standard XP X43-058 (AFNOR, 2007b), both particulate (filter)
156 and gaseous (PUF and resin) phases were extracted simultaneously using an accelerated
157 solvent extractor (ASE 350, Dionex). Each sample was introduced in a 99 mL stainless-steel
158 cell with two internal standard solutions of TPP (20 µL; 50 mg L⁻¹) and anthracene-d10 (20

159 μL ; 40 mg L^{-1}). The optimized extraction conditions were as follows: extraction solvent,
160 dichloromethane; temperature, 100°C; pressure, 100 bars; heat up time, 5 min; static time, 6
161 min. The flush volume amounted to 70% of the extraction cell volume. The extracted analytes
162 dissolved in dichloromethane were purged from the sample cell using pressurized nitrogen
163 (100 bars) for 300 s. Four cycles per cell were done.

164 Afterward, the extracts were concentrated under a nitrogen flow using a concentration
165 workstation (TurboVap II, Biotage) with pressure 1.1 bar and a water bath at 40°C, until a
166 500 μL extract was obtained.

167 A first aliquot portion was directly analyzed by gas chromatography coupled to tandem mass
168 spectrometry (GC-MS/MS), with a Trace GC Ultra (Thermo Scientific) coupled to a TSQ
169 Quantum™ Triple Quadrupole (Thermo Scientific) using electron impact ionization (70 eV)
170 according to the following parameters: column THERMO TG-5MS (internal diameter 0.25
171 mm, length 30 m, film thickness 0.25 μm), carrier gas: helium with 1 mL min^{-1} flow rate,
172 split/splitless injector: splitless time of 2 min with surge pressure of 300 kPa during 2 min,
173 injection volume: 1 μL , inlet temperature: 250°C, interface temperature: 330°C, with the
174 following temperature program: hold 3 min at 75°C; increase temperature to 180°C at a rate
175 of 25°C min^{-1} ; increase temperature to 300°C at 5°C min^{-1} ; hold 3 min at 300°C. The
176 characteristic selected ions for pesticides quantification and limits of detection (LOD) are
177 presented in Table S2. Data acquisition and treatments of selected-reaction mass
178 chromatograms were provided by the Xcalibur software (v.2.2, Thermo Scientific).

179 DCM was removed from the second aliquot portion and was replaced by acetonitrile
180 (TurboVap II) prior to an analysis by ultra-performance liquid chromatography (Acquity,
181 Waters) interfaced with a Quadrupole-Time-of-Flight Mass Spectrometer (Synapt G2 HDMS,
182 Waters) (UPLC-MS/MS) equipped with an electrospray ion source (ESI). The mass
183 spectrometer was used in its resolution mode, up to 18 000 FWHM (Full width at half
184 maximum) at 400 Th. The chromatographic separation was carried out on an Acquity UPLC
185 column BEH C18, 1.7 μm particle size, 100 mm \times 2.1 mm i.d. (Waters), at 40°C. The mobile
186 phase consisted in (A) UHQ water + 0.1% formic acid and (B) ACN + 0.1% formic acid. The
187 gradient elution was performed at a flow rate of 0.6 mL min^{-1} using 5% to 80% of B within
188 2.5 min and held at 80% of B for 0.5 min. The injection volume was 7.5 μL . Optimum ESI
189 conditions were found using a -1 kV capillary voltage in negative mode and 0.5 kV in positive
190 mode, 450°C desolvation temperature, 150°C source temperature, 20 L h^{-1} and 1000 L h^{-1}
191 cone gas and desolvation gas flow rate, respectively. Dwell times of 0.20 s scan^{-1} were

192 chosen. For MS/MS experiment, collision gas was Argon 99.995% (Linde) with a pressure of
 193 approximately $1.4 \cdot 10^{-4}$ mbar in the collision cell. The characteristic selected ions for
 194 pesticides quantification, optimum cone voltage, collision energy, and limits of detection
 195 (LOD) are presented in Table S3. Data acquisition and treatments of selected-reaction mass
 196 chromatograms were provided by the MassLynx software (v.4.1, Waters).

197 The extraction and analysis methods have been validated by a national intercomparison
 198 exercise (Marliere, 2015).

199

200 3. Results and discussion

201 3.1. Detection frequencies and atmospheric concentrations

202 The maximum and median concentrations and the frequency of detection of measured
 203 pesticides in the eight sampling sites are summarized in Table 3. The minimum concentration
 204 is below the LOD for each compound, except for Lindane (min. 0.007 ng m^{-3}) and
 205 Chlorpyrifos-methyl (min. 0.180 ng m^{-3}) at Aléria where these pesticides were quantified in
 206 all samples.

207 4 fungicides (Dimethomorph, Fenhexamid, Folpet, and Tebuconazole), 5 herbicides
 208 (Chlorpropham, Diflufenican, Oxadiazon, Pendimethalin, and Propyzamide), and 6
 209 insecticides (Chlorpyrifos, Cypermethrin, Lambda-cyhalothrin, Lindane, Permethrin, and
 210 PBO) were quantified in all sampling sites.

211

212 Table 3. Frequency of detection, maximum, and median concentrations of pesticides in all
 213 sampling sites.

	Aléria			Arles			Avignon			Cannes		
	Detection	Max	Median	Detection	Max	Median	Detection	Max	Median	Detection	Max	Median
	%	ng m^{-3}	ng m^{-3}	%	ng m^{-3}	ng m^{-3}	%	ng m^{-3}	ng m^{-3}	%	ng m^{-3}	ng m^{-3}
Fungicides (19)												
Boscalid	22	0.169	0.012	non-targeted			62	0.303	-	non-targeted		
Cymoxanil	3	0.018	-	0	-	-	3	1.230	-	0	-	-
Cyprodinil	9	0.686	-	9	0.050	-	8	1.103	-	0	-	-
Difenoconazole	9	4.087	-	4	0.074	-	14	0.571	-	0	-	-
Dimethomorph	30	1.226	-	17	0.603	-	30	0.342	-	11	0.091	-
Epoxiconazole	0	-	-	non-targeted			29	0.014	-	non-targeted		
Fenhexamid	9	0.020	-	20	0.042	-	11	0.072	-	14	0.300	-
Fenpropidin	0	-	-	non-targeted			0	-	-	non-targeted		
Fenpropimorph	0	-	-	22	0.037	-	14	0.153	-	0	-	-
Fluazinam	0	-	-	non-targeted			0	-	-	non-targeted		
Flusilazole	6	0.338	-	4	0.007	-	1	0.051	-	0	-	-
Folpet	14	26.435	-	48	16.705	-	29	24.001	-	9	2.481	-

Iprodione	6	0.504	-	non-targeted			10	0.737	-	non-targeted		
Kresoxim-methyl	12	0.063	-	22	0.074	-	23	0.177	-	0	-	-
Pyrimethanil	3	0.030	-	13	0.024	-	22	0.212	-	3	0.004	-
Spiroxamine	22	0.692	-	non-targeted			10	1.304	-	non-targeted		
Tebuconazole	53	0.782	0.005	87	0.290	0.014	78	0.284	0.013	71	0.038	0.003
Tetraconazole	0	-	-	48	0.037	-	25	0.048	-	9	0.002	-
Tolylfluanid	0	-	-	non-targeted			7	0.049	-	non-targeted		
Herbicides (25)												
2,4D	0	-	-	4	0.320	-	5	2.690	-	0	-	-
2,4MCPA	0	-	-	2	0.160	-	1	0.270	-	6	0.080	-
Aclonifen	0	-	-	0	-	-	0	-	-	0	-	-
Amitrole	0	-	-	0	-	-	0	-	-	0	-	-
Chlorpropham	11	0.046	-	59	0.072	0.010	19	0.159	-	51	0.052	0.008
Clomazone	0	-	-	non-targeted			0	-	-	non-targeted		
Diclofop-methyl	0	-	-	7	0.004	-	3	0.004	-	3	0.001	-
Diiflufenican	14	0.051	-	37	0.036	-	40	0.080	-	43	0.011	-
Dimethenamid-P	0	-	-	non-targeted			0	-	-	non-targeted		
Flazasulfuron	0	-	-	0	-	-	0	-	-	0	-	-
Flumioxazin	0	-	-	non-targeted			0	-	-	non-targeted		
Flurochloridone	0	-	-	15	0.016	-	11	0.013	-	0	-	-
Fluroxypyr	0	-	-	0	-	-	0	-	-	0	-	-
Isoproturon	0	-	-	non-targeted			0	-	-	non-targeted		
Lenacil	0	-	-	non-targeted			0	-	-	non-targeted		
Linuron	0	-	-	0	-	-	0	-	-	0	-	-
Metazachlor	0	-	-	15	0.039	-	15	0.113	-	0	-	-
S-Metolachlor	42	1.206	-	non-targeted			28	0.195	-	non-targeted		
Oxadiazon	9	0.143	-	50	0.461	0.002	17	0.105	-	54	0.715	0.011
Pendimethalin	6	0.065	-	93	0.527	0.030	84	2.300	0.036	69	0.061	0.005
Propyzamide	28	0.075	-	74	0.200	0.017	32	0.083	-	11	0.065	-
Prosulfocarb	0	-	-	24	0.881	-	20	0.385	-	0	-	-
Sulcotrione	0	-	-	0	-	-	0	-	-	0	-	-
Terbuthylazine	0	-	-	0	-	-	0	-	-	0	-	-
Triallate	0	-	-	non-targeted			43	0.159	-	non-targeted		
Insecticides (15)												
Chlorpyrifos	53	0.899	0.013	93	1.542	0.124	78	1.927	0.039	83	0.120	0.019
Chlorpyrifos-methyl	100	2.922	0.810	non-targeted			50	1.143	0.014	non-targeted		
Cypermethrin	6	0.085	-	17	0.083	-	22	0.197	-	9	0.056	-
Deltamethrin	0	-	-	0	-	-	3	0.407	-	0	-	-
Diiflubenuron	0	-	-	0	-	-	1	0.440	-	0	-	-
Esbiothrin	0	-	-	0	-	-	0	-	-	0	-	-
Fenoxycarb	0	-	-	28	0.201	-	12	0.334	-	54	0.160	0.007
Fipronil	0	-	-	17	0.010	-	6	0.067	-	20	0.038	-
Imidacloprid	0	-	-	2	7.300	-	1	3.300	-	0	-	-
Lambda-cyhalothrin	9	0.336	-	9	0.050	-	3	0.080	-	11	0.038	-
Lindane	100	0.108	0.031	98	0.620	0.190	99	1.066	0.078	97	0.586	0.112
Permethrin	9	0.243	-	7	0.465	-	5	0.424	-	44	0.608	-
Piperonyl butoxide (PBO)	17	0.061	-	70	0.343	0.028	53	0.251	0.006	60	0.304	0.013
Pirimicarb	0	-	-	0	-	-	0	-	-	0	-	-
Thiamethoxam	0	-	-	non-targeted			0	-	-	non-targeted		

214

	Cavaillon			Nice			Port-de-Bouc			Toulon		
	Detection	Max	Median	Detection	Max	Median	Detection	Max	Median	Detection	Max	Median
	%	ng m ⁻³	ng m ⁻³	%	ng m ⁻³	ng m ⁻³	%	ng m ⁻³	ng m ⁻³	%	ng m ⁻³	ng m ⁻³
Fungicides (19)												
Boscalid	57	0.297	-	23	0.048	-	42	0.169	-	34	0.154	-
Cymoxanil	4	1.500	-	0	-	-	0	-	-	0	-	-
Cyprodinil	6	0.855	-	9	0.446	-	5	1.243	-	0	-	-

Difenoconazole	27	3.876	-	5	0.234	-	10	8.478	-	3	0.066	-
Dimethomorph	32	0.747	-	12	0.053	-	21	0.150	-	18	0.179	-
Epoxiconazole	7	0.011	-	0	-	-	0	-	-	non-targeted		
Fenhexamid	15	0.056	-	4	0.020	-	6	0.021	-	2	0.008	-
Fenpropidin	0	-	-	0	-	-	0	-	-	non-targeted		
Fenpropimorph	10	0.030	-	0	-	-	4	0.052	-	4	0.006	-
Fluazinam	7	0.102	-	0	-	-	0	-	-	non-targeted		
Flusilazole	1	0.006	-	1	0.016	-	4	0.096	-	2	0.004	-
Folpet	34	24.593	-	3	2.530	-	13	26.869	-	20	31.410	-
Iprodione	5	1.233	-	3	0.225	-	5	0.701	-	0	-	-
Kresoxim-methyl	25	0.141	-	2	0.019	-	18	0.089	-	7	0.051	-
Pyrimethanil	77	5.580	0.061	0	-	-	10	0.169	-	1	0.013	-
Spiroxamine	18	1.357	-	3	0.088	-	4	0.101	-	6	0.129	-
Tebuconazole	75	1.647	0.014	35	0.031	-	53	0.301	0.004	62	0.186	0.005
Tetraconazole	56	1.209	0.004	7	0.158	-	12	0.031	-	12	0.023	-
Tolylfluanid	0	-	-	64	0.246	0.056	8	0.032	-	non-targeted		
Herbicides (25)												
2,4D	4	0.470	-	0	-	-	0	-	-	3	0.180	-
2,4MCPA	1	0.490	-	0	-	-	0	-	-	3	0.540	-
Aclonifen	0	-	-	0	-	-	0	-	-	0	-	-
Amitrole	0	-	-	0	-	-	0	-	-	0	-	-
Chlorpropham	36	0.048	-	25	0.086	-	12	0.053	-	26	0.068	-
Clomazone	0	-	-	0	-	-	0	-	-	non-targeted		
Diclofop-methyl	4	0.010	-	2	0.015	-	0	-	-	4	0.004	-
Diflufenican	30	0.020	-	5	0.011	-	23	0.051	-	29	0.040	-
Dimethenamid-P	0	-	-	0	-	-	0	-	-	non-targeted		
Flazasulfuron	0	-	-	0	-	-	0	-	-	0	-	-
Flumioxazin	0	-	-	0	-	-	0	-	-	0	-	-
Flurochloridone	13	0.006	-	1	0.010	-	6	0.050	-	2	0.002	-
Fluroxypyr	1	0.570	-	0	-	-	0	-	-	0	-	-
Isoproturon	0	-	-	0	-	-	0	-	-	0	-	-
Lenacil	0	-	-	0	-	-	0	-	-	non-targeted		
Linuron	0	-	-	0	-	-	0	-	-	0	-	-
Metazachlor	25	0.125	-	17	0.069	-	18	0.061	-	0	-	-
S-Metolachlor	59	0.591	-	0	-	-	21	0.097	-	1	0.030	-
Oxadiazon	22	0.217	-	3	0.297	-	11	0.141	-	18	0.223	-
Pendimethalin	99	13.350	0.180	17	0.158	-	68	0.785	0.013	46	0.189	-
Propyzamide	39	0.132	-	7	0.056	-	14	0.036	-	11	0.439	-
Prosulfocarb	21	0.519	-	1	0.050	-	12	0.692	-	2	0.058	-
Sulcotrione	0	-	-	0	-	-	0	-	-	0	-	-
Terbuthylazine	0	-	-	0	-	-	0	-	-	0	-	-
Triallate	43	0.164	-	14	0.011	-	38	0.181	-	non-targeted		
Insecticides (15)												
Chlorpyrifos	89	407.790	0.171	59	0.066	0.013	47	0.175	-	68	0.269	0.017
Chlorpyrifos-methyl	57	0.372	-	36	0.036	-	23	0.118	-	non-targeted		
Cypermethrin	12	0.134	-	47	0.195	-	6	0.051	-	33	0.237	-
Deltamethrin	4	0.158	-	3	0.353	-	0	-	-	0	-	-
Diflubenzuron	0	-	-	0	-	-	0	-	-	1	0.420	-
Esbiothrin	0	-	-	0	-	-	0	-	-	0	-	-
Fenoxycarb	28	0.590	-	10	0.316	-	2	0.132	-	20	0.223	-
Fipronil	21	0.085	-	5	0.113	-	0	-	-	24	0.102	-
Imidacloprid	1	7.300	-	0	-	-	0	-	-	1	7.300	-
Lambda-cyhalothrin	6	0.158	-	3	0.165	-	4	0.460	-	2	0.017	-
Lindane	99	3.005	0.078	98	0.170	0.045	99	0.175	0.038	98	1.359	0.121
Permethrin	13	0.437	-	55	0.808	0.048	11	0.351	-	22	0.393	-
Piperonyl butoxide (PBO)	37	0.280	-	80	0.300	0.025	39	0.189	-	63	0.663	0.011
Pirimicarb	9	0.346	-	0	-	-	3	0.031	-	0	-	-
Thiamethoxam	0	-	-	0	-	-	0	-	-	0	-	-

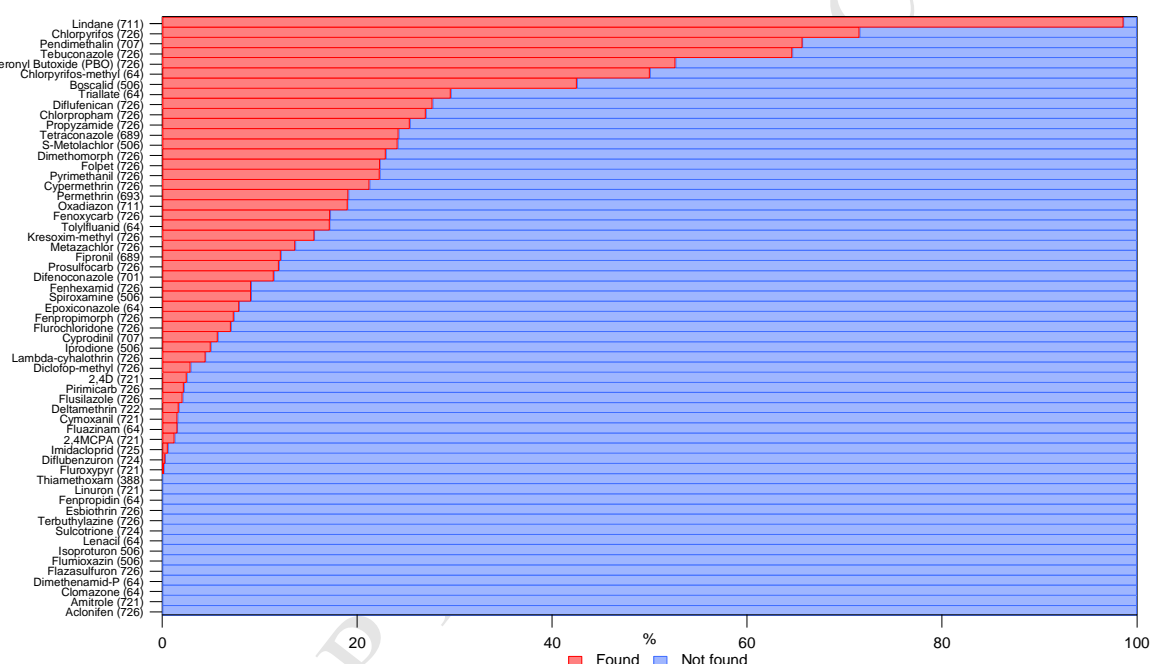
215 (-) means < Limit of Detection

216

217 *Detection frequencies*

218 Figure 1 presents the detection frequency of the 59 active substances. The number in brackets
 219 refers to the total samples where the active substance was searched. This number of samples
 220 differ from a compound to another either because of sampling or analytical problems or
 221 because of the inclusion of the active substance during the period under study (e.g.,
 222 Thiamethoxam was sampled for the first time in 2015).

223



224

225 Figure 1. Detection frequency of the 59 active substances. 'Found' is based on samples with
 226 concentrations above the limit of detection, and the number in brackets refers to total samples
 227 where the active substance was searched.

228

229 45 active substances (i.e., 76.3% of searched compounds) were detected in the PACA and
 230 Corsica atmosphere at least in one sample, at frequencies ranging from 0.1 to 98.6%. The
 231 detection frequency is equal or exceeds 50% for 6 active substances (i.e., 10.2% of searched
 232 compounds): Chlorpyrifos-methyl (I, 50.0%), PBO (I, 52.6%), Tebuconazole (F, 64.6%),
 233 Pendimethalin (H, 65.7%), Chlorpyrifos (I, 71.5%), and Lindane (I, 98.6%).

234 Among the 14 active substances (i.e., 23.7% of searched compounds) which have never been
235 detected, there are 1 fungicide (Fenpropidin), 2 insecticides (Esbiothrin and Thiamethoxam),
236 and 11 herbicides (Aclonifen, Amitrole, Clomazone, Dimethenamid-P, Flazasulfuron,
237 Flumioxazin, Isoproturon, Lenacil, Linuron, Sulcotrione, and Terbutylazine). In France,
238 even though they were authorized during the sampling period, some of them were subject to
239 restrictive derogation. Thiamethoxam was only used for ornamental crops because of their
240 potential responsibility in the mortality of pollinating insects (Tsvetkov et al., 2017).
241 Terbutylazine was only used for corn because of their genotoxic effects such as DNA
242 damage (Lovakovic et al., 2017). On the other hand, Esbiothrin was only used as a biocide
243 against household pest insects, making its ambient air detection more unlikely.

244 *Fungicides*: The most frequently detected fungicide was Tebuconazole (64.6%). It is used to
245 treat the upper parts of plants and have a broad range of applications against fungi such as
246 oïdium, rusts, septoria, scab, black-rot... (Index Acta Phytosanitaire, 2018). Although
247 Tebuconazole has already been detected in 9 out of 10 samples in the urban atmosphere of
248 Strasbourg, France (2007; Schummer et al., 2010), recent studies in Ile-de-France region,
249 France (2013-2014; Airparif, 2016) and in Valencia region, Spain (2008-2014; Coscollà et al.,
250 2013; Yusà et al., 2014; López et al., 2017) report detection frequencies lower than 20%. Five
251 other fungicides were detected with a detection frequency ranging from 20 to 25%, i.e.,
252 Pyrimethanil (22.3%), Folpet (22.3%), Dimethomorph (22.9%), Tetraconazole (23.0%), and
253 Boscalid (29.6%). These fungicides are also used to treat the upper parts of plants but have
254 more targeted actions than Tebuconazole against dead arm disease (Folpet), mildew
255 (Dimetomorph, Folpet), oïdium (Boscalid, Tetraconazole), scab (Boscalid, Pyrimethanil), or
256 botrytis (Boscalid, Pyrimethanil) (Index Acta Phytosanitaire, 2018).

257 It should be noted that Flusilazole (2.1%) was banned since 2013 and that its detections were
258 all made during 2012. Tolyfluanid (17.2%) was banned for agricultural uses but was
259 authorized as antifouling agent biocide. Therefore, it is not unusual to find it from sampling
260 sites close to ports (mainly Nice).

261 *Herbicides*: Of the 14 herbicides detected, four have a detection frequency higher than 20%
262 namely Pendimethalin (65.7%), Diflufenican (27.7%), Chlorpropham (27.0%), and
263 Propyzamide (25.4%). Pendimethalin is a selective dinitroaniline herbicide used in pre- and
264 post-emergence applications to control certain broadleaf weeds and most annual grasses
265 (Koblizkova et al., 2012). Table 1 reports its broad range of applications which, combined to
266 its relatively high volatility ($> 10^{-3}$ Pa) and its atmospheric half-life (Socorro et al., 2015,

267 2016; Mattei et al., 2018), might explain its highest detection frequency. Similar detection
268 frequencies ranging from 33 to 100% were reported for Pendimethalin, in various region in
269 France: Ile-de-France region (2013-2014; Airparif, 2016), Centre region (2006-2013;
270 Coscollà et al., 2017), Nouvelle-Aquitaine region (2007-2015; Atmo Nouvelle-Aquitaine,
271 2017), Grand Est region (2007; Schummer et al., 2010; 2012-2015; Villiot et al., 2018). In
272 Tuscany region (Italy), Pendimethalin was less frequently detected (25%) but sampling was
273 made using polyurethane foam disks as passive air samplers which do not take into account
274 the particulate phase (2008-2009; Estellano et al., 2015).

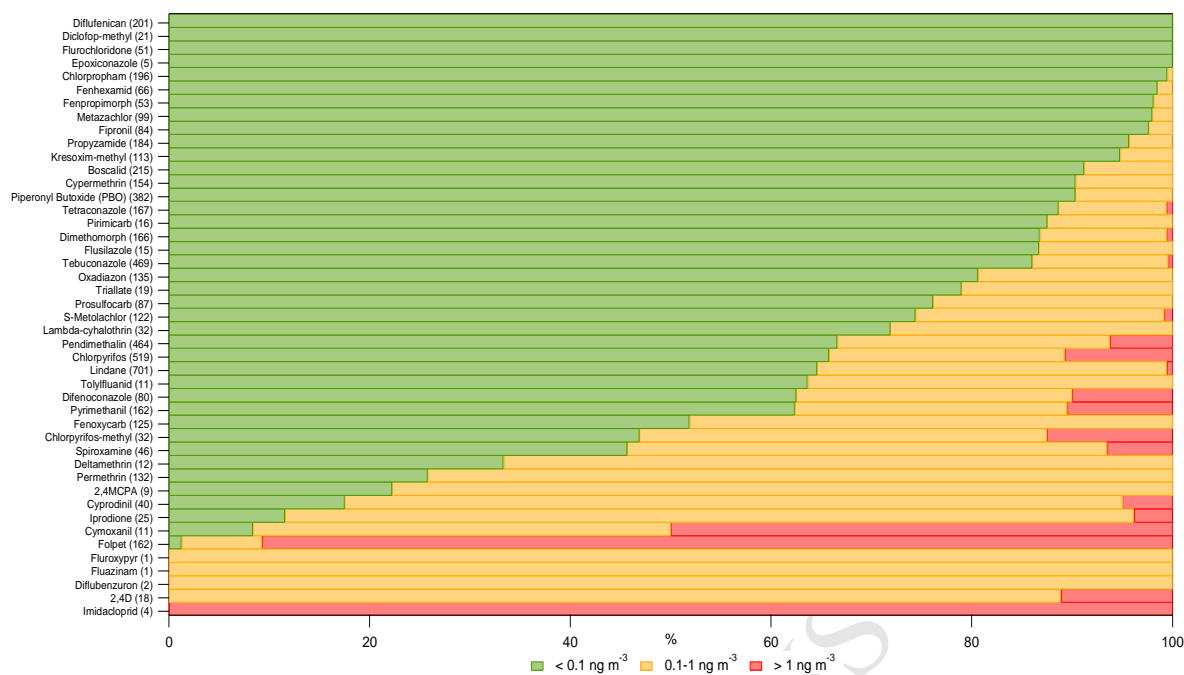
275 The detection frequencies of Diflufenican (non-detected) and Propyzamide (4%) in Ile-de-
276 France region (2013-2014; Airparif, 2016) were much lower than those found in PACA and
277 Corsica, except for Nice. According to the sales data for areas under study (BNVD, 2017),
278 Diflufenican was sold for rapeseed crop areas but also non-cropped areas while Propyzamide
279 was sold for a wide range of uses, such as seed crops, vineyards, orchards, rapeseed, and
280 ornamental crops. The difference could be due to the LOD, lower in this study. In the same
281 way, Chlorpropham, used for potatoes, was detected in a lower frequency (5%) in the
282 Valencia region (2008-2014; López et al., 2017).

283 *Insecticides*: 13 insecticides were detected including four above 50% of detection:
284 Chlorpyrifos-methyl (50.0%), PBO (52.6%), Chlorpyrifos (71.5%), and Lindane (98.6%).
285 PBO is a synergist widely used with insecticides as pyrethroids and carbamates. It was rarely
286 monitored in the ambient atmosphere but its wide presence in samples implies the presence of
287 other active substances. Field of uses of Chlorpyrifos and Chlorpyrifos-methyl currently
288 concerns vineyards and orchards (Index Acta Phytosanitaire, 2018), both agricultural areas
289 broadly represented around most of the sampling sites.

290 Despite its ban since 1998 for agricultural uses and 2007 for biocidal treatments, Lindane is
291 the most frequently detected active substance. Classified as a persistent organic pollutant
292 (UNEP, 2001), its persistence in the environment could explain its highest detection
293 frequency.

294 *Atmospheric concentrations*

295 With respect to atmospheric concentrations, it is still difficult to classify them because there is
296 no regulatory threshold. However, 3 categories of atmospheric concentrations such as, below
297 0.1 ng m^{-3} , between 0.1 and 1 ng m^{-3} , and above 1 ng m^{-3} , allow a distribution of detected
298 active substances, with 74.4%, 20.5%, and 5.1% of samples, respectively (Figure 2).



299

300 Figure 2. Distribution of the active substances between concentration below 0.1 ng m^{-3} ,
 301 between 0.1 and 1 ng m^{-3} . The number in brackets refers to total samples where the active
 302 substance was quantified.

303

304 Only four active substances never exceeded the 0.1 ng m^{-3} threshold, i.e., Diclofop-methyl
 305 (H), Diflufenican (H), Flurochloridone (H), and Epoxiconazole (F). These results are
 306 consistent with measurements carried out in the Centre region, France (2006-2013; Coscollà
 307 et al., 2017), Ile-de-France region, France (2013-2014; Airparif, 2016), Grand Est region,
 308 France (2007; Schummer et al., 2010), and Québec, Canada (2004; Aulagnier et al., 2008).
 309 Nevertheless, in this literature, exceptions with concentrations higher than 1 ng.m^{-3} are
 310 observed on a few samples, i.e., Diflufenican until 2.25 ng m^{-3} (Ineris, 2008) and
 311 Epoxiconazole until 3.99 ng m^{-3} (Coscollà et al., 2017).

312 17 active substances exceeded an atmospheric concentration of 1 ng m^{-3} for at least one
 313 sample. The most frequently detected at this concentration level were Imidacloprid (I, 4
 314 times/4 detections), Folpet (F, 147/162), Chlorpyrifos (I, 56/520), and Pendimethalin (H,
 315 29/464).

316 Imidacloprid was always detected at atmospheric concentrations higher than 1 ng m^{-3} . Only
 317 one pesticide was always detected at atmospheric concentrations above 1 ng m^{-3} . Indeed, on 2
 318 July 2012, it was simultaneously detected at concentrations ranging from 3.3 to 7.3 ng m^{-3} in
 319 Arles, Avignon, Cavaillon, and Toulon. Imidacloprid is a neonicotinoid insecticide like

320 Thiamethoxam which may induce substantial bee mortality (Zhu et al., 2017). Hence, there is
321 a limitation of its use and a mandatory program to control the red palm weevil was put in
322 place in summer 2012 in Toulon (JORF, 2012). The calculated trajectories (NOAA
323 HYSPLYT model) show the surrounding air mass from Toulon to Arles, Avignon, and
324 Cavaillon (Figure S2), which could explain the detection of Imidacloprid at several tens of
325 kilometers away, suggesting a transport at a regional scale.

326 Folpet (max. 31.41 ng m⁻³) is a broad-spectrum fungicide generally used on vineyards (Index
327 Acta Phytosanitaire, 2018). Its atmospheric monitoring has already regularly shown
328 concentrations above 1 ng m⁻³ in British Columbia, Canada (2004-2006; Raina et al., 2009)
329 and in many French regions (2006-2013; Schummer et al., 2010; Coscollà et al., 2017)
330 reaching the highest concentration at 3,950 ng m⁻³ in Grand Est region (2005; Marliere, 2009).

331 French monitoring reported the presence of Pendimethalin (max. 13.35 ng m⁻³) at high
332 concentrations ranged from 0.32 to 7.83 ng m⁻³ in Grand Est region (Schummer et al., 2010;
333 Villiot et al., 2018) and from 0.13 to 117.32 ng m⁻³ in Centre region (Coscollà et al., 2017).
334 These maximum atmospheric concentrations were significantly higher than those measured in
335 other countries, such as in Canada (max. 140 pg m⁻³; Gouin et al., 2008) or Australia (max.
336 200 pg m⁻³; Koblizkova et al., 2012).

337 Chlorpyrifos (max. 407.79 ng m⁻³) is one of the most searched pesticides in the atmosphere.
338 Surveys performed in France (range from 0.01 to 956.30 ng m⁻³; Marliere, 2009; Airparif,
339 2016; Coscollà et al., 2017; Villiot et al., 2018), in Italy (range from 3 to 580 pg m⁻³;
340 Estellano et al., 2015), in Spain (range from 1 to 210 pg m⁻³; Yusà et al., 2014), in Czech
341 Republic (max. 360 pg m⁻³; Koblizkova et al., 2012), in Canada (range from 7 to 868 pg m⁻³;
342 Yao et al., 2006; Aulagnier et al., 2008; Gouin et al., 2008; Hayward et al., 2010), in USA
343 (max. 2.9 ng m⁻³; Peck and Hornbuckle, 2005; Rudel et al., 2010), in Japan (max. 51 ng m⁻³;
344 Kawahara et al., 2005), and in China (range from 0.072 to 2.901 ng m⁻³; Li et al., 2014), have
345 shown variable concentrations but often associated with a high detection frequency (as in this
346 study).

347

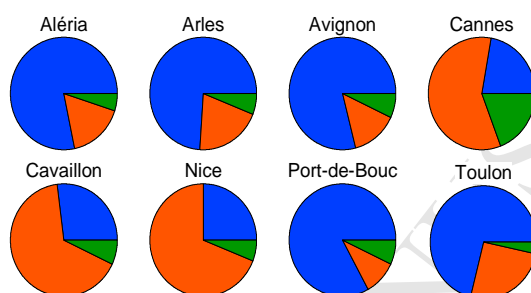
348 **3.2. Spatial distribution of pesticides**

349 Each sampling site has a specific typology (rural or urban) and is characterized by its
350 environment, in particular by the surrounding crops (Table 2). However, none of the 8
351 sampling sites seem to be impacted by only one type of crop, since, in South of France,

352 agricultural practices associate generally several crops. The spatial distribution shows how
 353 important the use of some pesticide families (and sometimes some active substances) is at
 354 each sampling sites. The distribution between urban and rural typologies for individual active
 355 substance highlights the atmospheric transport phenomenon at local and regional scales.

356 *Pesticide family distribution by sampling sites*

357 Figure 3 represents the distribution of pesticide family, i.e., herbicide, fungicide, and
 358 insecticide, for each sampling site. The percentage is determined from the sum of the
 359 atmospheric concentrations of each pesticide family during the 6-years sampling.



360
 361 Figure 3. Geographical distribution – sum of atmospheric concentrations by sampling sites.
 362 Fungicide = blue, Insecticide = orange, Herbicide = green.

363
 364 In view of atmospheric concentrations, two trends of pesticide distribution emerge 1/ a
 365 majority of fungicides, like Aléria, Arles, Avignon, Port-de-Bouc, and Toulon, and 2/ a
 366 majority of insecticides, like Cannes, Cavaillon, and Nice. On the eight sites, the herbicides
 367 contribution was negligible or at least minority (Cannes, 19%) although the herbicides family
 368 was the most represented in the searched pesticide list (25 out of 59 pesticides).

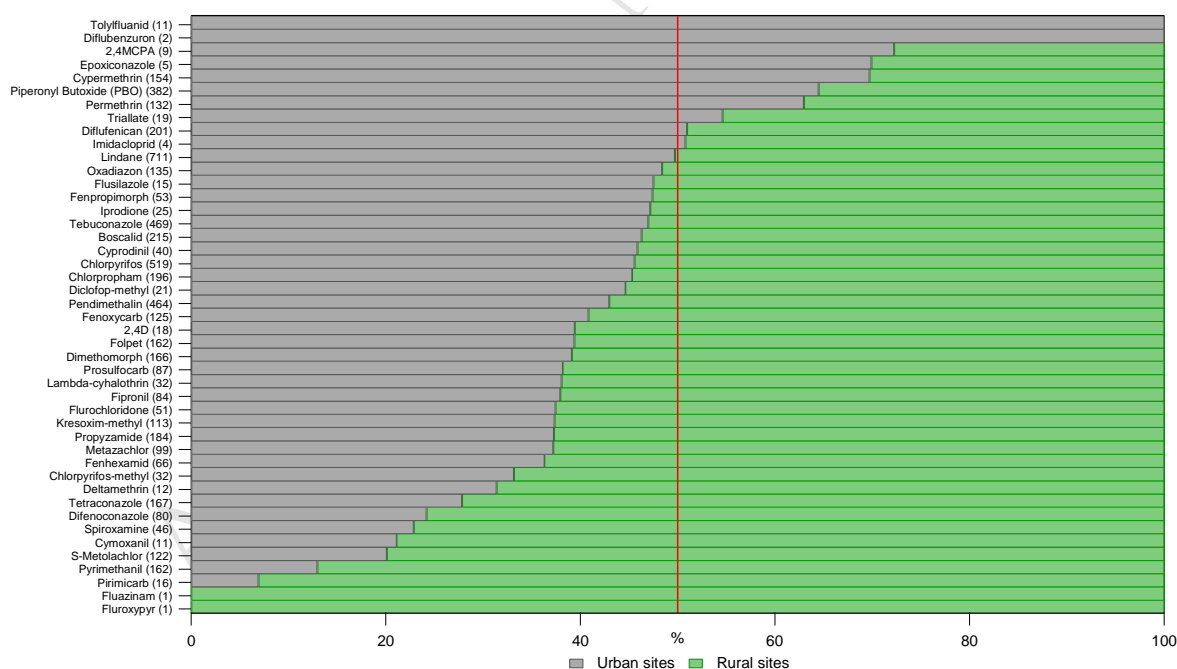
369 Although it was not detected in 2016, Folpet was the most concentrated active substance in
 370 the five sampling sites where fungicides were predominant. In France, it is one of the most
 371 widely used fungicides in vineyards (De Lozzo, 2015) with around 360 tons sold (2012-2016)
 372 for the sampling areas (BNVD, 2017). Moreover, within a radius of 10 km around the
 373 sampling sites (Table 2), Avignon has the highest land-use rate by vineyards (30%). Folpet
 374 can also be used to cure the cancerous disease (*Crumenulopsis* mainly) of some
 375 Mediterranean forests (Morelet et al., 1987). The development of this fungus favored by a
 376 higher rainfall was identified during the measurement campaign close to the three other
 377 sampling sites in PACA (DRAAF PACA, 2015).

378 With regard to insecticides, samples of Cannes and Nice were mainly composed by Lindane,
 379 Permethrin, and PBO (synergist widely used with pyrethroids and carbamates). Within a
 380 radius of 10 km, the urban fabric is the most important for Cannes (46%) and Nice (47%).
 381 More, both cities have adopted a ‘zero pesticide’ policy for the maintenance of green spaces
 382 and roads. The ban on agricultural uses of Permethrin suggests therefore individual biocidal
 383 uses. From Cavaillon, Chlorpyrifos was the insecticide the most concentrated (Maximum:
 384 407.79 ng m⁻³) which is consistent with the presence of apple, pear, and cherry orchards.

385 The largest contributions of herbicides were also at Cannes (Oxadiazon (mainly quantified in
 386 2012), Pendimethalin, Chlorpropham, and Diflufenican). Except for Diflufenican which is
 387 only used for cereals, all other active substances can be used for ornamental and flower crops
 388 (Index Acta Phytosanitaire, 2018) as logical as Alpes-Maritimes (Cannes) is the most
 389 important area for horticulture and the production of cut flowers (France AgriMer, 2013).

390 *Pesticide distribution by typology: rural vs. urban*

391 Figure 4 shows the distribution of active substances between urban and rural sampling sites.
 392 The number of detections is weighted by the number of samples collected on each site
 393 typology (urban and rural).



394
 395 Figure 4. Typological distribution of active substances between urban (grey) and rural (green)
 396 sites. The number in brackets refers to total samples where the active substance was detected.

397

398 Of the 45 active substances detected, 41 compounds were detected both in urban and rural
399 sites. Tolyfluanid (F) and Diflubenzuron (I) were detected only in urban sites, while
400 Fluazinam (July 2017) and Fluroxypyr (May 2012) were found only once in the rural site of
401 Cavaillon.

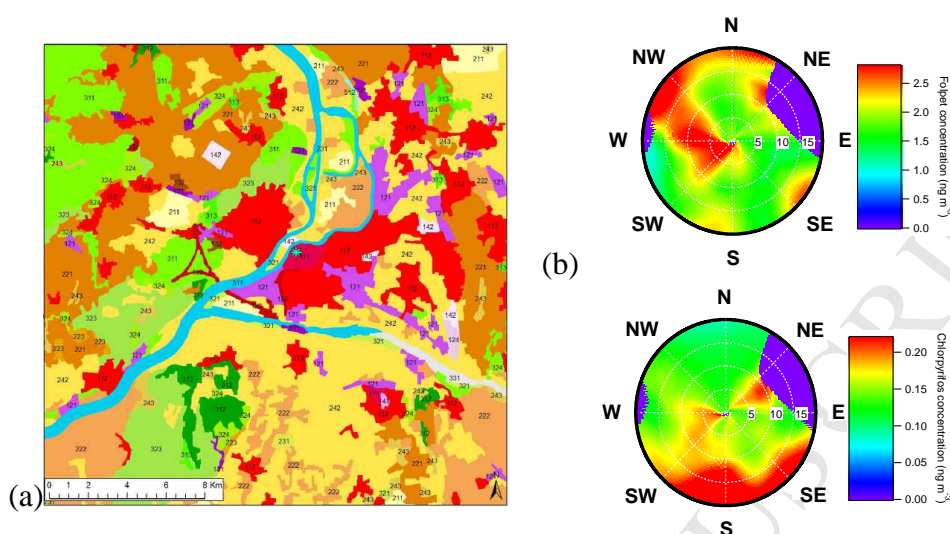
402 Compounds the most frequently detected in urban sites, such as Tolyfluanid (Product-Type
403 (PT) 7: Film preservatives, PT 8: Wood preservatives, PT 21: Antifouling products),
404 Diflubenzuron (PT 18: Insecticides, acaricides and products to control other arthropods),
405 Cypermethrin (PT 8, PT 18), PBO (PT 18), Permethrin (PT 8, PT 18), Imidacloprid (PT 18),
406 Fenpropimorph (PT 8), and Tebuconazole (PT 7, PT 8, PT 10: Masonry preservatives), were
407 authorized as biocide (Index Acta Phytosanitaire, 2018), suggesting wider urban uses than
408 rural uses.

409 Moreover, according to the sales data for studied areas (BNVD, 2017), Diflubenzuron
410 (flowers, green plants), 2,4MCPA (grass weedkiller), and Diflufenican (urban weed control)
411 are also used in the urban sites. In contrast, Epoxiconazole (cereals, beet) and Triallate
412 (oleaginous, beet) have only agricultural uses, and their presence in urban samples suggests an
413 atmospheric transport from rural to urban areas.

414 Overall, active substances were generally more frequently found in rural sites (35 active
415 substances over 45 detected). However, many compounds showed similar patterns and
416 atmospheric concentrations on both site typologies (rural and urban) suggesting their
417 important use even on urban sites.

418 Nevertheless, according to both the atmospheric persistence of the active substances and the
419 small distances between agricultural areas and cities, pesticides can undergo atmospheric
420 transport at the local and regional scale which contribute to explain their presence in urban
421 sites. To test this hypothesis, wind speed and direction have to be considered. As an example,
422 at the urban sampling site of Avignon, a very good fit is observed between the pollution roses
423 of Folpet and Chlorpyrifos (Figure 5.b) and their spreading areas (Figure 5.a). According to
424 the pollution rose, Folpet comes mainly from the North-West of Avignon with some
425 additional sources coming from the North-North-East, South-East, and south while
426 Chlorpyrifos comes from South-West, South, South-East, and for a small part from North-
427 East. Folpet is a fungicide mainly used on vineyards (code 221; Figure 5.a) and Chlorpyrifos
428 is an insecticide characteristic of orchards (code 222; Figure 5.a). When wind direction and
429 speed are appropriate, Folpet and Chlorpyrifos spread on these specific crops areas are
430 observed at the Avignon sampling site, suggesting a local scale atmospheric transport up to

431 Avignon. Moreover, back-trajectories calculated using the NOAA HYSPLYT model, suggest
 432 an atmospheric transport of Imidacloprid from Toulon to Arles, Avignon, and Cavaillon
 433 (Figure S2).



434 Figure 5. Geographical origin analysis of Folpet (top) and Chlorpyrifos (down) in Avignon
 435 urban sampling site: (a) zone of 10 km radius around the urban sampling site of Avignon
 436 (Corine Land Cover nomenclature: 11X/12X-Urban fabric, 21X-Arable land, 221-Vineyards,
 437 222-Fruit trees and berry plantations, 223-Olive groves, 24X-Heterogeneous agricultural
 438 areas, 31X-Forests, 32X-Scrub and/or herbaceous vegetation associations) and (b) ZeFir
 439 model (v. 3.60, Petit et al., 2017).

440

441 3.3. Temporal distribution of pesticides

442 The atmospheric contamination level by pesticides can be described from a temporal
 443 viewpoint for each detected active substance. Therefore, based on a sampling dataset of 6-
 444 years, a bunch of statistical distributions of the data can be calculated for monthly and yearly
 445 patterns. Ideally, the temporal distributions should be represented either by types of crops or
 446 sampling site typologies (urban or rural). However, it is difficult to consider a sampling area
 447 as wholly owned by one type of crop, since several crop types are generally associated (Table
 448 2). Moreover, for pesticides having too low detection frequencies, it is impossible to realize
 449 monthly profiles.

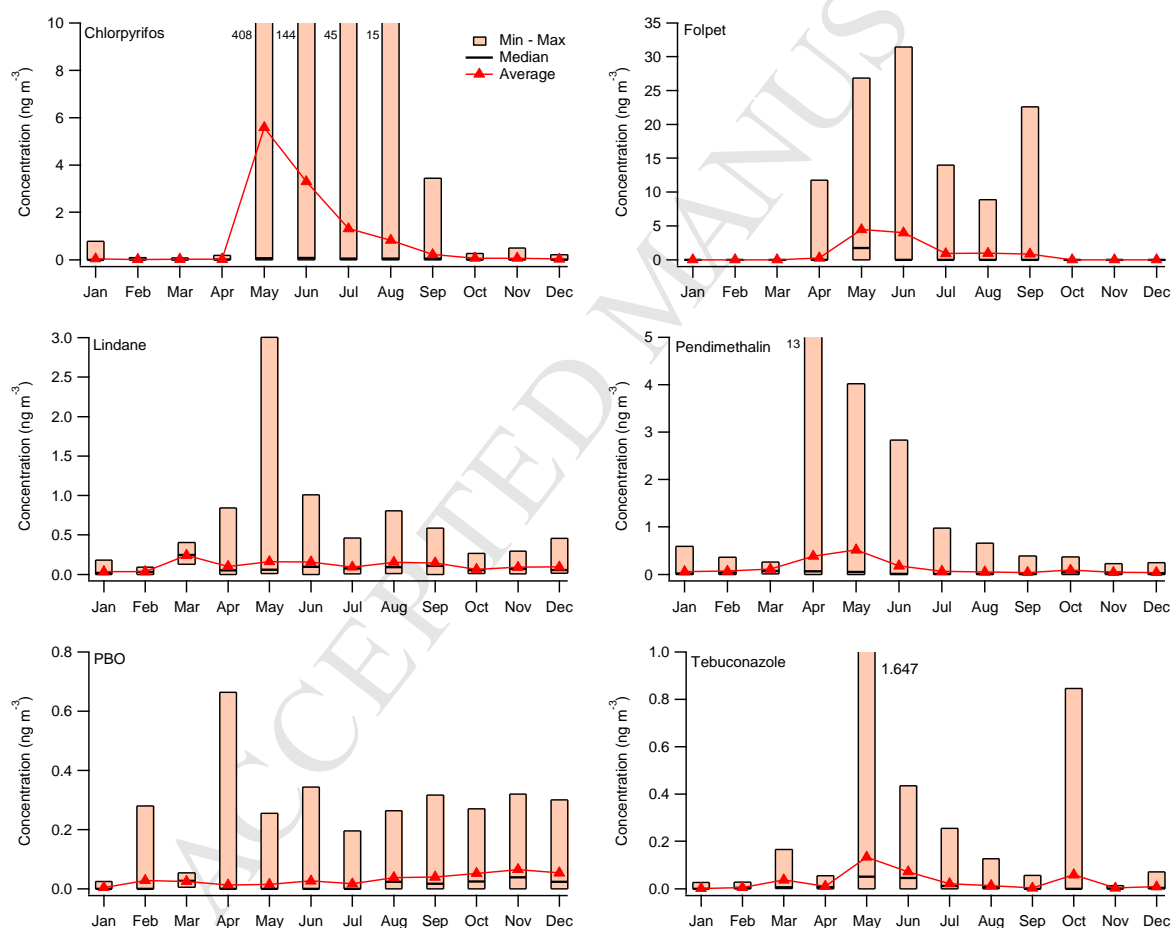
450 Therefore, the monthly distributions were described considering all sampling sites (i.e., for all
 451 types of crops) while the yearly distributions depicted each sampling site. Both monthly
 452 (Figure 6) and yearly (Figure 7) distributions were only presented for the six active substances

453 the most representative in terms of detection frequency and atmospheric concentration, i.e.,
 454 Chlorpyrifos (I), Folpet (F), Lindane (I), Pendimethalin (H), PBO (I), and Tebuconazole (F).

455 *Monthly distribution for all sampling sites*

456 The monthly distribution provides information on seasonal applications of the active
 457 substances. Because of a lack of information about the farming practices (applied amounts
 458 and nature of commercial formulations, dates of treatment, application equipment) at each
 459 sampling area, these detection periods were not always easily correlated with their uses.
 460 However, this detection timeline highlights the period(s) of population exposure and will be
 461 used to set up sampling strategies.

462



465 Figure 6. Monthly distribution – minimum, maximum, median, and average of atmospheric
 466 concentrations for all sampling sites.
 467

468

469 The soil and climate conditions (relative humidity (RH), temperature...) are important
 470 parameters for the development of adventitious flora and fungi. Indeed, high relative humidity

471 (RH > 90%) and temperate (10-25°C) periods favor fungus growth. It is therefore logical that
472 fungicides were mainly detected during the spring and early summer periods (April to July),
473 and to a lesser extent, during the fall period (October to December) (Figure S3). The
474 difference of action modes, preventive and curative actions for Tebuconazole and only
475 preventive action for Folpet (Index Acta Phytosanitaire, 2018), could explain that Folpet was
476 not detected during the fall period (Figure 6).

477 The weed control is ongoing throughout the year, due to the pre-emergence and post-
478 emergence treatments for a wide range of crops, such as winter and spring cereals, vegetable
479 crops... A general trend is therefore hard to find. For example, due to their different fields of
480 application, Propyzamide, Pendimethalin, and Prosulfocarb were more frequently detected
481 during the winter, spring, and fall periods, respectively (Figure 6 and Figure S3). These
482 observations are consistent with the conclusions of the French Agency for Food,
483 Environmental and Occupational Health & Safety (ANSES, 2010).

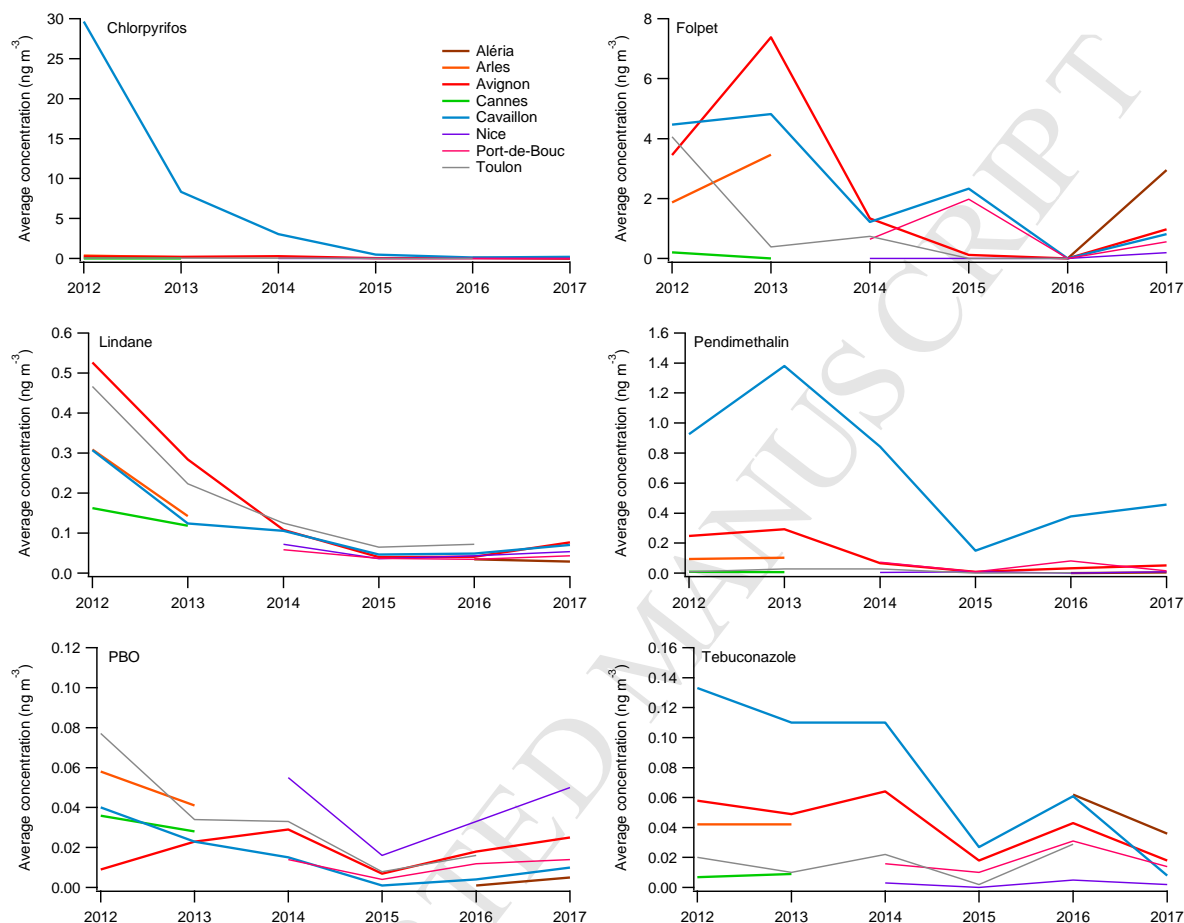
484 The insecticide Chlorpyrifos was used extensively during the spring and summer periods
485 especially in Cavaillon, which is characterized by intensive orchard crops. This timeline is
486 consistent with atmospheric concentrations measured in Tuscany region (2008-2009;
487 Estellano et al., 2015) and in Canada (2006-2007; Hayward et al., 2010). Lindane is a
488 particular case because it was banned since 1998 and 2007 for agricultural and biocidal uses,
489 respectively. Despite these strong restrictions, moderate but regular concentrations were
490 observed through the year in all sampling sites (Median: 0.065 ng m⁻³). The same pattern was
491 previously observed in other French regions such as in the Centre region (2006-2008;
492 Coscollà et al., 2010). Finally, according to French (2012-2015; Villiot et al., 2018) and
493 Chinese (2011-2012; Li et al., 2014) studies, the other insecticides (including PBO) were
494 detected throughout the year (Figure 5 and Figure S3).

495 *Pesticide distribution for each sampling site*

496 Figure 7 and Figure S4 represent the annual average concentration of the detected active
497 substances for each sampling site during the 6-years sampling. This inter-annual variation is
498 related to the annual quantities sold that are often dependent on the pest pressure. In France,
499 between 2012 and 2016, the sales for professional uses of fungicides (and bactericides),
500 herbicides, and insecticides (and acaricides) increased by 16.7%, 8.4%, and 56.3%,
501 respectively (Eurostat, 2018). For now, the sales data are available for individual compounds
502 only at department-wide (i.e., Alpes-Maritimes for Cannes and Nice, Bouches-du-Rhône for
503 Arles and Port-de-Bouc, Haute-Corse for Aléria, Var for Toulon, and Vaucluse for Avignon

504 and Cavaillon) (BNVD, 2017). In contrast to the national data, sales at department-wide for
 505 Alpes-Maritimes, Bouches-du-Rhône, Haute-Corse, Var, and Vaucluse have trended
 506 downwards.

507



508

509

510

511 Figure 7. Yearly distribution – annual average concentrations for each sampling site.

512

513 Therefore, a downward trend was observed for most of the atmospheric pesticide
 514 concentrations (Figure 7). This trend is particularly important for two insecticides,
 515 Chlorpyrifos and Lindane. Chlorpyrifos was detected at the highest concentrations in
 516 Cavaillon due to the large presence of orchards. In the Vaucluse department, since 2013, sales
 517 of Chlorpyrifos dropped by 97% (BNVD, 2017) and simultaneously the annual average
 518 concentration dropped by 98%. Moreover, at the national level, Chlorpyrifos was banned
 519 since the beginning of 2018 (Index Acta Phytosanitaire, 2018), suggesting a possible
 520 continuum in the decrease of their atmospheric concentrations. For Lindane, banned since

521 1998, there's no sales data available but the slow and continuous decrease of the atmospheric
522 background concentration was explained by its slow environmental degradation.

523 By contrast, for some pesticides such as Metazachlor (H) and Propyzamide (H), an increase of
524 atmospheric concentrations is observed during the last sampling year (Figure S4).
525 Unfortunately, the step back is not enough to know if this increase is exceptional or if it is the
526 start of a new upward trend in the concentrations of these active substances.

527 A sequential decrease (i.e., increase and decrease phases over the years) was observed for
528 Pendimethalin (H), Folpet (F), and Tebuconazole (F) (Figure 7). Even if the sold quantities
529 were smaller and smaller, these active substances remained the most used in the PACA and
530 Corsica regions (BNVD, 2017). Some active substances like PBO (Figure 7), Boscalid (H),
531 Prosulfocarb (F), and s-Metolachlor (F) (Figure S4) showed temporal profiles with similar
532 concentrations throughout the six years.

533

534 **4. Conclusion**

535 The monitoring of atmosphere of six urban and two rural sites in the PACA and Corsica for 6-
536 years enabled the detection of 45 active substances, involving 18 fungicides, 14 herbicides, 12
537 insecticides, and 1 synergist. The most detected pesticides were Pendimethalin (H, 64.6%),
538 Tebuconazole (F, 65.9%), Chlorpyrifos (I, 71.5%), and Lindane (I, 98.6%). Atmospheric
539 concentrations can vary from few pg m^{-3} to several hundreds of ng m^{-3} , including pesticides
540 regularly quantified above 1 ng m^{-3} such as Folpet, Chlorpyrifos, and Pendimethalin.

541 Although having mainly agricultural uses, the active substances were both detected in rural
542 and urban sampling sites, suggesting a possible atmospheric transport from agricultural areas
543 to city centers at local and regional scales. In an atmospheric concentration point of view, the
544 spatial distribution also shows that fungicides were more quantified than insecticides and
545 herbicides. Temporal monitoring shows a seasonally trend for each pesticide, depending on
546 pest pressure. Fungicide concentrations were higher during the spring and early summer
547 periods (April to July), whereas herbicide and insecticide concentrations were quite constant
548 throughout the year. Inter-annual variation suggests a downward trend which is consistent
549 with the available regional sales data.

550 From 2018, France will strengthen its pesticide air monitoring to develop regulations
551 regarding the pesticide toxicity. However, the implementation of an extensive air monitoring
552 network in Europe for pesticide control is needed.

553

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561

562 Competing financial interests

563 The authors declare no competing financial interests.

564

565 Reference

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Table 1: Physicochemical properties, agricultural uses, and legal situation of pesticides.

Pesticides	CAS	Molecular weight (g mol ⁻¹)	Vapor pressure (Pa, 25°C) ^a	Acceptable Daily Intake (mg kg bw ⁻¹ day ⁻¹) ^b	Substance group	Principal agricultural uses ^c	Legal situation for agricultural uses	
							in France (expiration of approval) ^c	in European Union ^d
<i>Fungicides (19)</i>								
Boscalid	188425-85-6	343.2	7.2·10 ⁻⁷	0.06	Carboxamide	Rapeseed, oleaginous, vegetable crops, vineyards, seed crops, ornamental crops	08/2018	08/44/ECReg. (EU) No 540/2011
Cymoxanil	57966-95-7	198.2	1.5·10 ⁻⁴	0.013	Acetamide	Potatoes	09/2021	2008/125Reg. (EU) No 540/2011
Cyprodinil	121552-61-2	225.3	5.1·10 ⁻⁴	0.02	Anilinopyrimidine	Cereals, orchards	05/2018	06/64/ECReg. (EU) No 540/2011Reg. (EU) No 678/2014
Difenoconazole	119446-68-3	406.3	3.3·10 ⁻⁸	0.01	Triazole	Beet, rapeseed, vegetable crops, orchards, vineyards, seed crops, ornamental crops	01/2019	2008/69Reg. (EU) No 1100/2011Reg. (EU) No 540/2011
Dimethomorph	110488-70-5	387.9	9.9·10 ⁻⁷	0.06	Morpholine	Vineyards	08/2018	07/25/ECReg. (EU) No 540/2011
Epoxiconazole	135319-73-2	329.8	1.0·10 ⁻⁵	0.01	Triazole	Cereals, beet	05/2019	2008/107Reg. (EU) No 540/2011
Fenhexamid	126833-17-8	302.2	4.0·10 ⁻⁷	0.2	Hydroxyanilide	Vegetable crops, orchards, seed crops, vineyards	01/2031	Reg. (EU) 2015/1201Reg. (EU) No 540/2011 (01/28/EC)
Fenpropidin	67306-00-7	273.5	1.7·10 ⁻²	-	Unclassified	Cereals, seed crops	01/2019	2008/66Reg. (EU) No 540/2011
Fenpropimorph	67564-91-4	303.5	3.9·10 ⁻³	0.003	Morpholine	Cereals, Sunflower	01/2019	2008/107Reg. (EU) No 540/2011
Fluazinam	79622-59-6	465.1	7.5·10 ⁻³	0.004	Pyridine	Potatoes, ornamental crops	03/2019	2008/108Reg. (EU) No 540/2011
Flusilazole	85509-19-9	315.4	3.9·10 ⁻⁵	0.002	Triazole	Cereals, beet, orchards, seed crops	05/2013	06/133/EC,Reg. (EU) No 540/2011
Folpet	133-07-3	296.6	2.1·10 ⁻⁵	0.1	Phthalimide	Vineyards	08/2018	07/5/ECReg. (EU) No 540/2011
Iprodione	36734-19-7	330.2	5.0·10 ⁻⁷	0.04	Dicarboximide	Vegetable crops, orchards, ornamental crops, seed crops, vineyards, turf	11/2017	Reg. (EU) 2017/2091 (03/31/EC,Reg. (EU) 2016/950,Reg. (EU) 2017/1511,Reg. (EU) No 540/2011,Reg. (EU) No 823/2012)
Kresoxim-methyl	143390-89-0	313.4	2.3·10 ⁻⁶	0.4	Strobilurin	Orchards, ornamental crops, vineyards	01/2022	Reg. (EU) No 540/2011Reg. (EU) No 810/2011 (2007/21/EC,99/01/EC)
Pyrimethanil	53112-28-0	199.3	1.1·10 ⁻³	0.2	Anilinopyrimidine	Beans, vegetable crops, orchards, seed crops, ornamental crops	05/2018	2006/74/ECReg. (EU) No 540/2011Reg. (EU) No 678/2014
Spiroxamine	118134-30-8	297.5	3.5·10 ⁻³	0.02	Morpholine	Vineyards	01/2022	Reg. (EU) No 797/2011 (2007/21/EC,99/73/EC,Reg. (EU) No 540/2011)
Tebuconazole	107534-96-3	307.8	1.3·10 ⁻⁶	0.03	Triazole	Cereals, vegetable crops, orchards, seed crops, vineyards, ornamental crops	09/2019	2008/125Reg. (EU) No 540/2011Reg. (EU) No 921/2014
Tetraconazole	112281-77-3	372.2	1.8·10 ⁻⁴	0.004	Triazole	Cereals, beet, orchards, vineyards	01/2022	2009/82/EUReg. (EU) No 540/2011
Tolyfluanid	731-27-1	347.3	7.7·10 ⁻⁵	-	Sulfamide	Orchards	12/2010	2010/20/EU
<i>Herbicides (25)</i>								

2,4-D (2,4-Dichlorophenoxyacetic acid)	94-75-7	221.0	$9.0 \cdot 10^{-6}$	0.01	Alkylchlorophenoxy	Cereals, vegetable crops, orchards, ornamental crops, turf	01/2031	01/103/ECReg. (EU) 2015/2033Reg. (EU) No 540/2011 (2010/77/EU,Reg. (EU) 2015/1885)
2,4-MCPA (2-methyl-4-chlorophenoxyacetic acid)	94-74-6	200.6	$4.0 \cdot 10^{-4}$	0.01	Aryloxyalkanoic acid	Cereals	11/2018	05/57/ECReg. (EU) 2017/1511Reg. (EU) No 540/2011 (Reg. (EU) No 762/2013)
Aclonifen	74070-46-5	264.7	$1.6 \cdot 10^{-5}$	0.07	Diphenyl ether	Vegetable crops, seed crops, ornamental crops	08/2022	2008/116Reg. (EU) 2017/195Reg. (EU) No 540/2011
Amitrole	61-82-5	84.1	$3.3 \cdot 10^{-5}$	0.0003	Triazole	Cereals, orchards, vineyards	10/2017	Reg. (EU) 2016/871 (01/21/EC,2010/77/EU,Reg. (EU) 2015/1885,Reg. (EU) No 540/2011)
Chlorpropham	101-21-3	213.5	$2.4 \cdot 10^{-2}$	0.05	Carbamate	Vegetable crops, ornamental crops	08/2018	04/20/ECReg. (EU) 2017/841Reg. (EU) No 540/2011
Clomazone	81777-89-1	239.7	$1.9 \cdot 10^{-2}$	0.1	Unclassified	Beet, vegetable crops, seed crops, ornamental crops	11/2018	2007/76Reg. (EU) No 540/2011
Diclofop-methyl	51338-27-3	341.2	$2.5 \cdot 10^{-5}$	0.002	Aryloxyphenoxy propionate	Cereals, turf	06/2021	2011/45/EUReg. (EU) No 540/2011
Diflufenican	83164-33-4	394.3	$4.3 \cdot 10^{-6}$	0.2	Carboxamide	Cereals	01/2019	2008/66Reg. (EU) No 540/2011
Dimethenamid-P	163515-14-8	275.8	$2.5 \cdot 10^{-3}$	0.03	Amide	Beans, beet, ornamental crops, vineyards	11/2017	03/84/ECReg. (EU) 2017/1511Reg. (EU) No 540/2011Reg. (EU) No 823/2012 (Reg. (EU) 2016/950)
Flazasulfuron	104040-78-0	407.3	$1.3 \cdot 10^{-5}$	0.013	Sulfonylurea	Orchards, vineyards	02/2018	Reg. (EU) 2017/805Reg. (EU) No 540/2011Reg. (EU) No 823/2012 (04/30/EC,Reg. (EU) 2016/2016)
Flumioxazin	103361-09-7	354.3	$3.2 \cdot 10^{-4}$	0.003	N-phenylphthalimide	Orchards, vineyards	07/2018	02/81/ECReg. (EU) 2016/549Reg. (EU) 2017/841Reg. (EU) No 540/2011 (2010/77/EU,Reg. (EU) 2015/1885)
Flurochloridone	61213-25-0	312.1	$2.7 \cdot 10^{-4}$	0.04	Unclassified	Vegetable crops, seed crops, ornamental crops	06/2021	2011/34/EUReg. (EU) No 540/2011 (2008/934/EC)
Fluroxypyr	69377-81-7	255.0	$3.8 \cdot 10^{-9}$	0.2	Pyridine	Cereals, vegetable crops, orchards, seed crops, ornamental crops	01/2022	Reg. (EU) 2017/856Reg. (EU) No 736/2011 (00/10/EC,2007/21/EC,Reg. (EU) No 540/2011)
Isoproturon	34123-59-6	206.3	$5.5 \cdot 10^{-6}$	0.015	Urea	Cereals	10/2017	Reg. (EU) 2016/872 (02/18/EC,2010/77/EU,Reg. (EU) 2015/1885,Reg. (EU) No 540/2011)
Lenacil	2164-08-1	234.3	$1.7 \cdot 10^{-9}$	-	Uracil	Beet, seed crops, ornamental crops	01/2019	2010/39/EUReg. (EU) No 540/2011 (2008/69/EC)
Linuron	330-55-2	249.1	$5.1 \cdot 10^{-3}$	0.01	Urea	Cereals, vegetable crops, ornamental crops	06/2018	03/31/ECReg. (EU) 2016/950Reg. (EU) 2017/244Reg. (EU) No 540/2011Reg. (EU) No 823/2012
Metazachlor	67129-08-2	277.8	$9.3 \cdot 10^{-5}$	0.03	Chloroacetamide	Rapeseed, vegetable crops, seed crops, ornamental crops	08/2022	2008/116/EC2009/155/ECReg. (EU) No 540/2011
S-Metolachlor	87392-12-9	283.8	$1.7 \cdot 10^{-3}$	0.08	Chloroacetamide	Beet, cereals, vegetable crops, seed crops	04/2018	05/3/ECReg. (EU) 2017/841Reg. (EU) No 540/2011
Oxadiazon	19666-30-9	345.2	$6.7 \cdot 10^{-4}$	0.05	Oxidiazole	Vineyards, ornamental crops, non-cropped areas	01/2019	2010/39/EUReg. (EU) No 540/2011 (2008/69/EC)
Pendimethalin	40487-42-1	281.3	$1.9 \cdot 10^{-3}$	0.1	Dinitroaniline	Cereals, vegetable crops, orchards, seed crops, ornamental crops, vineyards	08/2018	Reg. (EU) 2017/1114 Reg. (EU) No 540/2011 (03/31/ECReg. (EU) 2016/950, Reg. (EU) 2017/841,

								Reg. (EU) No 823/2012)
Propyzamide	23950-58-5	256.1	$2.7 \cdot 10^{-5}$	0.02	Benzamide	Rapeseed, vegetable crops, orchards, seed crops, vineyards, ornamental crops, non-cropped areas	02/2018	03/39/ECReg. (EU) No 2016/2016Reg. (EU) No 540/2011Reg. (EU) No 823/2012Reg. (EU) No 84/2018
Prosulfocarb	52888-80-9	251.4	$7.9 \cdot 10^{-4}$	0.02	Thiocarbamate	Cereals, vegetable crops, seed crops, ornamental crops	11/2018	2007/76/ECReg. (EU) No 540/2011
Sulcotrione	99105-77-8	328.8	$5.0 \cdot 10^{-6}$	0.0004	Triketone	Cereals	09/2022	2008/125Reg. (EU) No 540/2011
Terbuthylazine	5915-41-3	229.7	$1.2 \cdot 10^{-4}$	0.003	Triazine	Corn	01/2022	Reg. (EU) No 820/2011 (2008/934/EC)
Triallate	2303-17-5	304.7	$1.2 \cdot 10^{-2}$	0.005	Thiocarbamate	Beet, rapeseed, cereals, vegetable crops	01/2022	2009/77/ECReg. (EU) No 540/2011
Insecticides (15)								
Chlorpyrifos	2921-88-2	350.6	$1.4 \cdot 10^{-3}$	0.003	Organophosphate	Cereals, orchards, vegetable crops	02/2018	05/72/ECReg. (EU) No 540/2011Reg. (EU) No 762/2013Reg. (EU) No 84/2018
Chlorpyrifos-methyl	5598-13-0	322.5	$3.0 \cdot 10^{-3}$	0.01	Organophosphate	Cereals, rapeseed, orchards, vineyards, ornamental crops	02/2018	05/72/ECReg. (EU) No 540/2011Reg. (EU) No 762/2013Reg. (EU) No 84/2018
Cypermethrin	52315-07-8	413.3	$2.3 \cdot 10^{-7}$	0.05	Pyrethroid	Cereals, rapeseed, oleaginous, vegetable crops, orchards, ornamental crops, vineyards, non-cropped areas	11/2017	05/53/ECReg. (EU) 2017/1511Reg. (EU) No 540/2011 (Reg. (EU) No 533/2013)
Deltamethrin	52918-63-5	505.2	$1.2 \cdot 10^{-8}$	0.01	Pyrethroid	Cereals, vegetable crops, orchards, seed crops, vineyards, ornamental crops	11/2017	03/5/ECReg. (EU) 2017/1511Reg. (EU) No 540/2011Reg. (EU) No 823/2012 (Reg. (EU) 2016/950)
Diflubenzuron	35367-38-5	310.7	$1.2 \cdot 10^{-7}$	0.02	Benzoylurea	Corn, orchards, ornamental crops	01/2019	2008/69/EC2010/39/EUReg. (EU) 2017/855Reg. (EU) No 540/2011
Esbiothrin	8403-86-4	302.4	$1.3 \cdot 10^{-4}$	0.03	Pyrethroid	Biocidal uses only	-	-
Fenoxycarb	72490-01-8	301.3	$8.7 \cdot 10^{-7}$	0.05	Carbamate	Orchards, vineyards	06/2021	2011/20/EUReg. (EU) No 540/2011
Fipronil	120068-37-3	437.1	$2.0 \cdot 10^{-6}$	0.0002	Phenylpyrazole	Ornamental crops, non-cropped areas	08/2017	Reg. (EU) 2016/2035Reg. (EU) No 540/2011Reg. (EU) No 781/2013 (07/52/EC,2010/21/EU)
Imidacloprid	138261-41-3	255.7	$4.0 \cdot 10^{-10}$	0.06	Neonicotinoid	Orchards, ornamental crops, non-cropped areas	08/2022	Reg. (EU) No 485/2013Reg. (EU) No 540/2011 (2008/116/EC,2010/21/EU)
Lambda-cyhalothrin	91465-08-6	449.9	$1.0 \cdot 10^{-12}$	0.001	Pyrethroid	Cereals, beet, oleaginous, rapeseed, vegetable crops, orchards, seed crops, vineyards, ornamental crops	04/2023	00/80/ECReg. (EU) 2016/146Reg. (EU) No 540/2011 (2010/77/EU,Reg. (EU) 2015/1885)
Lindane	58-89-9	290.8	$4.4 \cdot 10^{-3}$	0.003	Organochlorine	Orchards, non-cropped areas	06/2002	00/801/EC
Permethrin	52645-53-1	391.3	$7.0 \cdot 10^{-6}$	0.05	Pyrethroid	Biocidal uses only	07/2002	00/817/EC
Piperonyl butoxide	51-03-6	338.4	$5.3 \cdot 10^{-4}$	0.1	Unclassified	Insecticide synergist	07/2028	-
Pirimicarb	23103-98-2	238.4	$4.3 \cdot 10^{-4}$	0.02	Carbamate	Vegetable crops, orchards	05/2018	06/39/ECReg. (EU) No 487/2014Reg. (EU) No 540/2011
Thiamethoxam	153719-23-4	291.7	$6.6 \cdot 10^{-9}$	0.02	Neonicotinoid	Ornamental crops	05/2018	Reg. (EU) No 485/2013Reg. (EU) No 487/2014Reg. (EU) No 540/2011 (07/6/EC,2010/21/EU)

^a PPDB: Pesticide Properties DataBase (Lewis et al., 2016). ^b APVMA, 2017. ^c Index Acta Phytosanitaire, 2018. ^d EU Pesticides Database, 2016.

1 Highlights

- 2 • 45 active substances were detected at frequencies ranging from 0.1 to 98.6%.
- 3 • Active substances were detected both in rural and urban sampling sites.
- 4 • The insecticide Chlorpyrifos has reached a concentration exceeding 400 ng m⁻³.
- 5 • Pesticides can be transported from rural to urban areas at local scale.
- 6 • A downward trend was observed for most pesticides.