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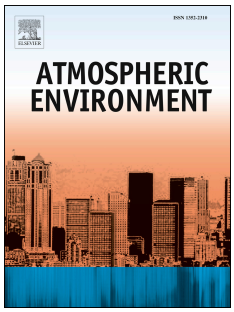

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Spatial and temporal distribution of Current-Use Pesticides in ambient air of Provence-Alpes-Côte-d'Azur Region and Corsica, France

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Abstract

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

Keywords

Pesticides; Atmosphere; Monitoring; Transport

Highlights

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

1. Introduction

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

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

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

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

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

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

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

2. Material and methods

2.1. Chemicals

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

115 Triphenyl phosphate (TPP; ≥ 99%) and anthracene-d10 (≥ 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 Teppe
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

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

The sampling was carried out according to the AFNOR standard XP X43-058 (AFNOR, 2007a) using a high-volume sampler (Digitel Aerosol Sampler DHA-80) equipped with a Total Suspended Particulates (TSP) inlet. Samplings were done two meters above ground-level. Particulate and gaseous samples were collected simultaneously on 150 mm diameter ashless quartz microfibre filter (ALBET LabScience) for particulate pesticides followed by a combination of two polyurethane foams (PUF; Tisch Environmental, Inc.) and 20 g of Amberlite XAD-2 resin (Supelco) for gaseous pesticides. Prior to use, filters, PUF, and resin were subject to clean-up by warming at 900°C and with DCM and acetone, respectively. The sampling flow was 10 m^3 h^{-1} for 48 h, giving a total volume of filtered air around 480 m^3.

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

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

2.3. Sample extraction and analysis

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

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

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

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

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

chosen. For MS/MS experiment, collision gas was Argon 99.995% (Linde) with a pressure of approximately $1.4.10^{-4}$ mbar in the collision cell. The characteristic selected ions for pesticides quantification, optimum cone voltage, collision energy, and limits of detection (LOD) are presented in Table S3. Data acquisition and treatments of selected-reaction mass chromatograms were provided by the MassLynx software (v.4.1, Waters).

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

3. Results and discussion

3.1. Detection frequencies and atmospheric concentrations

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

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

Table 3. Frequency of detection, maximum, and median concentrations of pesticides in all 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	-
Diflufenican	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	-	-
Diflubenzuron	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		

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	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	-	-

(-) means < Limit of Detection

Detection frequencies

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

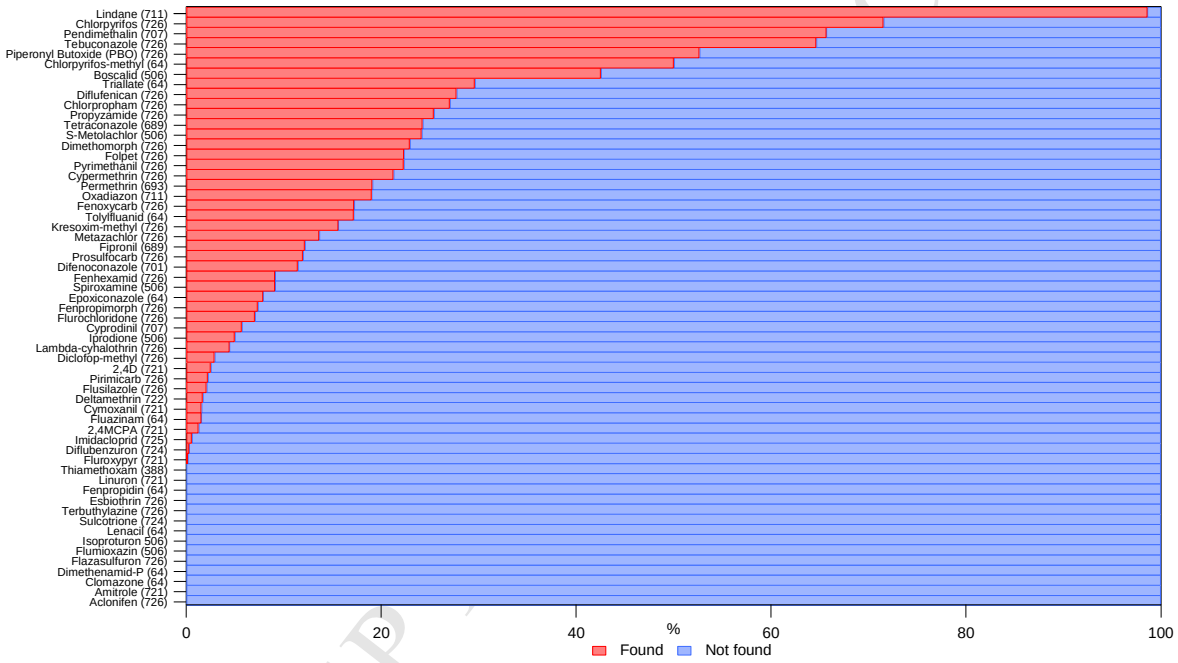

Figure 1. Detection frequency of the 59 active substances. ‘Found’ is based on samples with concentrations above the limit of detection, and the number in brackets refers to total samples where the active substance was searched.

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

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

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

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

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

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

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

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

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

Atmospheric concentrations

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

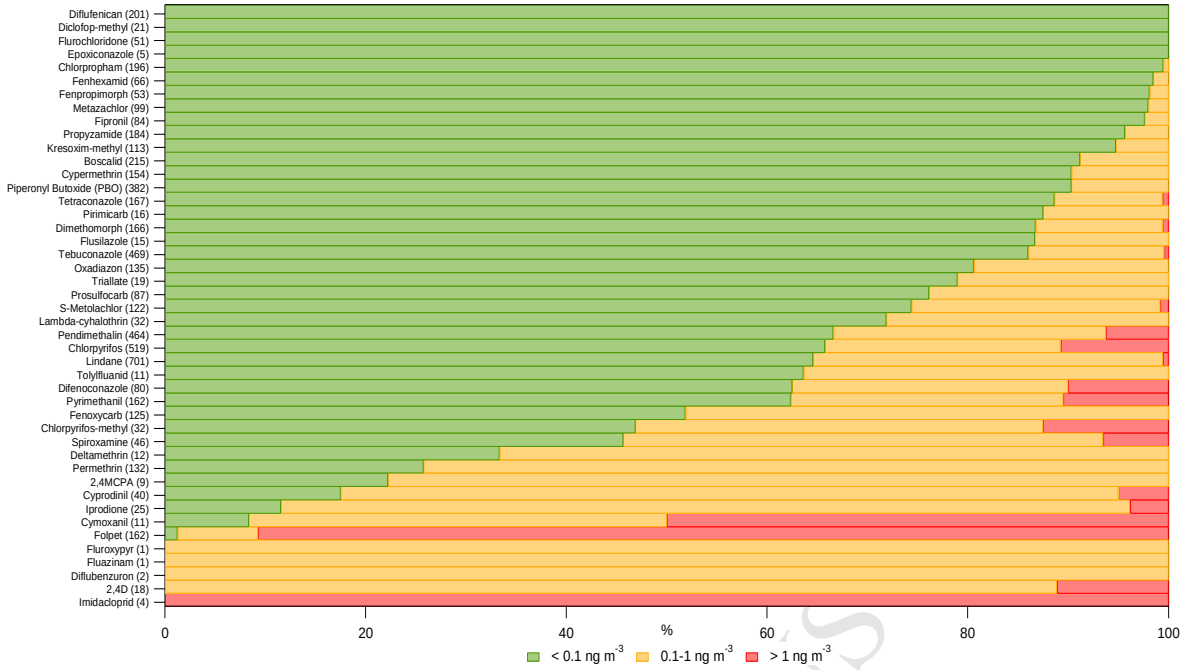

Figure 2. Distribution of the active substances between concentration below 0.1 ng m^{-3}, between 0.1 and 1 ng m^{-3}. The number in brackets refers to total samples where the active substance was quantified.

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

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

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

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

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

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

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

3.2. Spatial distribution of pesticides

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

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

Pesticide family distribution by sampling sites

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

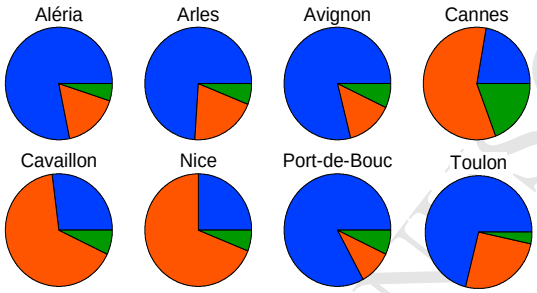

Figure 3. Geographical distribution – sum of atmospheric concentrations by sampling sites. Fungicide = blue, Insecticide = orange, Herbicide = green.

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

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

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

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

Pesticide distribution by typology: rural vs. urban

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

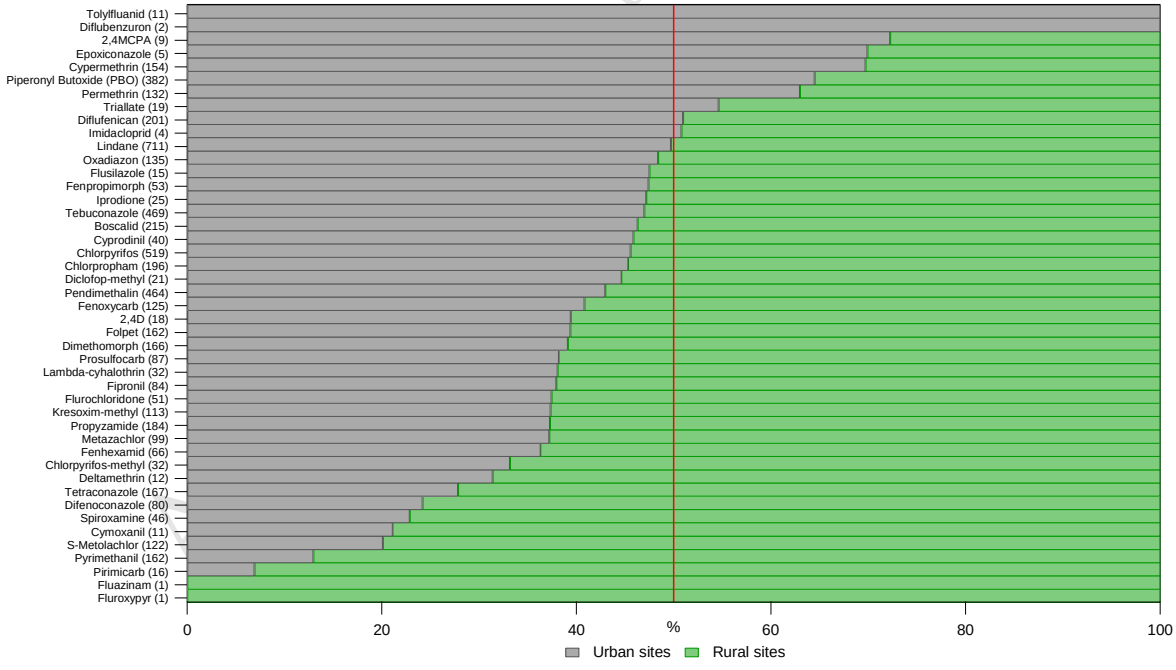

Figure 4. Typological distribution of active substances between urban (grey) and rural (green) sites. The number in brackets refers to total samples where the active substance was detected.

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

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

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

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

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

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

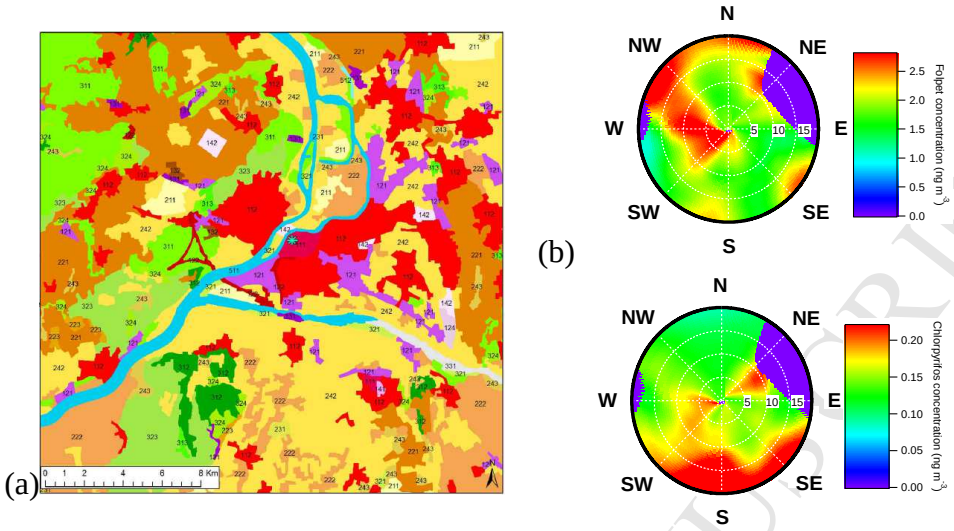

Figure 5. Geographical origin analysis of Folpet (top) and Chlorpyrifos (down) in Avignon urban sampling site: (a) zone of 10 km radius around the urban sampling site of Avignon (Corine Land Cover nomenclature: 11X/12X-Urban fabric, 21X-Arable land, 221-Vineyards, 222-Fruit trees and berry plantations,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

3.3. Temporal distribution of pesticides

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

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

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

Monthly distribution for all sampling sites

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

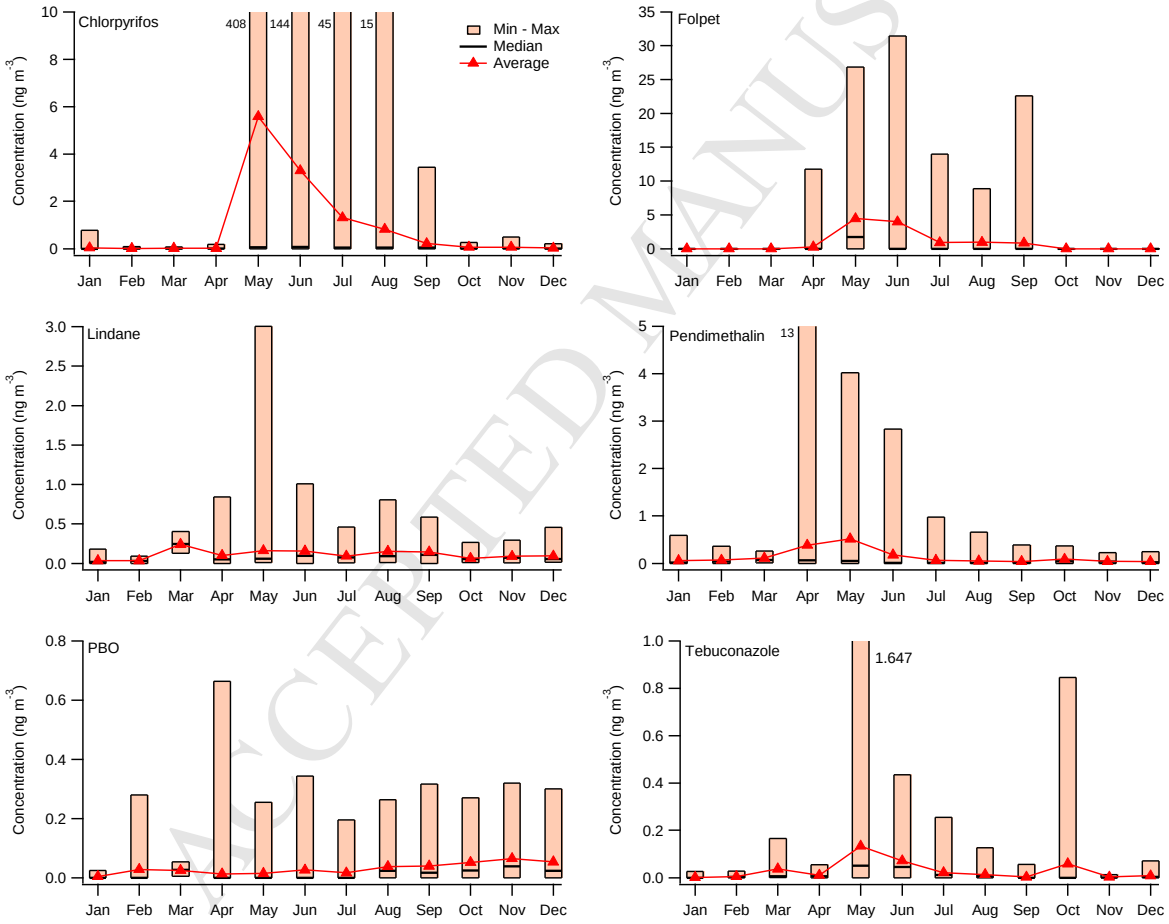

Figure 6. Monthly distribution – minimum, maximum, median, and average of atmospheric concentrations for all sampling sites.

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

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

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

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

Pesticide distribution for each sampling site

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

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

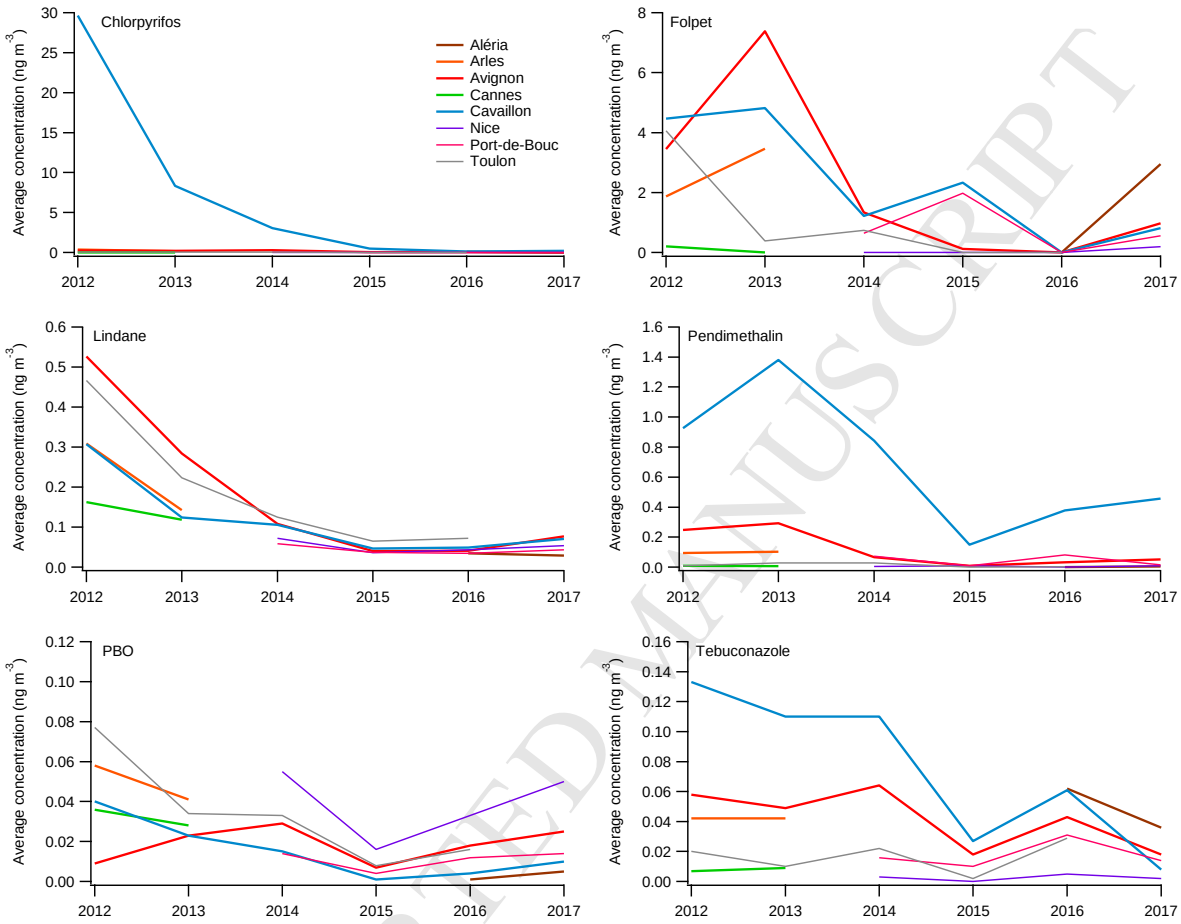

Figure 7. Yearly distribution – annual average concentrations for each sampling site.

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

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

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

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

4. Conclusion

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

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

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

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Competing financial interests

The authors declare no competing financial interests.

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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]
Fungicides (19)								
Boscalid	188425-85-6	343.2	$7.2 \cdot 10^{-7}$	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	$1.5 \cdot 10^{-4}$	0.013	Acetamide	Potatoes	09/2021	2008/125Reg. (EU) No 540/2011
Cyprodinil	121552-61-2	225.3	$5.1 \cdot 10^{-4}$	0.02	Anilinopyrimidine	Cereals, orchards	05/2018	06/64/ECReg. (EU) No 540/2011Reg. (EU) No 678/2014
Difenoconazole	119446-68-3	406.3	$3.3 \cdot 10^{-8}$	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	$9.9 \cdot 10^{-7}$	0.06	Morpholine	Vineyards	08/2018	07/25/ECReg. (EU) No 540/2011
Epoxiconazole	135319-73-2	329.8	$1.0 \cdot 10^{-5}$	0.01	Triazole	Cereals, beet	05/2019	2008/107Reg. (EU) No 540/2011
Fenhexamid	126833-17-8	302.2	$4.0 \cdot 10^{-7}$	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	$1.7 \cdot 10^{-2}$	-	Unclassified	Cereals, seed crops	01/2019	2008/66Reg. (EU) No 540/2011
Fenpropimorph	67564-91-4	303.5	$3.9 \cdot 10^{-3}$	0.003	Morpholine	Cereals, Sunflower	01/2019	2008/107Reg. (EU) No 540/2011
Fluazinam	79622-59-6	465.1	$7.5 \cdot 10^{-3}$	0.004	Pyridine	Potatoes, ornamental crops	03/2019	2008/108Reg. (EU) No 540/2011
Flusilazole	85509-19-9	315.4	$3.9 \cdot 10^{-5}$	0.002	Triazole	Cereals, beet, orchards, seed crops	05/2013	06/133/EC,Reg. (EU) No 540/2011
Folpet	133-07-3	296.6	$2.1 \cdot 10^{-5}$	0.1	Phthalimide	Vineyards	08/2018	07/5/ECReg. (EU) No 540/2011
Iprodione	36734-19-7	330.2	$5.0 \cdot 10^{-7}$	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	$2.3 \cdot 10^{-6}$	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	$1.1 \cdot 10^{-3}$	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	$3.5 \cdot 10^{-3}$	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	$1.3 \cdot 10^{-6}$	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	$1.8 \cdot 10^{-4}$	0.004	Triazole	Cereals, beet, orchards, vineyards	01/2022	2009/82/EUReg. (EU) No 540/2011
Tolylfluanid	731-27-1	347.3	$7.7 \cdot 10^{-5}$	-	Sulfamide	Orchards	12/2010	2010/20/EU
Herbicides (25)								

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-phenylphtalamide	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.

Highlights

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