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Passive Sampling as a Tool to Assess Atmospheric Pesticide Contamination Related to Vineyard Land Use

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Abstract: The massive use of pesticides in agriculture has led to widespread contamination of the environment, particularly the atmospheric compartment. Thirty-six pesticides, most used in viticulture, were monitored in ambient air using polyurethane foams as passive air samplers (PUF-PAS). Spatiotemporal data were collected from the samplers for 10 months (February–December 2013), using two different sampling times (1 and 2 months) at two different sites in a chateau vineyard in Gironde (France). A high-volume active air sampler was also deployed in June. Samples were extracted with dichloromethane using accelerated solvent extraction (ASE) (PUFs from both passive and active) or microwave-assisted extraction (MAE) (filters from active sampling). Extracts were analyzed by both gas and liquid chromatography coupled with tandem mass spectrometry. A total of 23 airborne pesticides were detected at least once. Concentrations in PUF exposed one month ranged from below the limits of quantification (LOQs) to 23,481 ng PUF^{-1}. The highest concentrations were for folpet, boscalid, chlorpyrifos-methyl, and metalaxyl-m—23,481, 17,615, 3931, and 3324 ng PUF^{-1}. Clear seasonal trends were observed for most of the pesticides detected, the highest levels (in the ng m^{-3} range or the μg PUF^{-1} range) being measured during their application period. Impregnation levels at both sites were heterogeneous, but the same pesticides were involved. Sampling rates (*Rs*) were also estimated using a high-volume active air sampler and varied significantly from one pesticide to another. These results provide preliminary information on the seasonality of pesticide concentrations in vineyard areas and evidence for the effectiveness of PUF-PAS to monitor pesticides in ambient air.

Keywords: passive sampling; pesticides; air quality

1. Introduction

Intensive use of anthropogenic organic compounds such as current-use pesticides in agriculture is of environmental and public health concerns. In 2018, worldwide pesticide use for agriculture reached 4.1 million tons, a twofold increase in consumption since 1990 [1]. The total quantity of active substances sold in France in 2018 was 85,000 tons. The massive use of pesticides has led to contamination of all three environmental media, water, soil, and atmosphere [2–8]. Current use pesticides are subject to marketing authorization with the aim of controlling their use, but the absence of regulations on the level of pesticides permitted in the air can lead to health issues linked to chronic exposure, particularly among farmers, workers, and children [9,10].

Air has been described as the preferred medium for pesticide dispersal and transport over long distances, and pesticides can reach urban and remote areas [11]. Airborne

pesticides have been found all over the world, as shown by studies in Europe [12,13], Africa [14,15], Asia [16], North America [17], and even at the North and South Poles [18–20]. This ubiquity is the consequence of both the physicochemical properties of the pesticides (e.g., volatility, viscosity) and the meteorological factors (e.g., temperature, wind force, and direction, relative humidity) that facilitate their transfer into the atmosphere [21,22]. However, most contamination occurs as a result of spray drift during application, when, depending on the weather conditions, application techniques, and the operator ability, up to 30–50% of the sprayed compounds are directly emitted into the air and may reach nontarget organisms [23].

Active air samplers (AAS) are generally used to measure the concentrations of pesticides in the air [24,25]. AAS allow short-term sampling, provide information on gas/particle partitioning, continuous sampling data at high temporal resolution. However, as the AAS technique is costly, it requires a power source or daily maintenance, passive air samplers (PAS) have been used as a low-cost and simple semiquantitative methodology. PAS function based on molecular diffusion from air to an adsorbent with a free flow and provide time-weighted average (TWA) concentrations. In order to determine concentrations of airborne pollutants (in ng m^{-3} or pg m^{-3}), the airflow that diffuses through the adsorbent needs to be known. This is why calibration data are needed to access parameters including sampling rates (*Rs*). In scarce studies, *Rs* was determined by modeling using chemistry and physics, fluid dynamics, hourly meteorological data, and the physical and chemical properties of the target compounds and deployment dates [26,27]. Another accepted way to determine *Rs* is the use of depuration compounds (DCs), e.g., isotopically labeled compounds [28–30]. This method is valid as DCs are spiked and recovered in a reproductible way. The third and the most direct way to determine *Rs* is in situ calibration through the combined use of active and passive samplers. *Rs* can be estimated using the concentrations measured by active sampling and levels accumulated in PAS [31–33].

Since 2002, polyurethane foam passive air samplers (PUF-PAS) have been the most widely used tools to monitor historical semivolatile organic compounds (SVOCs), including polychlorinated biphenyls [34], polybrominated diphenyl ethers [35], organochloride pesticides [36], polycyclic aromatic hydrocarbons [37] or emerging compounds like phthalates [38] or chlorinated paraffins [39]. Given the growing interest in pesticides, monitoring has been carried out at local, national [31,40] and continental scales [41]. Although PUF disk samplers are the most used for SVOCs including currently used pesticides (together with XAD-2 resin samplers in a lesser extent regarding pesticides), their use has been limited by the fact that some currently used pesticides are too volatile to be captured effectively by PUF disks [41]. Other samplers have been developed, such as sorbent-impregnated PUF or SIP disk samplers [41] or new NMC@SiC (adsorbent based on nitrogen-doped carbon coated on silicon carbide foam) samplers [42], exhibiting higher sorptive capacity needed for capturing the more volatile and polar compounds.

Massive applications of pesticides have resulted in a large number of pesticides in ambient air at concentrations ranging from a few pg m^{-3} to several ng m^{-3}. For instance, 41 pesticides have been detected in concentrations ranging from 0.1 to 117.3 ng m^{-3} in central France [43]. In Spain, two studies reported contamination levels for 17 pesticides ranging from 6.8 to 2 892 pg m^{-3} in one remote, one urban, and three rural sites [44] and average concentrations ranging between 1.63 and 117.01 pg m^{-3} for 20 pesticides in a rural station [45]. In France, 28 pesticides have been quantified at concentrations ranging from 0.12 to 14.87 ng m^{-3} in atmospheric samples collected in four sampling years (2012–2015) in a vineyard environment [46]. In addition, AAS detected 19, 22, and 23 pesticides at concentrations ranging from 0.1 to 14.2 ng m^{-3} in three periods between 2013 and 2015 [42].

In this study, PUF-PAS disks were installed at two sites (one in a vineyard plot and one located at a distance of 100 m from the nearest vineyard plot) during a 10-month sampling campaign in 2013. The main goals were to exploit the advantages of passive sampling, test the efficiency of PUF-PAS as adsorbent for pesticide multiresidue monitoring related to vineyard land use, test sampling duration, and derive sampling rates for each pesticide

accumulated in PUF disks. We have chosen to test the performance of PUF material because it is readily available, simple to use, and comparable to what is used for active gas phase sampling. The data provided information on the most frequently detected pesticides, the frequency of detection, and potential drift from the vineyard to a neighboring plot. It helped us draw up preliminary occurrence profiles for 36 pesticides with their seasonal variations. Moreover, even if the data correspond to a past period, they provide a reference to be compared with more recent ones which could allow to address trends in air contamination through the past ten years taking into consideration changes in uses and regulations.

2. Materials and Methods

2.1. Chemicals

All solvents were HPLC grade. Methanol (MeOH) was purchased from Atlantic Labo (Eysines, France); ethyl acetate (EA) and dichloromethane (DCM) from ICS (Belin-Beliet, France). Milli-Q grade water was obtained from a Milli-Q system (Millipore SA, Saint-Quentin-les-Yvelines, France). Pesticide standards (>95% purity) (Table 1) were supplied by Cluzeau Info Labo (Sainte-Foy-la-Grande, France) and Sigma-Aldrich (Saint-Quentin-Fallavier, France).

2.2. Sampling Procedure

Prior to exposure in the field, PUF-PAS disks (14 cm diameter, 1.35 cm thick, 0.0028 g cm^{-3} density, 365 cm^2 surface area, 207 cm^3 volume; Tisch Environmental, Hamilton, OH, USA) were precleaned by pressurized liquid extraction (PLE) using DCM at 1500 psi for 30 min (2 cycles), dried in a fume hood covered in foil and then individually wrapped in aluminum foil. PUF-PAS were housed in precleaned stainless steel chambers [47] and installed at a height of 1.5 to 2 m from the ground at two sites in a vineyard for 7 sampling periods of one month or two months from February to December 2013. More details on the sampling campaigns are given in Tables S1 and S2 in the Supplementary Materials.

The investigated vineyard was located in the periurban area of Bordeaux in Gironde. Three samplers were set up in the vineyard plot where the pesticides were applied (treated zone TZ), the three others in a nearby nontreated area located 100 m from the closest vineyard plot (NTZ). At each site, one sampler was used for a one-month monitoring and the two others for monitoring over two months (each within a month of the other). After sampling, PUF were retrieved, covered in aluminum foil, sealed in bags, and stored at -18 °C until analysis. Fourteen samples were obtained, plus laboratory and field blanks.

As part of PUF-PAS calibration, a DIGITEL DA80 high-volume active sampler (HV-AAS) (30 m^3 h^{-1} flow rate; PM10; PUF & QF/F 150 mm filter) was installed in the courtyard of the wine chateau (located between TZ and NTZ) for five consecutive days in June 2013 (4 to 8 June). A one-month PUF-PAS was also installed in June close to the HV-AAS for the purpose of comparison. Meteorological conditions (air temperature, rainfall, wind speed, and wind direction) were also recorded daily in the same week (Table S2). PUF plugs and filters were collected every 24 h. All samples were stored at -18 °C until extraction.

2.3. Sample Extraction and Analysis

Air samples were screened for 36 pesticides, fungicides (*n* = 21), insecticides (*n* = 6), herbicides (*n* = 7) and transformation products (TPs) (*n* = 2) (see Table 1). PUF disks and filters were spiked with 11 isotopically labeled compounds (selected according their commercial availability and also in order to cover the range of the native targeted pesticides, at least isotopologs of 11 native pesticides of the study). PUFs were extracted by PLE (ASE 350©, Dionex, Courtaboeuf, France) (1500 psi at 90 °C for two 10-min static cycles) and filters by microwave-assisted extraction (MAE) (Start E©, Milestone, Sorisole, Italy) (5 min at 800 W, followed by 5 min at 400 W) using DCM. Filter extracts were then filtered on precleaned glass wood. The resulting extracts (PUFs and filters) were concentrated to 3 mL using a RapidVap® system (Labconco, Kansas City, MO, USA) (45 °C, 750 mbar). An aliquot of 1.5 mL was taken, blown down under a gentle stream of ultrapure nitrogen and

solvent exchanged into MeOH for liquid chromatography (LC) analysis. The remaining 1.5 mL were also evaporated under a nitrogen stream and solvent exchanged into EA for gas chromatography (GC) analysis.

Table 1. Use and physicochemical properties of the pesticides investigated in this study.

Name	Type	Analysis	Vapor Pressure [a] at 20 °C (mPa)	Henry's Law Constant [a] at 25 °C (Pa m³ mol⁻¹)	log K_{oa} [a]	Approved in France (in 2013)	Applied on the Vineyard Plot in 2013
Ametoctradin	F	LC-MS/MS	2.1×10^{-7}	4.13×10^{-7}	14.1	Y	Y (17 May)
Atrazine	H	LC-MS/MS	3.9×10^{-2}	1.5×10^{-4}	9.9	N	-
Azoxystrobin	F	LC-MS/MS	1.1×10^{-7}	7.4×10^{-9}	14.0	Y	-
Bifenthrin	I	GC-MS/MS	1.78×10^{-2}	7.74×10^{-5}	10.8	N	-
Boscalid	F	LC-MS/MS	7.2×10^{-2}	5.18×10^{-5}	10.6	Y	Y (8 July)
Carbendazim	F	LC-MS/MS	9.0×10^{-2}	3.60×10^{-3}	5.9	N	-
Carbetamide	H	LC-MS/MS	3.0×10^{-4}	1.93×10^{-8}	12.9	Y	-
Chlorpyrifos-methyl	I	GC-MS/MS	3.0	0.235	8.0	Y	Y (1 July + 1 August)
Cyazofamid	F	LC-MS/MS	1.33×10^{-2}	4.03×10^{-2}	7.9	Y	Y (2 August)
Cymoxanil	F	LC-MS/MS	1.5×10^{-1}	3.3×10^{-5}	8.5	Y	-
Cyprodinil	F	LC-MS/MS	5.10×10^{-1}	6.6×10^{-3}	9.5	Y	-
Desipropylatrazine (DIA)	TP	LC-MS/MS	-	$9.8 \times 10^{+2}$	1.5	-	-
Diuron	H	LC-MS/MS	1.15×10^{-3}	2.0×10^{-6}	11.9	N	-
Fipronil	I	GC-MS/MS	2×10^{-3}	2.31×10^{-4}	10.7	N	-
Fipronil sulfide	TP	GC-MS/MS	-	-	-	-	-
Fipronil sulfone	TP	GC-MS/MS	-	-	-	-	-
Flazasulfuron	H	LC-MS/MS	1.33×10^{-2}	2.58×10^{-6}	8.9	Y	-
Fludioxonil	F	GC-MS/MS	3.9×10^{-4}	5.4×10^{-5}	11.7	Y	-
Flusilazole	F	LC-MS/MS	3.9×10^{-2}	2.7×10^{-4}	10.8	N	-
Folpet	F	GC-MS/MS	2.1×10^{-2}	8.0×10^{-3}	8.5	Y	Y (7 May + 17 June + 17 July)
Imidacloprid	I	LC-MS/MS	4.0×10^{-7}	1.7×10^{-10}	13.7	Y	-
Iprovalicarb	F	LC-MS/MS	7.9×10^{-5}	1.4×10^{-6}	12.4	Y	Y (17 June)
Kresoxim-methyl	F	LC-MS/MS	2.3×10^{-3}	3.6×10^{-4}	10.2	Y	Y (16 July)
Mandipropamid	F	LC-MS/MS	9.4×10^{-4}	9.2×10^{-5}	10.6	Y	Y (27 May)
Metalaxyl-M	F	LC-MS/MS	3.3	3.5×10^{-5}	9.5	Y	Y (7 May)
Metolachlor (S)	H	LC-MS/MS	3.7	2.2×10^{-3}	9.1	Y	-
Metrafenone	F	LC-MS/MS	0.15	1.32×10^{-1}	8.6	Y	Y (27 May)
Myclobutanil	F	LC-MS/MS	0.198	4.33×10^{-4}	9.6	Y	Y (7 June)
Propiconazole	F	LC-MS/MS	5.6×10^{-2}	9.2×10^{-5}	11.1	Y	-
Quinoxyfen	F	GC-MS/MS	1.2×10^{-2}	3.08×10^{-2}	10.0	Y	Y (17 May)
Simazine	H	LC-MS/MS	8.1×10^{-4}	5.6×10^{-5}	9.9	N	-
Spiroxamine	F	LC-MS/MS	3.5	3.8×10^{-3}	8.7	Y	Y (17 June)
Tebufenpyrad	I	LC-MS/MS	1.6×10^{-3}	1.1×10^{-3}	11.2	Y	-
Terbuthylazine	H	LC-MS/MS	0.152	2.3×10^{-3}	9.4	Y	-
Tetraconazole	F	GC-MS/MS	0.18	3.6×10^{-4}	10.4	Y	Y (1 July)
Thiamethoxam	I	LC-MS/MS	6.6×10^{-6}	4.7×10^{-10}	12.6	Y	-
Trifloxystrobin	F	LC-MS/MS	3.4×10^{-3}	2.3×10^{-3}	10.5	Y	-
Zoxamide	F	LC-MS/MS	1.3×10^{-2}	6.59×10^{-3}	9.3	Y	Y (1 July)

[a] Data from the Pesticide Properties DataBase (PPDB) website; Abbreviations: F = fungicide, H = herbicide, I = insecticide, TP = transformation product; LC-MS/MS = liquid chromatography coupled to tandem mass spectrometry, GC-MS/MS = gas chromatography coupled to tandem mass spectrometry, K_{oa} = octanol/air partition coefficients, N = no, Y = yes.

The 36 investigated pesticides were analyzed by liquid or gas chromatography coupled with tandem mass spectrometry (LC-MS/MS and GC-MS/MS). Polar compounds were separated by high-performance liquid chromatography (HPLC, 1290 Agilent Technologies, Santa Clara, CA, USA) using a Kinetex C18 column (100 mm × 2.1 mm; 1.7 µm; Phenomenex, Torrance, CA, USA) thermoregulated at 35 °C. Mobile phases were MeOH and Milli-Q water (with 0.1% of acetic acid and 5 mM of ammonium acetate). Analytes were detected with a tandem mass spectrometry triple quadrupole (6460, Agilent Technologies, Santa Clara, CA, USA) under positive electrospray ionization (ESI+) and multiple reaction monitoring (MRM) with nitrogen as collision gas. Apolar and nonthermosen-

sitive compounds were analyzed using a gas chromatography instrument (7890 Agilent Technologies, Santa Clara, CA, USA) equipped with an injector at 250 °C (pulsed split-less mode, 25 psi for 1.5 min). Compounds were separated on a HP 5 MS UI column (30 m × 0.25 mm × 0.25 μm film thickness; 5% phenyl methyl siloxane, Agilent J&M GC columns) with Helium (6.0) as carrier gas set at a constant flow of 1.3 mL min^{-1}. Detection was carried out by a triple quadrupole mass spectrometer (7000 A Agilent Technologies, Santa Clara, CA, USA). The mass spectrometer was operated under electron impact ionization (EI) at 70 eV and multiple reaction monitoring (MRM) was used for all analytes. Analytical parameters for LC-MS/MS and GC-MS/MS analysis are reported in Supplementary Tables S3 and S4, respectively.

2.4. Quality Assurance and Quality Control (QA/QC)

The glassware was dedicated, cleaned, and calcinated at 450 °C overnight. Samples were prepared in a room dedicated to ultratrace analyses. Field blanks and laboratory procedural blanks were collected and analyzed; most of the target pesticides were not detected or at low concentrations. A few nanograms of ametoctradin and kresoxim-methyl were quantified on the PUF HV-AAS field blank on day 2. Levels in the field samples were blank-subtracted.

Instrumental limits of quantification (LOQs) were below 0.7 pg injected (except for cymoxanil and fludioxonil) (Tables S3 and S4). Linearity was validated over the concentration range 1–3 000 pg injected (*n* = 6 for LC-MS/MS and *n* = 7 for GC-MS/MS) (Tables S3 and S4). The accuracy of the method was determined from passive PUF disks spiked at 100–500 ng (*n* = 5). The accuracy of the method was satisfactory for 32 pesticides out of the 36 targeted with recoveries ranging from 70% to 135% (median recovery = 104%), except for carbendazim, carbetamide, flazasulfuron, and propiconazole (55, 160, 36, and 149% recovery, respectively) (Table S5). LOQs were obtained by extracting spiked PUF disks. Signal to noise ratios (S/N) were determined using the peak-to-peak method and LOQs were calculated for S/N = 10. The LOQ of 29 molecules was <3 ng PUF-PAS^{-1} and the LOQ of 7 molecules was between 3 and 35 ng PUF-PAS^{-1} (median LOQ = 0.7 ng PUF-PAS^{-1}). PAS LOQs in pg m^{-3} were also extrapolated using a sampled air volume of 150 m^3 (1-month sampling). Detailed performances are listed in Supplementary Table S5.

2.5. Derivation of Sampling Rates and Estimation of Air Concentrations from PUF-PAS

Both passive and active air samplers were installed at the same site. In this way, the sampling rate (*Rs*) of the PUF-PAS can be calculated in the linear uptake phase using the following equation [37]:

$$Rs = \frac{M(PAS)}{Cair * t}$$

where *Rs* (m^3/day) is the sampling rate, M(PAS) is the amount of pesticide accumulated in the PUF (ng PUF^{-1}), C$_{air}$ is the concentration of pesticides in the air from the active air sampling (ng m^{-3}), and t is the sampling duration (days).

3. Results and Discussion

Overall, in all samples (i.e., active and passive), among the 36 targeted pesticides, 23 were detected at least once, the majority being fungicides. Fourteen pesticides were applied in 2013, mainly between May and August (Table 1), and were all detected in PUFs (ametoctradin, boscalid, chlorpyrifos-methyl, cyazofamid, folpet, iprovalicarb, kresoxim-methyl, mandipropamid, metalaxyl-m, metrafenone, myclobutanil, quinoxyfen, spiroxamine, zoxamide). Several molecules that were not applied by the wine chateau were nevertheless detected and quantified, including azoxystrobin, carbendazim, trifloxystrobin, fludioxonil, *S*-metolachlor or fipronil as well as two of its TPs (fipronil sulfide and fipronil sulfone). Other pesticides (atrazine, bifenthrin, carbetamide, diuron, flazasulfuron, imidacloprid, simazine, tebufenpyrad, terbuthylazine, and thiametoxam), not applied on this vineyard plot or banned, were never detected.

3.1. Pesticide Air Concentrations Determined by Active Sampling

Pesticide air concentrations were monitored on five consecutive days in June (4–8 June 2013) using a DA80 HV-AAS, in both the particle (PM10) and gaseous phases. The total (gaseous and particle phases) daily pesticide concentrations (in pg m^{-3}) are listed in Table 2. Among the 36 investigated pesticides, 22 pesticides were quantified at least once, including two banned fungicides (carbendazim and flusilazole, banned in 2009), 15 pesticides were detected every day and six pesticides were detected four days out of five (either in the particulate phase or in the gaseous phase). It has to be noticed that only myclobutanil was applied on day 2 of the sampling week. Myclobutanil concentrations ranged from 36 pg m^{-3} on the day before treatment to 1238 pg m^{-3} on the day of treatment, i.e., a concentration 35 times higher. Interestingly, the maximum level was reached the day after treatment (1779 pg m^{-3}). Among the other pesticides detected that were not sprayed on vineyard plots during the sampling week, five pesticides (e.g., azoxystrobin and propiconazole) exhibited median concentrations ranging from 3 to 50 pg m^{-3}, 15 pesticides (e.g., *S*-metolachlor, cymoxanil or boscalid) ranging from 50 to 500 pg m^{-3}, and three pesticides higher than 500 pg m^{-3}. Folpet was detected at the highest levels, with a median concentration of 20,856 pg m^{-3}, followed by chlorpyrifos-methyl (median and maximum concentrations of 771 pg m^{-3} and 2338 pg m^{-3}, respectively) and spiroxamine (median concentration of 665 pg m^{-3}). Ametoctradin was observed at a maximum concentration of 1238 pg m^{-3} at day 3. Overall, the highest median concentrations were observed for pesticides that have been already sprayed before (in May) or during the sampling week. However, the concentrations of chlorpyrifos-methyl and spiroxamine were surprisingly high, even though they were never applied before the week of sampling. Other studies have reported the presence of pesticides at similar levels of contamination. Azoxystrobin (7.3–9.5 pg m^{-3}), carbendazim (12–230 pg m^{-3}), cyprodinil (11–20.4 pg m^{-3}), or iprovalicarb (6.9–10 pg m^{-3}) were detected in the particulate phase (PM 2.5) in Spain [48]. In France, *S*-metolachlor (11–20.4 pg m^{-3}) and spiroxamine (150–2010 pg m^{-3}) were present in the air [43]. From 2012 to 2015, several pesticides used in vineyards or crops were identified, and also found in our study, such as cymoxanil, spiroxamine, cyazofamid, or quinoxyfen, at concentrations ranging from 100 to 13,900 pg m^{-3} [46]. Other studies conducted in rural areas in France, particularly near vineyards, also reported the predominance of folpet in Aquitaine, Centre, and Alsace regions, with maximum concentrations in the range 10,000–80,000 pg m^{-3} [43,49–51].

Measured air concentrations showed also a high short-term variability (CV ranged from 20% to 100%), even for pesticides that were not sprayed on the sampling site during the week (i.e., all except myclobutanil). This variability appeared to be related to global meteorological conditions and most particularly to highly heterogeneous wind directions both intra- and interday (backward air mass trajectories computed using NOAA's HYSPLIT model, see Table S2), although low wind speeds (0.4–0.8 m s^{-1}) were locally recorded during the week (Table S2). In addition, for all detected pesticides (except myclobutanil), the lowest concentrations were reported at day 5; the drop in the concentrations can be explained by the heavy rainfall (71 mm) that occurred on that day (it did not rain for the first four days) (Table S2). This interday variability also highlighted the fact that a better representativeness of the measurements could be obtained using low volume active sampling or passive sampling instead, in particular, in risk assessment studies of chronic exposure to pesticides. Thus, active sampling, carried out at a high temporal frequency (a few hours), allows to study the different sources and potential atmospheric reactivity of pollutants, whereas passive sampling makes it possible to obtain an integrated vision (integrates all these sources of variability) and to pinpoint the most problematic compounds.

Table 2. Number of detections, median, minimum, maximum, and total concentrations (pg m^{-3}) of pesticides detected using HV-AAS.

Name	Detection Number (/5)	Total Concentrations [1] pg·m^{-3}									
		Day 1	Day 2	Day 3	Day 4	Day 5 (Rainy)	Median	Mean	Day 1 to Day 4 CV (%)	Minimum	Maximum
Ametoctradin	5	234.1	880.5	1237.8	197.8	6.5	234.1	511.3	80%	6.5	1237.8
Azoxystrobin	4	6.8	3.1	2.7	13.0	<LQ	3.1	5.1	75%	<LQ	13
Boscalid	4	54.8	65.4	53.2	38.3	<LQ	53.2	42.3	21%	<LQ	65.4
Carbendazim	4	15.8	5.8	4.4	3.8	<LQ	4.4	6.0	76%	<LQ	15.8
Chlorpyrifos-methyl	5	2338.2	771.1	1494.9	691.5	285.6	771.1	1116.3	58%	285.6	2338.2
Cyazofamid	4	51.0	121.5	62.6	59.6	<LQ	59.6	58.9	44%	<LQ	121.5
Cymoxanil	5	102.2	156.8	122.2	77.0	17.2	102.2	95.1	29%	17.2	156.8
Cyprodinil	5	10.1	32	17.8	8.2	3.7	10.1	14.4	64%	3.7	32
Flusilazole	2	3.9	<LQ	<LQ	2.9	<LQ	<LQ	1.4	21%	<LQ	3.9
Folpet	4/4	13,302.5	24,814.9	23,685.0	18,027.3	na *	20,856.2	19,957.4	27%	13,302.5	24,814.9
Iprovalicarb	4	1.5	163.8	131.3	49.9	<LQ	49.9	69.3	86%	<LQ	163.8
Kresoxim-methyl	5	89.5	230.5	125.6	143.5	53.6	125.6	128.5	41%	53.6	230.5
Mandipropamid	5	162	383.6	182.3	115.2	2.4	162.0	169.1	56%	2.4	383.6
Metalaxyl-M	5	195.3	411.2	291.4	177.1	108.7	195.3	236.7	40%	108.7	411.2
Metolachlor (S)	5	210.3	165.3	142.3	99.6	68.6	142.3	137.2	30%	68.6	210.3
Metrafenone	5	193.8	520.3	158.7	124.7	15.8	158.7	202.7	73%	15.8	520.3
Myclobutanil [2]	5	35.6	1237.7	1779.1	235.2	87.4	235.2	675.0	101%	35.6	1779.1
Propiconazole	4	10.4	16.1	5.7	3.5	<LQ	5.7	7.1	63%	<LQ	16.1
Quinoxyfen	5	28.2	59.2	169.7	54.0	16.8	54.0	65.6	81%	16.8	169.7
Spiroxamine	5	726.2	980.6	665.4	437.5	23.5	665.4	566.6	32%	23.5	980.6
Trifloxystrobin	5	51.8	253.9	181.8	136.8	20.9	136.8	129.0	54%	20.9	253.9
Zoxamide	5	24.5	73.1	111.8	63.1	1.4	63.1	54.8	53%	1.4	111.8

* na: not analyzed [1] Total concentrations: gas + particulate phases. [2] Myclobutanil was sprayed at day 2, underlined: pesticides sprayed before this sampling week (in May).

In the atmosphere, pesticides can be found either in the gaseous or particulate phase, depending on their properties (octanol air partition coefficient logK_{oa}, vapor pressure, Henry's law constant), on the environmental conditions (temperature, relative humidity, particle concentrations, etc.), and on the characteristics of ambient particles [52]. Gas and particle partitioning (G/P) affects the deposition of pesticides, their long-range transport, degradation, and impacts on human and ecosystem [52]. Almost all the compounds were only present in the PM10 particulate range (Figure 1). Chlorpyrifos-methyl was the only compound found almost entirely in the gaseous phase (99%) over the 5-day sampling period. A mean of 56% of Folpet was found in the gaseous phase, in agreement with distributions reported in other studies [12,45]. Five percent of Kresoxim-methyl was found in the gas phase (from day 3 to 5), and metalaxyl-M (<1%) was found only once as gaseous.

The octanol air partition coefficient (log K_{oa}) is one of the most reliable parameter to predict the distribution of the molecules between the atmospheric phases [53]. The higher the value, the more it will guarantee the presence of a molecule in the particulate phase. Using the K_{oa}-based partitioning model, compounds with log K_{oa} values below 10 are likely to be in the gaseous phase [45]. Chlorpyrifos-methyl (high vapor pressure) and folpet, which are the only two pesticides systematically quantified in the gaseous phase, have a log K_{oa} of less than 9 (Table 1). Kresoxim-methyl and metalaxyl-m, quantified once in the gaseous phase, have log K_{oa} values below 10.5. However, some pesticides with log K_{oa} in the range 8–10 were present at higher proportions in the particle phase (i.e., 100%) than predicted, including *S*-metolachlor, flusilazole, cyprodinil, and myclobutanil. Although the LOQs of the compounds were higher in the PUFs than in the filters and may explain some of the nondetections in the gas phase (this could be the case for *S*-metolachlor, flusilazole, and cyprodinil detected at low levels in the particulate phase), they were nevertheless sufficient to determine a least 1% gas phase partitioning for myclobutanil. The dominance toward the particulate phase observed for almost pesticides could be related

to mass transport kinetics limitations (nonequilibrium) following pesticide application as hypothesized by [54,55]. The aerosol composition, the pesticide formulation, and/or application technique can affect the gas-particle partitioning of pesticides. The aerosol composition was not characterized in this study, but it has been shown that a significant amount of mineral or soot constituents of the particles can increase the adsorption of polar compounds [54]. Several studies have suggested that the formulation adjuvants could affect the pesticide volatilization from surfaces and soils [56,57], or that the size of droplets projected by different nozzle types during application could influence the pesticide capacity to evaporate from sprayed droplets [55,58]. Regarding myclobutanil, which was sprayed during the sampling week, it was partitioned at 100% in the particulate phase. As mentioned previously, one possible explanation could be that, during the application, the sampler trapped the aerosol on the filter without the compound diffusing into the PUF. More research conducted during spraying activities are needed. In addition, sorption to aerosol particles may significantly increase the half-lives of pesticides in the atmosphere (from several days to one month), implying that they can be both persistent and therefore transported over long distances [59,60].
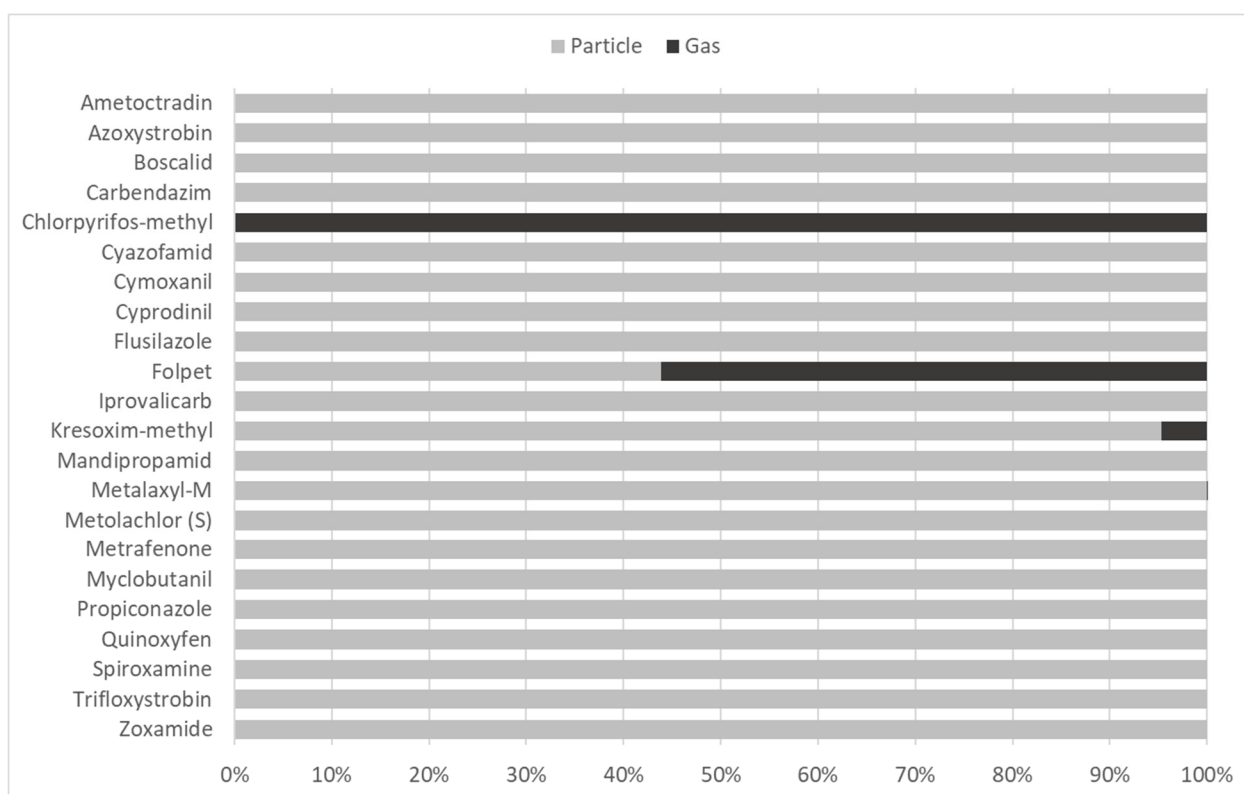

Figure 1. Mean gas and PM10 particle distribution (%) of the 22 pesticides quantified using a DA80 HV-AAS on five consecutive days in June 2013 (Gironde, France).

3.2. Pesticide Air Concentrations Determined by PAS

PUF-PAS were deployed for a period of one month or two months over a period of 10 months at two locations in a vineyard in a periurban area: one inside a vineyard plot (treated zone, TZ) and one located 100 m from the closest vineyard plot (nontreated zone, NTZ). All individual results are given in the Supplementary Table S6. Among the 36 pesticides monitored, 23 were detected at least once including 14 that were applied over the course of the year by the wine chateau (Figure 2). The detection frequency over all samples (independently of the site and of the sampling duration) was highest for folpet, boscalid, chlorpyrifos-methyl, zoxamide, and cyazofamid (respectively detected in 94%, 86%, 75%, 75%, and 71% of samples).
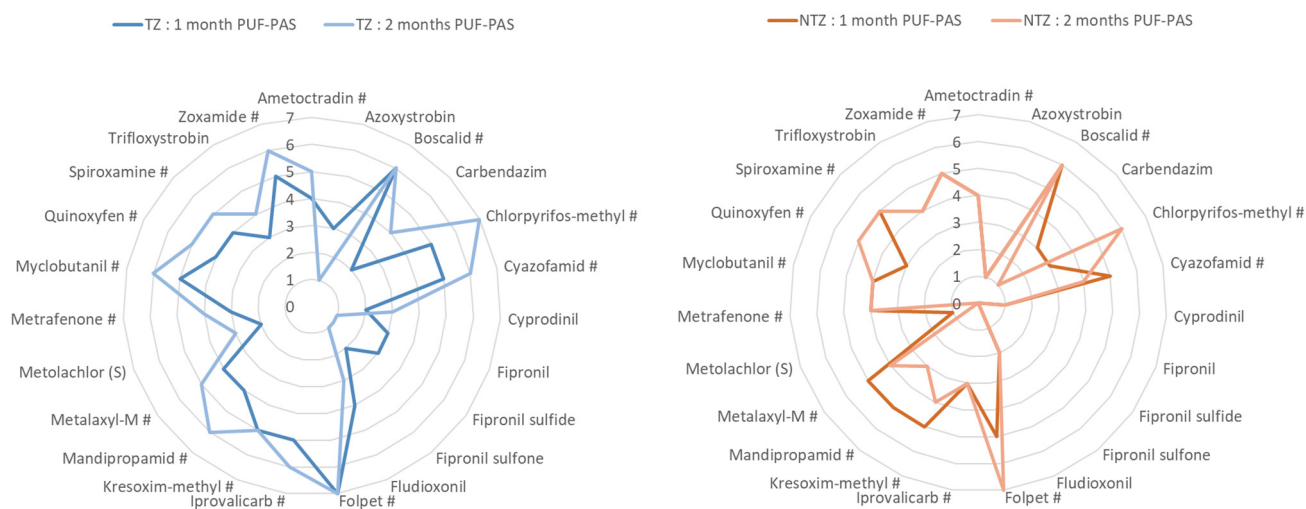
Figure 2. Detection frequencies by the PUF-PAS sampled for a period of one or two months from February to December 2013 in the treated zone (TZ) (**left**) and nontreated zone (NTZ) (**right**). #: Applied on the vineyard plot in 2013.

Compared to AAS performed in June, cymoxanil (with relatively high LOQs in PUF), and cyprodinil, propiconazole, flusilazole, azoxystrobin (only present at the lowest levels in the PM10 particle phase) were not detected by passive sampling at this period, which is consistent with the fact that PUF mainly collect the gaseous phase. On the contrary, fludioxonil was observed in June in PUF-PAS but was not sampled by HV-AAS, possibly due to its use by the surrounding growing farms at the end of June, after the HV-AAS sampling week. All other pesticides, almost exclusively distributed in the particle phase and not detected in the PUF-AAS (except chlorpyriphos-methyl, which was only present in the gaseous phase), were quantified in the PUF-PAS. These results confirm that PUF-PAS should be assumed to represent bulk rather than gas-phase compound concentrations due to the sampling of particle-bound compounds (e.g., [61,62]).

All pesticides applied and detected at least once in TZ were also detected at least once in NTZ. The two sampling sites showed heterogeneous impregnation levels but were marked by the same pesticides. Given the short distance between TZ and NTZ (a few hundred meters), it is unlikely that the lower quantities observed in NTZ were due to atmospheric degradation. However, NTZ is "protected" from prevailing winds by trees, which may be a vector for pesticides used at the chateau but also by other surrounding winegrowers. It should be noted that the problem of transport of pesticides from the atmosphere is important, in particular because of human exposure in the vicinity of farms. For example, a South African study analyzed pesticide concentration levels in the air in schools located near vineyards [63], and found kresoxim-methyl, cyprodonil, and boscalid concentrations of around 100 pg m^{-3}. In the Netherlands, outdoor air concentrations were 5–10 times higher at homes located within 250 m of agricultural fields than at homes located at a distance of more than 500 m during applications of pesticides. Chlorpropham and pendimethalin were found at concentrations of up to 2754 and 123 pg m^{-3}, respectively [64].

As little information was available on the passive accumulation of the pesticides of interest in the PUFs, two exposure periods were tested: 1 and 2 months. For applied pesticides, the PUFs deployed over the two time periods clearly discriminated the period of pesticide application, as shown by the levels highlighted in bold in Table S6. For these pesticides, the levels accumulated in each PUF were relatively comparable between 1 and 2 months PUF-PAS, both during and outside the application periods. The only exception was for quinoxyfen for which significant amounts of quinoxyfen were found in PUFs exposed for two months (March–May and April–June) and not in the PUF exposed for only one month (29 April–29 May), this compound having been sprayed on 17 May. For nonapplied pesticides (azoxystrobin, cyprodinil, fludioxonil, trifloxystrobin, fipronil, and

S-metolachlor), similar levels were also observed, accumulated amounts being relatively low (except for *S*-metolachlor exhibiting a peak in May during its application in the surrounding areas). Similar results were obtained for chlorpyriphos-ethyl and pyrimethanil captured by PUF-PAS after 30 and 60 days of exposure in rural area [65]. These results underlined the need to establish pesticide accumulation kinetics to define the best exposure time. Finally, extracts from the PUFs exposed for two months showed more matrix effects than PUFs exposed for one month, which could bias the quantification. Thus, for future passive monitoring of pesticides, it is recommended to choose an exposure time of one month as it is sufficient to detect the pesticides of interest, allows a better temporal resolution, and limits matrix effects.

Seasonal variations in time-weighted-average concentrations (ng PUF-PAS^{-1}) in the one-month PUF-PAS installed in TZ and NTZ area are presented in Figure 3. As already mentioned, PUFs were able to evidence the different pesticide applications, with greatly higher concentrations being registered the month of their application compared to the rest of the year (Table S6, values in bold).
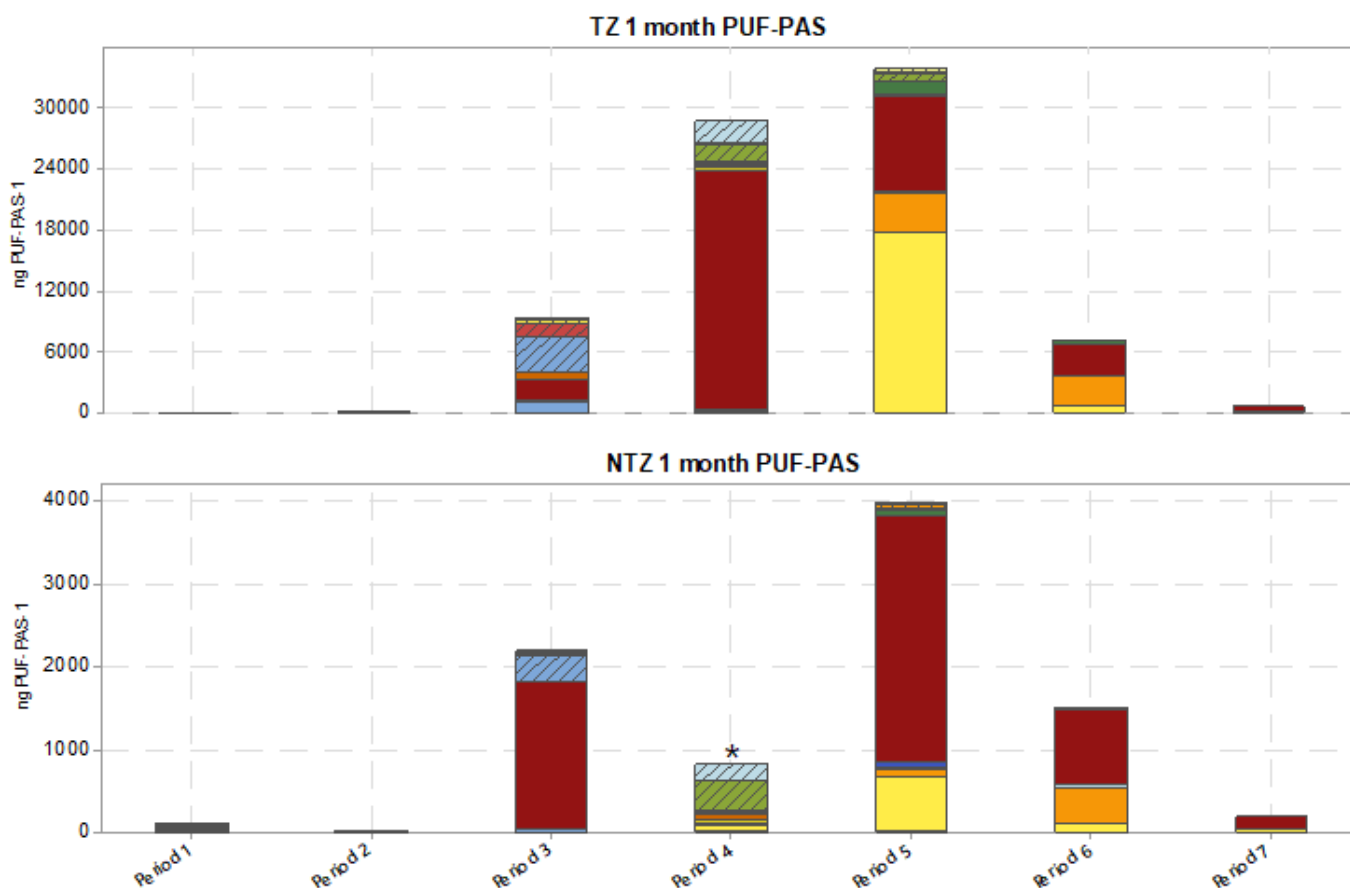

Figure 3. Monthly cumulative amounts (ng PUF-PAS^{-1}) found in the treated (TZ) and nontreated (NTZ) zones by PUF-PAS in 2013 and correspondence periods (period 1: 20 February–21 March, period 2: 21 March–23 April, period 3: 23 April–29 May, period 4: 29 May–26 June, period 5: 26 June–24 July, period 6: 24 July–11 September, period 7: 11 September–17 October). * Folpet and some other CUPs not analyzed (see Table S6).

Some pesticides were observed at low levels in the one-month PUF-PAS in NTZ in period 1 (February–March), whereas they were neither quantified in TZ nor in the PUF deployed in NTZ during two months. Their nondetection in TZ could be explained by the variability in sampling as well as in sources especially at such low levels close to the LQs; regarding the difference between the 1-month and 2-month PUFs on NTZ, desorption of compounds may have occurred and/or increased matrix effects in the 2-month PUF may

have affected sensitivity. Only folpet was identified (61 ng PUF-PAS^{-1}) in TZ in period 1. Small amounts of folpet (143 ng PUF-PAS^{-1}), cyprodinil (16 ng PUF-PAS^{-1}), boscalid (7 ng PUF-PAS^{-1}), and fipronil and two of its transformation products (3–6 ng PUF-PAS^{-1}) were found in period 2 (March–April) in the TZ. A spring peak was observed in period 3 (April–May) linked with wine-growing practices. Cumulative amounts of 9306 and 2195 ng PUF-PAS^{-1} were observed in TZ and NTZ, respectively, where folpet, metalaxyl-m, and ametoctradin represented 21%, 36%, and 13% of the PUF-PAS mass in the TZ (Figure 3). In NTZ, with the exception of period 1, folpet accounted for 60% to 80% of the quantity of pesticides accumulated in the PUFs during all the sampling periods (although a data was lacking for June in the one-month PUF, it was nevertheless observed in the two-month PUF). In TZ, total pesticide concentrations increased from May (period 3) to July (period 5), mainly due to the applications of folpet and boscalid. In period 4 (May–June), the total amount accumulated in the PUF was 28,634 ng PUF-PAS^{-1}, where folpet contributed for 82%, and myclobutanil and spiroxamine for 6–8%. Total pesticide levels reached their maximum in July (period 5) with a total concentration of 33,884 ng PUF-PAS^{-1}, where boscalid, folpet, and chlorpyriphos-methyl accounted for 52%, 28%, and 12%, respectively. In more detail, the highest levels of metalaxyl-m, mandipropamid, and metrafenone were found in May (period 3), of folpet, myclobutanil, spiroxamine, iprovalicarb, and quinoxyfen in June (period 4), and of zoxamide, kresomyl-methyl, azoxystrobin, chlorpyriphos-methyl, boscalid, and cyazofamid in July (period 5). Comparison with NTZ confirmed these observations: except for metrafenone and ametoctradin, the maximum quantities accumulated were obtained at the same time as in TZ, i.e., at the time of spraying. In addition, in TZ, folpet and boscalid were still detected in high quantities more than 2 months after their last application (Table S6).

The seasonality of pesticides in the atmosphere, with peak concentrations in spring and early summer, has already been reported in many studies [43,51,66]. In the category of nonsprayed pesticides in the vineyard, *S*-metolachlor reached a peak in May (period 3), in agreement with its use on maize crops at regional scale. Fludioxonil and trifloxystrobin also showed seasonal trends with peaks in May–June and June–July, which may correspond to its use by other vineyards in the neighborhood. Levels of cyprodinil and carbendazim showed no seasonality.

3.3. PAS-Derived Air Concentrations

Using the equation given in Section 2.5, it is possible to go from the quantities found on the PUF-PAS to real atmospheric concentrations by determining a sampling rate (*Rs*) thanks to air concentrations obtained with an active sampler codeployed during the sampling period (Table 3). This value is specific to each compound and depends on the meteorological parameters [47]. This calibration then makes it possible to compare the concentrations of pesticides found in this study but also with the results of other monitoring studies in different sites and years and with other sampling materials (XAD, SIP, SiC).

The previous section highlighted the marked variability of the quantities of pesticides accumulated in the PUFs from one month to the next, reflecting the impact of crop application. It is therefore difficult to consider that the average concentration of a molecule during the short active sampling campaign (4–8 June) could correspond to that in the passive sampling month (28 May–26 June). The active sampling campaign also showed that the concentrations could vary from one day to the next. However, *Rs* (Table 3) can be determined thanks to the equation given in Section 2.5 to estimate semiquantitative pesticide air concentrations using PUF-PAS (Table 4). *Rs* were determined from amounts accumulated in PUF of June at each of the three sites (TZ, NTZ, and in the courtyard of the wine chateau where the HV-AAS has been installed) for our information but only those determined in the courtyard of the wine chateau (where both AAS and PAS was performed) are discussed here and used to derive semiquantitative concentrations of pesticides (Table 3). The calculated *Rs* values ranged from 2 for chlorpyriphos-methyl to 155 m^3 d^{-1} for iprovalicarb. Of the 16 pesticides for which the individual *Rs* could be calculated, eleven

had Rs in the range 2–9 m^3 d^{-1} (ametoctradin, chlorpyriphos-methyl, cyazofamid, folpet, kresomil-methyl, metalaxyl-m, metrafenone, myclobutanil, quinoxyfen, trifloxystrobin, and zoxamide), two with Rs about 20 m^3 d^{-1} (mandipropamide and carbendazim), and 3 with high Rs between 80 and 155 m^3 d^{-1} (boscalid, spiroxamine, and iprovalicarb). Similar variability in Rs has been observed in other PAS studies for PAHs, PCBs, OCPs, and PBDEs (see [62,67]). Some of these high Rs, notably the two highest ones obtained for iprovalicarb and spiroxamine, are explained by the high quantities accumulated in the PUF-PAS compared to those obtained in AAS since they were sprayed in the second half of June, whereas the active sampling was carried out just before. It is therefore clear that these high values ($Rs > 10$) are not representative of true sampling rates for these five pesticides; for these five ones and for those without calculated Rs, a constant value of 4 m^3 d^{-1} supported by numerous previous investigations has been used (e.g., [30,31,34,42]). Then, using the values quantified in PUF-PAS over the entire passive sampling campaign and sampling times (Table S6), the average pesticide concentrations were able to be estimated (Table 4).

Table 3. Accumulated quantities in PUF-PAS (ng), average pesticide concentrations (pg m^{-3}), and derived individual sampling rates (Rs) during the codeployment of passive and active samplers in June 2013 (Gironde, France).

Compound	Quantities Found in PUF-PAS (ng) on TZ in June (Period 4)	Quantities Found in PUF-PAS (ng) on NTZ in June (Period 4)	Quantities Found in PUF-PAS (ng) Next to HV-AAS Area in June	Average Concentration (Gas and Particulate Phases) Obtained during 5 Days (June) by DA80 HV-AAS (pg·m^{-3})	Estimated Rs for TZ (m^3.d^{-1})	Estimated Rs for NTZ (m^3.d^{-1})	Estimated Rs Next to HV-AAS Area (m^3.d^{-1})	Mean Rs for TZ, NTZ, and HV-AAS Area (m^3.d^{-1})
Ametoctradin	58	34	**46**	511	4.1	2.4	**3.3**	3.2
Azoxystrobin	<LQ	<LQ	**<LQ**	5	-	-	-	-
Boscalid	79	56	**93**	42	67.2	47.6	**79.1**	64.6
Carbendazim	2	6	**4**	6	11.9	35.7	**23.8**	23.8
Chlorpyrifos-methyl	137	<LQ	**61**	1116	4.4	-	**2.0**	3.2
Cyazofamid	18	11	**12**	59	10.9	6.7	**7.3**	8.3
Cymoxanil	<LQ	<LQ	**<LQ**	95	-	-	-	-
Cyprodinil	<LQ	<LQ	**<LQ**	14	-	-	-	-
Fludioxonil	31	<LQ	**<LQ**	<LQ	-	-	-	-
Flusilazole	<LQ	<LQ	**<LQ**	1	-	-	-	-
Folpet	23,481	* na	**5016**	19,957	42.0	-	**9.0**	25.5
Iprovalicarb	414	54	**299**	69	214.3	28.0	**154.8**	132.3
Kresoxim-methyl	21	10	**14**	129	5.8	2.8	**3.9**	4.2
Mandipropamid	176	59	**94**	169	37.2	12.5	**19.9**	23.8
<u>Metalaxyl-M</u>	41	20	**25**	237	6.2	3.0	**3.8**	4.3
Metolachlor (S)	150	<LQ	**<LQ**	137	39.1	-	-	39.1
<u>Metrafenone</u>	42	17	**23**	203	7.4	3.0	**4.0**	4.8
Myclobutanil	1774	371	**117**	675	93.9	19.7	**6.2**	39.9
Propiconazole	<LQ	<LQ	**<LQ**	7	-	-	-	-
<u>Quinoxyfen</u>	51	<LQ	**13**	66	27.6	-	**7.3**	17.3
Spiroxamine	2193	189	**1463**	567	138.3	11.9	**92.2**	80.7
Trifloxystrobin	10	6	**9**	129	2.8	1.7	**2.5**	2.3
Zoxamide	6	3	**5**	55	3.9	1.9	**3.2**	3.0

* na: not analyzed; underlined: pesticides that have been applied before (in May) or during the sampling campaign of June; in bold: values that are used and discussed here (for information purposes regarding other data).

Table 4. Air concentrations (pg m^{-3}) estimated from the cumulative quantities in the PUF-PAS and Rs with correspondence periods (period 1: 20 February–21 March, period 2: 21 March–23 April, period 3: 23 April–29 May, period 4: 29 May–26 June, period 5: 26 June–24 July, period 6: 24 July–11 September, period 7: 11 September–17 October); * na: not analyzed; colors: distribution of air pesticides in 2013 in the treated (TZ) and nontreated (NTZ) zones with the lowest (from the most faintly colored) to the highest concentrations (to the most strongly colored).

| | Atmospheric Concentration (pg·m^{-3}) | | | | | | | | | | | | | | |
| | Period 1 | | Period 2 | | Period 3 | | Period 4 | | Period 5 | | Period 6 | | Period 7 | | | |
	TZ	NTZ	TZ	NTZ	TZ	NTZ	TZ	NTZ	TZ	NTZ	TZ	NTZ	TZ	NTZ	Max.	Min.
Ametoctradin	-	-	-	-	10,459	372	628	368	195	97	37	12	-	-	10,459	12
Azoxystrobin	-	-	-	-	7	-	-	-	188	152	-	-	7	-	188	7
Boscalid	-	233	61	53	79	-	705	500	157,277	5714	3908	602	1431	278	157,277	53
Carbendazim	-	-	-	-	43	21	18	54	-	-	-	5	-	-	54	5
Chlorpyrifos-methyl	-	-	-	-	714	-	2446	-	70,196	1714	28,602	4347	167	97	70,196	97
Cyazofamid	-	38	-	-	20	8	88	54	24	-	196	75	42	8	196	8
Cyprodinil	-	-	121	-	-	-	-	-	429	268	-	-	-	-	429	121
Fipronil	-	-	23	-	-	-	-	-	27	-	10	-	-	-	27	10
Fipronil sulfide	-	-	45	-	-	-	-	-	18	-	10	-	-	-	45	10
Fipronil sulfone	-	-	45	-	-	-	-	-	-	-	15	-	-	-	45	15
Fludioxonil	-	-	-	-	93	-	277	-	1107	607	56	41	-	-	1107	41
Folpet	234	-	481	81	6222	5597	93,179	na *	37,714	11,754	7465	2059	1426	475	93,179	81
Iprovalicarb	-	28	-	-	11	-	2957	386	507	50	33	-	11	-	2957	11
Kresoxim-methyl	-	27	-	-	44	15	192	92	10,888	476	858	21	57	-	10,888	15
Mandipropamid	-	78	-	-	6086	21	1571	527	304	54	77	10	-	-	6086	10
Metalaxyl-M	-	118	-	-	24,992	2489	385	188	179	28	21	16	-	-	24,992	16
Metolachlor (S)	-	-	-	-	10,579	-	1339	-	-	161	-	-	-	-	10,579	161
Metrafenone	-	52	-	-	1814	29	375	152	63	18	-	-	-	-	1814	18
Myclobutanil	-	83	-	-	32	5	10,219	2137	4303	52	46	-	18	-	10,219	5
Quinoxyfen	-	-	-	-	51	106	250	-	284	201	20	17	-	-	284	17
Spiroxamine	-	293	-	-	521	71	19,580	1688	509	54	26	15	-	-	19,580	15
Trifloxystrobin	-	14	-	-	34	11	143	86	43	29	-	-	-	-	143	11
Zoxamide	-	119	-	-	330	45	67	33	4777	145	140	19	61	-	4777	19

It should be noted that better Rs estimates could probably have been obtained by codeploying the HV-AAS throughout the PAS month (which was not possible in our case due to sampler availability and operational costs) and/or by codeploying low volume active samplers (LV-AAS) (not yet available in our laboratory at that time) rather than HV-AAS [62]. Given the differences in the physicochemical properties of the compounds studied (e.g., log K$_{oa}$ ranging from 6 to 14), the use of a single sampling rate for some of them involves high uncertainty in the determination of average concentrations. Nevertheless, estimated air concentrations were in agreement with the data available for banned and currently used pesticides in rural areas (e.g., [56,65,68,69]), especially close to cultivated plots as in this study [70,71]. Concentrations of pesticides that were detected but were not applied on the vineyard plot ranged from <LOQ to 1 ng m^{-3}, except for S-metolachlor with a maximum concentration about 10 ng m^{-3}. The same range was observed for applied pesticides outside their application periods (except for high levels of folpet from April to October), whereas their concentrations reached levels ranging from 2 to 157 ng m^{-3} during their application period. The highest levels were registered in TZ in June and July for boscalid, folpet, and chlorpyriphos-methyl with maximum concentrations of 157, 93, and 70 ng m^{-3}, respectively. In NTZ, their concentrations were in the range 0.5–12 ng m^{-3} during their application period. These results reveal general impregnation of pesticides, transfer to nontarget areas, and seasonality in the atmospheric environment consistent with that reported in other studies [43,51,66].

4. Conclusions

In the present study, the occurrence and the seasonal patterns of pesticides were monitored in a wine-growing environment using PUF-PAS over a period of 10 months and HV-AAS for one week. HV-AAS samples collected on five consecutive days provided information on the relatively high short-term variability of pesticide concentrations (for most pesticides) as well as in the (G/P) partition of pesticides, which, except for chlorpyriphos-methyl and folpet (and to a lesser extent kresomil-methyl), were mainly distributed in

the PM10 particulate phase. This study also showed that PUF-PAS are effective tools to monitor pesticides in ambient air and allowed to obtain an integrated vision of the pesticide contamination of air in a periurban area for almost a year. Twenty-three pesticides out of 36 were detected, with concentrations ranging from pg m^{-3} to ng m^{-3}. A sampling period of one month was sufficient to obtain high temporal PAS data and to evidence high seasonal variations in air concentrations, the highest variations being observed during the period of pesticide application (May–August). Several pesticides not used by the chateau or banned were nevertheless detected in the air, again underlining the ubiquity of these pesticides in the air and their transport to surrounding areas.

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