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1 **A multiresidue analytical method on air and rainwater for**
2 **assessing pesticide atmospheric contamination in untreated areas**

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21 **Abstract**

22 The use of pesticides in agriculture to protect crops against pests and diseases generates
23 environmental contamination. The atmospheric compartment contributes to their dispersion at
24 different distances from the application areas and to the exposure of organisms in untreated
25 areas through dry and wet deposition. A multiresidue analytical method using the same TD-
26 GC-MS analytical pipeline to quantify pesticide concentrations in both the atmosphere and
27 rainwater was developed and tested *in natura*. A Box-Behnken experimental design was used
28 to identify the best compromise in extraction conditions for all 27 of the targeted molecules in
29 rainwater. Extraction yields were above 80% except for the pyrethroid family, for which the
30 recovery yields were around 40-59%. TD-GC-MS proved to be a good analytical solution to
31 detect and quantify pesticides in both target matrices with low limits of quantification. Twelve
32 pesticides (six fungicides, five herbicides and one insecticide) were quantified in rainwater at
33 concentrations ranging from 0.5 ng.L⁻¹ to 170 ng.L⁻¹ with a seasonal effect, and a correlation
34 was found between the concentrations in rainwater and air. The calculated cumulative wet
35 deposition rates are discussed regarding pesticide concentrations in the topsoil in untreated
36 areas for some of the studied compounds.

37 **Keywords:** landscape, concentration, impact, wet deposition, SBSE

38 **Graphical abstract**

39 **Highlights:**

- 40 • A reliable method to quantify pesticides in rainwater and air was tested *in natura*
- 41 • 27 pesticides were monitored in rainwater during an agricultural season in France
- 42 • Collections were done by tenax tubes for air and stir bar sorption for rain.
- 43 • Fungicides, herbicides, and insecticides were detected in both air and rainwater
- 44 • The contribution of wet deposition to the exposure of untreated areas was evaluated

45 **1 Introduction**

46 Pesticides are commonly used in agriculture to protect crops from pests and diseases leading to
47 contamination of the environment. The atmospheric compartment contributes to their dispersal
48 at different distances from the application areas (van Dijk and Guicherit, 1999; FOCUS 2008).
49 Consequently, organisms in untreated areas (*e.g.* Pelosi et al., 2021) and also human populations
50 (*e.g.* Dereumeaux et al., 2020, Teyssere et al., 2020) can be exposed. Pesticides are emitted
51 into the atmosphere during application by dispersion of spray droplets and after application
52 mainly by volatilization. Once in the atmosphere, compounds can partition into their gaseous
53 and particulate phases, be degraded, transported in the wind, and finally deposited by dry
54 deposition (gaseous or particulate phases deposited by turbulence) or wet deposition (by rain)
55 (Woodrow et al., 2019).

56 Both dry and wet deposition should be considered in risk assessments for non-target
57 ecosystems. Indeed, FOCUS (2008) recommends that during registration procedures dry
58 deposition should be taken into account in risks assessments for non-target ecosystems located
59 close to the treated plots, in addition to the drift already considered. Through modeling studies
60 coupling volatilization and local atmospheric dispersion models, Asman et al. (2001) and Bedos
61 et al. (2013) found that the contribution of dry deposition to water surface contamination may
62 be higher than the contribution of drift for volatile pesticides. Regarding wet deposition, Potter
63 and Coffin (2017) analyzed three years of rainfall monitoring in a small watershed in the USA
64 and concluded that wet deposition should be included in pesticide risk assessments. Wet
65 deposition rates can reach high levels, depending on the compound. For instance, studies in
66 Europe (van Dijk and Guicherit, 1999 ; Asman et al., 2005) found wet deposition rates ranging
67 from a few $\text{mg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ to several $\text{g}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$. More recently in Sweden, Kreuger et al. (2017)
68 carried out long-term monitoring of pesticide concentrations in rainwater and calculated wet
69 deposition rates ranging from 9 to 800 $\text{mg}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$, which represents up to 0.1 % of the applied

70 dose for some compounds. All these deposition studies relied on pesticide monitoring in the air
71 and rainwater.

72 Regarding airborne pesticide concentrations, most monitoring studies, which are generally
73 carried out to assess population exposure, focused on background concentrations. Datasets on
74 background concentrations have been available in various regions of France since the early
75 2000s, thanks to campaigns conducted by the Approved Air Quality Monitoring Associations
76 (AASQAs) (data available in the Phytatmo database 2019; see also Désert et al., 2018 and
77 Villiot et al., 2018). There are however, no continuous monitoring programs of rainwater
78 contamination organized at the French national level. However, data is available in reviews
79 such as Dubus et al. (2000), Asman et al. (2001) or Bedos et al. (2002), which concluded that
80 the range of concentrations in rainwater was large, from non-detectable to values higher than
81 100 ng.L⁻¹. More recently, Scheyer et al., (2007) observed high pesticide concentrations in
82 Eastern France, particularly during periods of intensive applications on crops. The quantitative
83 assessment of the contribution of atmospheric contamination and deposition to untreated areas,
84 including exposure of the human population, remains a challenge as agricultural practices are
85 constantly evolving (e.g., banning, introducing new molecules on the market, using biocontrol
86 products). Monitoring programs are therefore still needed to assess the state of environmental
87 contamination and its temporal trends, as well as to evaluate the effectiveness of environmental
88 regulation policies, as stressed by Asman et al., (2005).

89 Various measurement systems are available to quantify pesticide contamination of the
90 atmosphere. This is a challenging measurement because the concentrations to be detected can
91 be relatively low, less than 2 ng.m⁻³ (Phyatmo 2019), and complex mixtures of compounds are
92 present. Regarding the gaseous and particulate phase, active and passive samplers are used to
93 trap pesticides from the air (Yusà et al., 2009; Coscollà and Yusa, 2016). Passive samplers
94 involve exposing a sorbing phase to ambient air to collect the gas phase. The sampled pesticides

95 migrate by molecular diffusion to the adsorbent where they are trapped (Namieśnik et al., 2005).
96 The sampling time varies from a few weeks to several weeks. Because an electricity supply is
97 not required, the use of passive samplers over long periods in remote areas remains a convenient
98 technique. The main drawback of this sampling technique is that the volume of air passing
99 through the adsorbent during exposure must also be accurately assessed (Wania et al., 2003;
100 Lévy et al., 2020). According to Coscollà and Yusa (2016), although improvements are
101 possible, passive sampling will always remain more uncertain than active sampling. Active
102 samplers actively pump air through an adsorbent to collect the pesticides present in particulate
103 and gaseous phases. The sampling time is shorter than for passive samplers, typically a few
104 hours to a few days, and it can be reduced depending on measurement objectives and the
105 sensitivity of chemical analyses. In contrast to passive samplers, active samplers allow accurate
106 measurement of the volume of air sampled using a flow meter, but require a power supply,
107 which can be difficult in remote areas and this is the main drawback of this method.

108 Once trapped in the adsorbent, extraction of the sorbing phase is required for both techniques.
109 This can be carried out either using organic solvents or thermal desorption (TD). Using solvents
110 increases the uncertainties due to the numerous preparation steps required before analysis
111 (extraction, concentration) and it is also time consuming. Thermal desorption does not require
112 a concentration step. Furthermore, when coupled directly with gas chromatography (GC) and
113 mass spectrometry (MS) systems, it has a lower limit of quantification than the solvent
114 extraction technique (Bedos et al., 2006). Thus, active sampling coupled with TD-GC-MS is an
115 interesting analytical technique for quantifying airborne pesticides. (Bedos et al., 2006 ;
116 Clément et al., 2000 ; Briand et al., 2002). Two drawbacks of this technique are that it can only
117 be used for non-thermosensitive compounds, and the sample is destroyed during the analysis,
118 preventing further analysis.

119 To quantify pesticide concentrations in rainwater, Stir Bar Sorptive Extraction (SBSE)
120 techniques (Baltussen et al., 1999) can be used, especially for small sample volumes. A larger
121 amount of sorptive extraction phase is available in comparison to other extraction techniques
122 such as SPME (Solid Phase Microextraction). As a result, more pesticides can be extracted
123 using SBSE, which increases the sensitivity and decreases the limits of quantification of this
124 technique (David and Sandra, 2007). The Stir Bars (Twister®) are directly extracted by TD
125 (Sandra et al., 2003) and analyzed by GC-MS. The same analytical pipeline can therefore be
126 used for both gas and rainwater matrices. This is an advantage that facilitates monitoring
127 concentrations in both air and water and reduces measurement uncertainties. The multiresidue
128 method has the advantage of decreasing the number of analyses. However, it is generally a
129 complex process that requires compromises due to the diversity of the chemical properties of
130 the compounds.

131 This study was part of a project being conducted in the Long Term Socio-Ecological Research
132 (LTSER) “Zone Atelier Plaine & Val de Sèvre” (ZAPVS) (Bretagnolle et al. 2018a), aiming to
133 investigate the contamination of several environmental matrices (air, rainwater and soils) and
134 soil macro-fauna (earthworms, carabids and small mammals) by pesticides in an intensive
135 agricultural landscape (Pelosi et al., 2021). Here, we focused on assessing the contribution of
136 atmospheric pollution to this exposure. Among the pesticides frequently used in the sampling
137 area and those showing potential emission to the atmosphere, 27 molecules were targeted. Our
138 objective was to develop a multiresidue analysis method using a single analytical pipeline to
139 quantify both atmospheric and rainwater pesticide concentrations in sample collected *in natura*.
140 Our objective was to develop a multiresidue analysis method using a single analytical pipeline
141 to quantify both atmospheric and rainwater pesticide concentrations in sample collected in
142 *natura*. A comparison of the data thus obtained on rainwater contamination with existing data
143 on air contamination in the same region is presented together with an analysis based on

144 compound physico-chemical properties. Wet deposition ($\mu\text{g}\cdot\text{m}^{-2}$) was calculated given the
145 rainfall amount and pesticide quantified concentration to assess its contribution to the
146 contamination of untreated areas.

147 **2 Materials and methods**

148 2.1 Study area, rainwater and air sampling

149 This study was carried out in the Long Term Socio-Ecological Research (LTSER) area, known
150 as the "Zone Atelier Plaine & Val de Sèvre (ZAPVS)" 46°11'N - 0°28'W Villiers-en-Bois,
151 France (Bretagnolle et al., 2018a). Biodiversity, ecological functions as well as farmer practices
152 and land use are annually monitored in this intensive cereal plain of 435km². In 2018,
153 agricultural practices were recorded (especially pesticides) during farmer interviews in at least
154 100 fields per year (see Bretagnolle et al. 2018a, b). Farmer interviews allow very accurate data
155 on pesticide use to be recorded (products, active molecules, timing of application etc.).
156 Rainwater was collected at the research station « Centre d'Etudes Biologiques de Chizé » on a
157 weakly basis from March to November 2018 with a refrigerated collector at 4°C (Eigenbrodt
158 NSA 181/KS, DE). The samples were stored in polyethylene terephthalate bottles at -20°C
159 before analysis. The amount of rainwater per week was measured with an ARG100 Tipping
160 Bucket rain gauge and was recorded with a CR10 data logger (Campbell Sci, USA). Rainwater
161 sampling was in a forested area and assumed to represent the background level of wet
162 deposition in the whole area.

163 For air sampling, two 1 km² landscapes windows with contrasting agricultural management
164 practices were selected: the first contains a high proportion of conventionally farmed arable
165 crops (98 % hereafter "CF landscape") and the second a high proportion of organically farmed
166 arable crops (69 % hereafter "OF landscape").

167 Air sampling was conducted daily from the 22nd May to 1st June 2018. Ambient air was sampled
168 at 1.6 m above the ground surface at a flow rate ranging from 0.52 to 1.13 L.min⁻¹ over 24 hour
169 sampling periods. Pesticides were trapped on cartridges filled with 60 mg Tenax TA adsorbent
170 (Gerstel®, DE). The deployed sampling system operated on a 12V supply and therefore did not
171 require a nearby power source. Volumetric controllers (Gallus 2000, Schlumberger, FR) were
172 used to measure the volume of air sampled by each cartridge. Before the sampling campaign,
173 cartridges were pre-conditioned by heating at 280°C under a helium stream of 60 L min⁻¹ for 6
174 hours. After exposure, cartridges were closed and stored in the dark at 4°C until analysis.

175 2.2 Selected pesticides

176 Herbicides, fungicides, and insecticides were studied. In total, 27 pesticides belonging to 14
177 chemical substance families were analysed (Table 1). These pesticides were chosen as they
178 were frequently used in the sampling area (see Pelosi et al., 2021), were compatible with
179 multiresidue analysis, and have significant potential for atmospheric emission. Some have
180 isomers as specified in Table 1 and a total of 33 molecules was thus considered.

181 2.3 Analytical method development

182 2.3.1 *Rainwater sample extraction*

183 SBSE was used to extract pesticides from rainwater. SBSE is based on the partitioning of
184 pesticides between the water sample studied and a specific polymeric phase supported by a
185 magnetic bar (called a "Twister", Gerstel®10mm×0.5mm with a 24 µL Polydimethylsiloxan
186 (PDMS) coating). Several factors can modify the equilibrium and affect the extraction yield.
187 Some factors were fixed according to Prieto et al. (2010), and based on our instrumentation: the
188 stirring speed (800 rpm), the extraction temperature (25°C), the sample volume (10mL) and the
189 acceptor phase volume (24 µL PDMS). A Box-Behnken experimental design (Box and
190 Behnken, 1960) was conducted to study the influence of the following factors : the addition of
191 an inert salt (NaCl, Factor A), the addition of an organic modifier (Acetone, Factor B) and the

192 extraction time (Factor C). Box-Behnken designs are based on three-level incomplete factorial
193 designs. A series of experiments was set up to study the relationships between factors and
194 response. The experimental domain and the Box-Behnken design used are detailed in Table S.1.
195 Statistical analysis was performed with the software “Statgraphics Plus 4.1”, to model the
196 response Y (peak areas corresponding to the quantity of extracted molecules) as a function of
197 the chosen factors A, B, C (extraction conditions). The obtained Pareto diagram was used to
198 identify which factors significantly affected the quantity of extracted molecules. The statistical
199 model allowed the factor levels that maximized the response (simulated optimum conditions)
200 to be determined (Bourdat-Deschamps et al., 2007) and followed the equation given in Eq.S1.

201 Before being used, Twister® were preconditioned using Gerstel TCD2 C200. They were heated
202 at 280°C under a helium stream of 60 mL.min⁻¹ for four hours. Up to two Twister® bars could
203 be extracted and analyzed at the same time (in the same analytical tube called a TDU TUBE)
204 by the analytical pipeline used in the laboratory. It was thus possible to choose up to two
205 different extraction conditions. This procedure helped determine the best compromise for the
206 extraction of all molecules, since one condition was more efficient for some compounds and
207 another for the other compounds. The optimised extraction method applied to rainwater samples
208 was the following: 30% (m/v) NaCl was added to 10 mL of rainwater sample and a first
209 extraction was carried out for 135 min (1st Twister®). 10% (v/v) acetone was added to a second
210 aliquot of 10 mL rainwater sample and a second extraction was carried out for 135 min with a
211 second stirring Twister®. Then both Twister® bars were placed together in a “Thermal
212 Desorption Unit” (TDU tube described in the following section) for analysis.

213 2.3.2 Analysis by TD-GC-MS

214 TD-GC-MS was used to analyze the pesticides in rainwater and air samples. Tenax tubes and
215 Twister® were desorbed using a Thermo Desorption Unit (TDU, Gerstel, DE). The TDU was
216 programmed to desorb pesticides from tubes and Twister® from 50 to 280 °C for 8 min at a

217 rate of 60 °C.min⁻¹. Pesticides were then cryo-focused in the programmable temperature
218 vaporization injector at -20 °C using a baffled glass liner. Compound separation was carried
219 out using an Agilent 7890B gas chromatograph equipped with a capillary column (30 m length,
220 0.25 mm internal diameter, 0.25 µm df, HP-5MSUI column, Agilent). The oven temperature
221 was initially set at 70 °C hold 2 min, heated at a rate of 25°C.min⁻¹ to 150 °C, then heated at a
222 rate of 3°C.min⁻¹ to 200°C and finally at 8°C.min⁻¹ to 300°C hold 1 min. Helium was used as
223 carrier gas, with a flow rate of 1.5 mL.min⁻¹. As mentioned in Table 1, several of the studied
224 pesticides have isomeric forms: cypermethrin (four isomers), cyproconazole (two isomers),
225 propiconazole (two isomers) and tau-fluvalinate (two isomers). With the chromatographic
226 conditions used, a total of 32 compounds out of the 33 possible compounds were separated: the
227 27 selected pesticides given in Table 1, three isomeric forms of cypermethrin separated in
228 addition to the main one, one isomeric form of propiconazole and one isomeric form of tau-
229 fluvalinate. We also found two isomers of cyproconazole but they could not be separated.
230 Therefore, only 32 molecules could be quantified. Pesticide detection was performed with an
231 Agilent 5977A mass spectrometer. The Electronic Impact (EI) mode was at +70 eV and a
232 SIM/SCAN mode was used. The SCAN monitoring range was set from 30 to 510 *m/z*. Two
233 ions per molecule were selected in the SIM mode (Table S. 2). The temperature of the ion source
234 and Quadrupole analyzer were set at 230 and 150°C, respectively. TD-GC-MS data were
235 processed with MassHunter software (version B.07.04.5560, Agilent Technologies Inc.). “To
236 ensure an accurate identification and quantification of the studied molecules, we worked on the
237 EIC (Extracted Ion Chromatogram) SIM chromatograms. The extracted ion chromatogram is
238 generated by separating the ions of interest from the SIM data file (Figure S.1). All the
239 chromatographic peaks were checked one by one by analyzing (a) the retention time of the
240 molecules (b) the presence for each molecule of its specific ions (c) the intensity ratios of the

241 SIM signals and the 2 specific ions. In case of noncompliance with the 3 criteria of
242 chromatographic peak, the results were not kept in the study.”

243 2.3.3 *Quantification step*

244 Standard solutions at $100 \text{ ng}\cdot\mu\text{L}^{-1}$ in acetone of each studied molecule were purchased from
245 Restek. To avoid inter-molecule reactivity, the supplier suggested separating the 27 pesticides
246 and their isomers into three batches. Dilutions in acetone (Carlo Erba) of these commercial
247 solutions were made to obtain standard concentrations from 0.01 to $2 \text{ ng}\cdot\mu\text{L}^{-1}$ (Table S.1). To
248 quantify pesticides in rainwater, a calibration curve was built using Twister® extraction of 10
249 mL of ultrapure water (MilliQ, Merck) placed in a light-resistant flask and spiked with $10 \mu\text{L}$
250 of each of the three batches of standard solutions at increasing concentrations (0.01 ; 0.02 ; 0.04 ;
251 0.05 ; 0.10 ; 0.20 ; $0.40 \text{ ng}\cdot\mu\text{L}^{-1}$). These calibration samples were extracted at the same time as
252 the rainwater samples, to obtain a calibration curve. For trueness recoveries (see section 2.4)
253 below 80 %, the results were corrected considering these recoveries”.

254 To quantify pesticides in the air, clean Tenax® tubes were spiked with $1 \mu\text{L}$ of standard solution
255 (0.04 ; 0.1 ; 0.2 ; 0.4 ; 0.6 and $2 \text{ ng}\cdot\mu\text{L}^{-1}$) taken up with a glass syringe and deposited on the grid
256 of the Tenax tube. The tubes were then dried to evaporate the acetone solvent with a helium
257 stream at $0.5 \pm 0.05 \text{ L}\cdot\text{min}^{-1}$ flow rate for 15 min. This was carried out three times to
258 successively spike the same calibration Tenax tube with each standard batch. To quantify the
259 mass of compound trapped, field tubes were analyzed on the same day as the calibration ones
260 to ensure that the analytical conditions were the same.

261 2.4 Method characterization

262 SBSE theoretical recovery of a compound from a water sample was calculated with the
263 following equation (Baltussen et al.,1999):

$$264 \quad \frac{m_{SBSE}}{m_0} = \frac{\left(\frac{K_{OW}}{v_W}\right)}{1 + \left(\frac{K_{OW}}{v_{SBSE}}\right)} * 100 \quad \text{Eq. 1}$$

265 where m_{SBSE} is the mass of analyte in the SBSE, m_0 is the amount of analyte present in the
 266 water sample, K_{OW} is the octanol-water partitioning coefficient, v_W and v_{SBSE} are the water
 267 sample volume and the volume of polydimethylsiloxane (PDMS) phase on the Twister[®],
 268 respectively.

269 To evaluate the efficiency of pesticide extraction from rainwater, the trueness experimental
 270 recovery was determined as follows: some ultrapure water (MilliQ, Merck) (free from
 271 pesticides) and a rainwater sample taken in the ZAPVS (previously analyzed and found to be
 272 free of pesticides) were spiked with each of the studied molecules from a standard solution at a
 273 concentration of 0.4 ng.L⁻¹. The SBSE protocol established above was then carried out on two
 274 replicates of each water sample. Experimental trueness of the recovery of each pesticide studied
 275 was evaluated by comparing the quantities of molecules extracted from the rainwater (P_{rain}) and
 276 the ultrapure water (P_{pure}). It was calculated as follows:

$$277 \quad \text{Experimental trueness} = P_{rain}/P_{pure} * 100 \quad \text{Eq. 2}$$

278 and compared to the theoretical one calculated with Eq1.

279 To evaluate the efficiency of the chosen extraction conditions, following the experimental
 280 design results, we compared them to the modeled optimum for each compound by calculating
 281 a ratio (given as a percentage of the optimum, PO) based on the following equation:

$$282 \quad PO = \frac{Y_{cond1} + Y_{cond2}}{Y_{opt}} \quad \text{Eq. 3}$$

283 with Y_{cond1} the peak area representing the quantity of molecules extracted in the first extraction,
 284 Y_{cond2} the peak area representing the quantity of molecules extracted in the second extraction,

285 Y_{opt} the peak area simulated representing the quantity of molecules extracted under simulated
286 optimum conditions.

287 To validate the effectiveness of standard tube preparation for air extractions, sequential doping
288 (three different spikes on the Tenax tube) as described in section 2.3.3 was compared to the
289 routinely used method for doping (only one spike on Tenax tube) (Figure S.2). The thermal
290 desorption efficiency step was also tested by analyzing the same sample twice and calculating
291 the ratio of the amount of compound measured after the second desorption to the amount
292 measured with the first desorption.

293 The limits of detection (LOD) and quantification (LOQ) were established for both air and water
294 matrices. For air, we used a Tenax tube spiked with 1 μL of standard solution at $0.1 \text{ ng}\cdot\mu\text{L}^{-1}$ of
295 all compounds. For water samples, we used 10 mL MilliQ water spiked with 10 μL of standard
296 solution at $0.01 \text{ ng}\cdot\mu\text{L}^{-1}$ for all compounds. LOD and LOQ were calculated as signal to noise
297 ratios of 3 and 10, respectively. Repeatability was also assessed for air and water samples ($n=3$)
298 including the sample preparation steps. Results are presented in Table S.3.

299 2.5 Wet deposition calculation

300 Given the pesticide concentrations in rainwater (C_i in $\text{ng}\cdot\text{L}^{-1}$) and rain intensity for each sample
301 (R_i in mm), wet deposition (w_d in $\mu\text{g}\cdot\text{m}^{-2}$) was calculated for each compound as cumulated over
302 all samples in the nine months according to the following equation:

$$303 \quad w_d = \sum C_i \frac{R_i}{1000} \quad \text{Eq. 4}$$

304 2.6 Monitoring data from ATMO Nouvelle Aquitaine: sampling location and selection.

305 The AASQAs monitor and assess ambient air quality in every French administrative region
306 (metropolitan and overseas). Even though pesticides are not subject to regulatory monitoring,
307 some AASQAs carry out ad hoc and local campaigns to assess pesticide contamination of the
308 atmosphere. Here we used the data measured weekly by “ATMO Nouvelle Aquitaine”

309 (AASQA ATMONA) from February to November 2018. Active sampling was carried out using
310 a PUF trapping media for the gas phase and a quartz filter (47mm) to trap the particles.

311 We selected four locations among the seven locations that the AASQA ATMONA monitors
312 (Figure 2). These were Poitiers and Limoges (urban sites) as they are located within a similar
313 agricultural profile as the ZAPVS studied (arable crops), as well as Medoc (a rural site vineyard)
314 and Cognaçais (a rural site, mixed environment of arable crops and vineyard) as they were
315 located almost upwind of the ZAPVS and thus pesticide applications in this area could result in
316 contamination of air masses near our site.

317 **3 Results and discussion**

318 3.1 Method development and characterization

319 *3.1.1 Experimental design results: choice of conditions for rainwater sample extraction*

320 Table S.4 summarizes the results obtained for all compounds and Figure 3 shows the
321 experimental design results for one compound, bifenthrin, as an illustration. The Pareto chart
322 (Figure 3a) represents the standardized effect (means of the effect divided by its standard error)
323 of the factors, and ranks the factors in order of importance. For bifenthrin, three factors were
324 statistically significant. The extraction time (C) and the addition of acetone (B) had a positive
325 effect, *i.e.* they improved its extraction, while the addition of NaCl (A) had a significantly
326 negative effect. One of the advantages of the experimental design approach was also to study
327 factor interactions. For bifenthrin, NaCl/Extraction time (AC) and NaCl/Solvent (AB)
328 interactions had negative effects. To find optimal conditions, the “optimisation function” of stat
329 graphics was used.

330 Statistical models explained more than 90% of the variability in the quantity of the extracted
331 molecules for each studied pesticide. The estimation of optimum extraction conditions was thus
332 reliable. Thiamethoxam was the only molecule that could not be extracted by SBSE due to its

333 very low octanol/water coefficient ($\text{LogK}_{\text{ow}} = -0.13$, Table 1): 31 molecules out of 32, which
334 could be separated chromatographically (see 2.3.2 subsection) were thus considered. According
335 to the optimum results of the Box-Behnken experiment, the first factor to enhance extraction of
336 a majority of molecules was the addition of salt (30%) (13 molecules out of 31) followed by
337 the addition of acetone (10 %) (nine out of 31 molecules). These two extraction conditions
338 seemed to be therefore unavoidable. The results were less contrasted for the remaining
339 molecules. For clomazone, pirimicarb, and propiconazole 1, adding salt had a significant
340 positive effect whereas acetone had a negative effect. Adding acetone did not have an effect on
341 cloquintocet-mexyl and diflufenican extraction. Salt addition had no effect on the extraction of
342 pyraclostrobin and metrafenone. Each molecule would therefore be extracted efficiently in both
343 cases. Overall, the addition of salt and acetone appeared to be a good compromise in the choice
344 of extraction conditions.

345 The results of Pareto diagrams also indicated that NaCl/acetone interactions had a significant
346 negative effect on twelve molecules. Therefore, the two extraction conditions were not carried
347 out on the same sample at the same time. However, since it is possible to analyze two Twister®
348 bars together in the same TDU tube, the two extraction conditions were carried out on two
349 separate aliquots of the rainwater samples. Concerning the extraction time, the simulations
350 predicted that more than 200 minutes would lead to optimum extraction. However to carry out
351 all the extractions in a reasonable time with good repeatability, a compromise was sought to
352 reduce the extraction time. Based on the simulations, 135 min was found as a good compromise
353 that only reduced the quantity of extracted molecules by less than 20% compared to the
354 optimum.

355 The following extraction conditions were hence chosen: 30% (m/v) NaCl was added to 10 mL
356 of rainwater sample and a first extraction was carried out for 135 min (1st Twister®). 10% (v/v)
357 acetone was added to a second aliquot of 10 mL rainwater sample and a second extraction was

358 carried out for 135 min with a second stirring Twister®. Both Twister® bars were extracted
359 and analyzed simultaneously by TD-GC-MS.

360 *3.1.2 Rainwater sample extraction efficiency*

361 As explained previously, it was difficult to choose optimum conditions for each studied
362 compound. The quantity of molecules extracted with the conditions fixed above represented
363 more than 80% (PO) of the response that would have been obtained under the optimum
364 conditions simulated by the models. Thus, the extraction conditions chosen above were a good
365 compromise to efficiently extract all the molecules under study. Experimental recoveries (Eq
366 2) were higher than 80% for 22 out of the 31 molecules, and ranged from 40% to 59% for only
367 eight molecules (Table S. 2: no available data for cypermethrin1). There was a significant
368 increase between theoretical recoveries (Eq 1) and experimental recoveries (Eq 2), of two to
369 ten fold for a majority of the molecules. However, five molecules and their isomers
370 (cypermethrin, deltamethrin, lambda-cyhalothrin, bifenthrin, tau-fluvalinate) showed lower
371 experimental recovery, two-fold lower than the theoretical yields, even though the experimental
372 design clearly showed that the solvent conditions were the most favorable conditions for
373 extracting them. These compounds all belong to the pyrethroid family. Serôdio and Nogueira
374 (2005) observed a decreased signal with higher stirring speeds, one of the parameters that was
375 not tested in the Box-Behnken design. The experimental extraction yield was taken into account
376 by applying a correction factor for these five molecules in final calculations of their
377 concentration in rainwater. SBSE was used here for 14 different chemical families covering a
378 wide range of physico-chemical properties ($\log K_{ow}$ ranging from 1.36 to 7.02). The choice of
379 contrasted extraction conditions described above allowed the best compromise for the majority
380 of the studied molecules.

381 All methodological tests and evaluations (LOD, LOQ, repeatability etc.) are summarized and
382 presented in Table S. 3. These criteria were taken into account in the analysis and interpretation
383 of the results.

384 3.2 Quantification of pesticides in rainwater samples

385 The cumulated rainfall amount over the experimental period was 621 mm, which is typical for
386 the Deux-Sèvres department at this time of the year (ranging from 417.5 to maximum 1071
387 mm, in 2009 to 2019, as indicated in the INRAE CLIMATIK database) (Table 2). No rainwater
388 was collected for nine of the weeks so a total of 22 samples was analyzed. The concentrations
389 of 12 pesticides belonging to nine different chemical families were quantified in rainwater,
390 ranging from 0.5 ng.L⁻¹ to 173.9 ng.L⁻¹. All pesticide types were detected: six fungicides, five
391 herbicides and one insecticide (Table 2). The highest concentrations were found for herbicides,
392 which also showed the largest variability in concentration. Bifenthrin was the only insecticide
393 detected with concentrations similar to those of fungicides. Over the entire period, rainwater
394 contamination was mostly observed in spring (end of March-beginning of June) for both
395 fungicides and herbicides (Figure S.3). The herbicides pendimethalin and diflufenican were
396 also found in early March, in October and November. Note that winter was less well represented
397 than the other seasons as no samples were taken before the 7th of March 2018 and none after
398 the 28th of November 2018.

399 Pendimethalin and S-metolachlor were the most frequently detected pesticides in this study and
400 are also among the most reported in rainwater with concentrations ranging from 160 to 350
401 ng.L⁻¹ and from 100 to 510 ng.L⁻¹, respectively, in Europe (Dubus et al., 2000; Asman et al.,
402 2005). Potter and Coffin (2017) observed even higher concentrations between 1.5 and 1700
403 ng.L⁻¹ for pendimethalin and 15 to 3800 ng.L⁻¹ for S-metolachlor. In another recent study,
404 Kreuger et al. (2017) detected boscalid, epoxiconazole, diflufenican, pendimethalin, and S-
405 metolachlor in 30% of the rainfall events between 2012 and 2015 in Sweden with

406 concentrations ranging from 1 (most frequently detected pesticides) to 100 ng.L⁻¹ (more
407 occasionally detected pesticides), which is closer to the range of concentrations found in this
408 study.

409 3.3 Quantification of pesticides in air samples

410 The developed analytical method (section 2.3) was carried out on the air samples collected in
411 May 2018.

412 Six pesticides were quantified in air samples: three fungicides, two herbicides and one
413 insecticide (Table 3). Concentrations ranged from 0.03 ng.m⁻³ to 1 ng.m⁻³ for the majority of
414 the compounds except for pendimethalin for which concentrations were higher, between 1.5
415 ng.m⁻³ to 22 ng.m⁻³. As for rainwater, we observed that herbicide concentrations were higher
416 than those of fungicides. Tau-fluvalinate, the only insecticide detected, showed the same range
417 of concentrations as fungicides. No significant variations in concentrations were observed
418 during this short sampling period except for S-metolachlor in the organic farming window on
419 the 30th and 31st of May, where there was a higher concentration for one sampling period over
420 the four sampling periods (by a factor of three). This could be due to a S-metolachlor application
421 close to the sampling location. Observed pesticide concentrations were relatively similar in the
422 two studied windows, except for pendimethalin for which a higher concentration was observed
423 in the CF (conventional farming) window (four fold higher). Six and four pesticides were
424 detected in the OF (organic farming) and CF windows, respectively. The OF window was close
425 to treated areas (Figure 1). The conventional farming fields may thus have had an impact on
426 pesticides in the air above this area. However, the sampling was short (24 hours) and the number
427 of samples collected was low, so these results should be considered with caution. It would be
428 necessary to interpret them with regards to the actual treatments carried out within the studied
429 1 km² landscapes and at their edges (information not available at this scale).

430 Coscolla et al. (2016) reported in their review measured air concentrations from French,
431 Canadian or American studies published before 2013, for a large number of pesticides,
432 including epoxyconazole, fenpropidine, pendimethalin and S-metolachlor, The concentrations
433 quantified in our study are within the ranges reported by Coscolla et al. (2016). To go further
434 on, we compared our results to the measurements performed by AASQA ATMONA at selected
435 representative sites in 2018. Among the 27 active substances (not taking into account isomers),
436 ten were not investigated in the AASQA ATMONA campaign: cloquintocet-mexyl,
437 cycloxydim, dimethachlor, metconazole, metrafenone, napropamide, pirimicarb,
438 pyraclostrobin, tau-fluvalnalate, and thiamethoxam. Among the 17 others, seven pesticides
439 were quantified by AASQA ATMONA: aclonifen, boscalid, diflufenican, fenpropidine,
440 metazachlor, S-metolachlor and pendimethalin. Two pesticides detected here (Table 3) were
441 also quantified by AASQA ATMONA in May 2018, namely S-metolachlor and pendimethalin.
442 While S-metolachlor concentrations were consistent with the AASQA ATMONA data (0.34 to
443 1.32 ng.m⁻³), the pendimethalin concentrations measured in this study were higher (AASQA
444 ATMONA data: 0.17 to 1.32 ng.m⁻³). Regarding fenpropidine, at the end of April, AASQA
445 ATMONA reported a concentration of 0.22 ng.m⁻³ in the air, which is very close to that we
446 measured. AASQA ATMONA did not detect epoxiconazole (LOQ < 0.15). The overall
447 agreement between this study and AASQA ATMONA shows that the method developed in the
448 present work is relevant for pesticide quantification in the atmosphere. These findings
449 correspond to farmer pesticide usage recorded through interviews in the study site. For instance,
450 pendimethalin and epoxiconazole were used in 23% and 15% of the fields for which data on
451 farming practices were collected in 2018 (see Bretagnolle et al. 2018a,b for details on inquiries).
452 We found only one surprising discrepancy for S-metolachlor. From the interviews, few farmers
453 used it (< 5% of fields for which data on agricultural practices are known) while it was
454 frequently found in the atmosphere in this study. This pesticide is mostly used in maize for

455 weeds. If maize is not a particularly frequent crop at ZAPVS scale (c.10% of the area,
456 representing 8% of agricultural practices datas collected from farmer interviews), it was
457 particularly abundant in this conventional farming landscape studied and sampled here (>50%),
458 which could explain our observations.

459 3.4 Seasonality of rainwater and airborne concentrations

460 Some pesticides (aclonifen, diflufenican, pendimethalin, S-metolachlor) were detected in
461 rainwater and reported by AASQA ATMONA in the atmosphere over the same periods. Both
462 datasets can be used to analyze the seasonal trend of these pesticides in the region as illustrated
463 in Figure 4 for pendimethalin and S-metolachlor, the two most frequent compounds quantified
464 in air by AASQA ATMONA and in rainwater in this study.

465 Overall, there was a good correlation between the seasonal variations in pesticide
466 concentrations measured in the rainwater and atmosphere. This is expected because of the
467 equilibrium between gaseous compounds and their solubilized counterparts in water. The ratio
468 between rainwater and atmospheric concentrations (Exp_{ratio}) was calculated and evaluated
469 theoretically as proposed by Ligocki et al. (1985) in order to parameterize the scavenging of
470 gaseous organic compounds by rain. Two estimates of this ratio were calculated either based
471 on Henry's law constant ($T1_{ratio}$), or on the ratio between vapour pressure and water solubility
472 ($T2_{ratio}$). This approach assumes that all the pesticide is in the gas phase. Theoretical and
473 experimental ratios were in the same order of magnitude except for those for pendimethalin,
474 which showed a much larger experimental ratio (Figure S.4). These differences may be due to
475 the uncertainty in the physico-chemical properties of these compounds. Indeed, Van Pul et al.
476 (1999) evaluated that the uncertainty in wet deposition of gaseous pesticides is a factor of two
477 to three, mainly because of uncertainties in Henry's law constant and its temperature
478 dependency. The observed differences may also be due to the assumption that the compounds
479 are entirely in the gas phase, while a fraction may be in the particulate phase, thus affecting the

480 scavenging of the compounds by rain. For further comparisons of the experimental ratios to the
481 theoretical ratios, the gas-particle partitioning of pesticides should be taken into account, which
482 is still a challenge.

483 3.5 Wet deposition and consequences for soil contamination

484 Kreuger et al. found similar orders of magnitude (2017) for propiconazole (somewhat lower
485 than $1 \mu\text{g}\cdot\text{m}^{-2}$) and epoxiconazole (close to $1 \mu\text{g}\cdot\text{m}^{-2}$). Higher deposition was found here for
486 pendimethalin and S-metolachlor compared to Kreuger's data but this is consistent with the fact
487 that the use of pendimethalin and S-metolachlor were forbidden in Sweden when the samples
488 were taken while they are still allowed and used in France. Our estimates were however lower
489 than the annual mean deposition of 92 and $80 \mu\text{g}\cdot\text{m}^{-2}$ found by Potter and Coffin (2017) for
490 pendimethalin and S-metolachlor, respectively. In terms of application dose (based on the
491 recommended application dose), for pendimethalin this deposition rate corresponded to 0.03%
492 of the application dose being deposited over the nine months. This result is in agreement with
493 Kreuger et al. (2017) who found that deposited amounts corresponded to 0.1-0.0001% of the
494 applied dose in the field. Potter and Coffin (2017) found 1.2% and 1% for pendimethalin and
495 S-metolachlor, over the agricultural watershed over 3 years.

496 Pelosi et al. (2021) detected diflufenican, epoxiconazole and boscalid in the top 5 cm of soils
497 (sampled in 2016) in untreated areas such as grasslands (temporary and permanent) and
498 hedgerows. The lowest concentrations (between 0.3 and $0.5 \text{ ng}\cdot\text{g}^{-1}$ dry soil) were found in
499 permanent grasslands (untreated). Combining our results and those from Pelosi et al. (2021),
500 bearing in mind that the sampling years were different in the two studies, we evaluated the
501 contribution of wet deposition to soil contamination based on the following assumptions. First,
502 since the sales of boscalid, diflufenican and epoxiconazole were relatively constant in the
503 French area "département des Deux-Sèvres" over 2016 to 2018 (BNVD 2021), we assumed
504 that the results of both experimental campaigns are representative of the overall contamination

505 of rainwater and soils. Second, we considered that wet deposited pesticide molecules remained
506 in the top 5cm of soil (depth sampled by Pelosi et al. (2021)), thus ignoring further infiltration
507 and degradation given the relatively high DT50lab (time required for the concentration to
508 decline to half of the initial value), of each compound in the soil (DT50lab,: 94.5, 353.5 and
509 484.4 days for diflufenican, epoxiconazole and boscalid respectively, from PPDB). Based on
510 these assumptions, the yearly contribution of wet deposition to soil concentrations was
511 evaluated to range between 1% and 2.4% of the pesticides found in untreated soil by Pelosi et
512 al. (2021). The rainwater was sampled in an area of the ZAPVS that is not located exactly in
513 the same fields as those sampled by Pelosi et al. (2021) and not in the direct vicinity of treated
514 fields, thus we may have underestimated the contribution of rainwater to the level of soil
515 contamination observed by Pelosi et al. (2021). Spatial and temporal synchronization of
516 sampling is necessary to go further with this analysis, which should also be extended to a wider
517 range of compounds. In addition, untreated areas may also be contaminated by gaseous
518 deposition of pesticides in the air or by droplets drifting from treatments into adjacent treated
519 areas. Modeling studies taking into account local plant protection practices and landscape
520 features are required to assess the contribution of each process.

521 **4 Conclusion**

522 This study developed a reliable method for quantifying mixtures of several pesticides in
523 rainwater and air. The proposed methodology based on using a single analytical method for
524 both compartments represents a clear advantage: sources of uncertainties associated with the
525 methods involving several laboratories and techniques can be reduced. The use of Box-Behnken
526 factorial experiments made it possible to identify the best compromise in conditions to extract
527 the 27 active substances in rainwater. The descriptive quality of the statistical models obtained
528 from this experimental design made it possible to model the influence of analytical choices on
529 extraction yields without conducting new laboratory experiments that would be time-, material-

530 and money-consuming. Using this statistical tool, we could study the influence of several
531 factors in a minimum number of experiments in the laboratory. With regards to the gas phase,
532 a sampling time of 24h may be possible to quantify atmospheric concentrations, in view of the
533 limits of quantification obtained, thus allowing the relatively fine monitoring of the temporal
534 evolution of concentrations, which may be rapid. TD-GC-MS appears to be a good analytical
535 solution to detect and quantify pesticides in both air and rainwater. The limits of quantification
536 obtained were low and could be further improved by avoiding molecule splitting towards the
537 analysis system. Nevertheless, the proposed approach also has some limits. For example : TD
538 is not suitable for thermolabile compounds and the sample is destroyed so additional analyses
539 of the same sample are not possible , GC is intended for volatile or semi-volatile molecules.

540 The feasibility of air monitoring using an approach based on a mobile active sampling system
541 that does not require a nearby power supply was confirmed by comparing the concentration
542 levels with AASQA ATMONA regional measurements in the region. To assess the involvement
543 of dry deposition in the contamination of untreated areas, a broader-scale deployment of the
544 measurements within agricultural landscapes would be required. Developed air sampling
545 systems that are self-contained, particularly in terms of energy supply, would meet this need.
546 For wet deposition, a seasonal effect was clearly observed showing a correlation between
547 molecules detected in rainwater and air. The differences between theoretical and measured air-
548 to-rainwater concentration ratios raise the question of uncertainties in rain scavenging processes
549 and points towards the need for further monitoring in field conditions. Using the same analytical
550 approach for both compartments is a real advantage for addressing this issue.

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A multiresidue analytical method on air and rainwater for assessing pesticide atmospheric contamination in untreated areas

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Compound	log K _{ow} pH 7, 20°C	Vapour pressure (mPa) 20 °C	Water solubility (mg.L ⁻¹) 20 °C	Henry's law constant 25 °C (Pa.m ³ .mol ⁻¹)	Molecular mass	Type	Chemical Substance family
Acetochlor	4.14	2.20E-02	282	2.10E-03	269.77	Herbicide	Chloroacetamide
Aclonifen	4.37	1.60E-02	1.4	3.03E-03	264.66	Herbicide	Diphenyl ether
Bifenthrin	6.6	1.78E-02	0.001	7.74E-05	422.87	Insecticide	Pyrethroid
Boscalid	2.96	7.20E-04	4.6	5.18E-05	343.21	Fungicide	Carboxamide
Clomazone	2.54	2.70E+01	1212	5.90E-03	239.7	Herbicide	Isoxazolidinone
Cloquintocet-mexyl	5.03	5.31E-03	0.59	3.02E-03	335.83	Herbicide	Unclassified
Cycloxydim	1.36	1.00E-02	53	6.14E-05	325.47	Herbicide	Cyclohexanedione
Cypermethrin ^a	5.5	6.78E-03	0.009	3.10E-01	416.3	Insecticide	Pyrethroid
Cyproconazole ^b	3.09	2.60E-02	93	5.00E-05	291.78	Fungicide	Triazole
Deltamethrin	4.6	1.24E-05	0.0002	3.10E-02	505.2	Insecticide	Pyrethroid
Diflufenican	4.2	4.25E-03	0.05	1.18E-02	394.29	Herbicide	Carboxamide
Dimethachlor	2.17	6.40E-01	2300	1.70E-04	255.74	Herbicide	Chloroacetamide
Epoconazole	3.3	3.50E-04	7.1	1.65E-05	329.76	Fungicide	Triazole
Fenpropidin	2.6	1.07E+01	530	1.07E+01	273.46	Fungicide	Unclassified
Lambda-Cyhalothrin	5.5	2.00E-04	0.005	2.00E-02	449.85	Insecticide	Pyrethroid
Metazachlor	2.49	9.30E-02	450	5.90E-05	277.75	Herbicide	Chloroacetamide
Metconazole	3.85	2.10E-05	30.4	2.21E-07	319.83	Fungicide	Triazole
Metrafenone	4.3	1.53E-01	0.492	1.32E-01	409.27	Fungicide	Benzophenone
Napropamide	3.3	2.20E-02	74	8.10E-05	271.36	Herbicide	Alkanamide
Pendimethalin	5.4	3.34E+00	0.33	1.27E+00	281.31	Herbicide	Dinitroaniline
Pirimicarb	1.7	4.30E-01	3100	3.30E-05	238.29	Insecticide	Carbamate
Prochloraz	3.5	1.50E-01	26.5	1.64E-03	376.67	Fungicide	Imidazole
Propiconazole ^c	3.72	5.60E-02	150	9.20E-05	342.22	Fungicide	Triazole
Pyraclostrobin	3.99	2.60E-05	1.9	5.31E-06	387.82	Herbicide	Strobilurin
S-metolachlor	3.05	3.70E+00	480	2.20E-03	283.79	Herbicide	Chloroacetamide
Tau-fluvalinate ^d	7.02	9.00E-08	0.00103	1.20E-04	502.9	Insecticide	Pyrethroid
Thiamethoxam	-0.13	6.60E-06	4100	4.70E-10	291.71	Insecticide	Neonicotinoid

^a 4 isomers, ^b 2 isomers, ^c 2 isomers, ^d 2 isomers

Table 1. List of the studied pesticides and their physico-chemical properties, type and chemical substance family. (PPDB Pesticide Properties DataBase University of Hertfordshire 2020)

Sampling period		FUNGICIDES						HERBICIDES					INSECTICIDES	Cumulated Rain	
Start	End	Boscalid	Epoxiconazole	Fenpropidin	Metconazole	Metrafenone	Propiconazole	Aclomifen	Cycloxydim	Diflufenican	Pendimethalin	S-metolachlor	Bifenthrin	in mm	
Quantification frequency		10	10	10	3	14	14	10	14	7	38	24	21	-	
MIN		0.5	5.5	1.9	47.1	1.4	14.3	19.6	2.6	4.0	15.8	0.8	7.5	-	
MAX		7.9	22.9	7.2	47.1	17.7	25.1	39.8	13.7	5.2	111.7	173.9	53.0	-	
WINTER	07/03/18	14/03/18	ND	ND	ND	ND	ND	ND	ND	ND	95.8	ND	< LOQ	56.0	
	14/03/18	21/03/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	28.2	
	21/03/18	28/03/18	ND	ND	ND	ND	ND	ND	ND	4.0	80.1	ND	18.1	25.4	
SPRING	28/03/18	04/04/18	ND	ND	ND	ND	21.8	ND	ND	ND	15.8	ND	ND	34.4	
	04/04/18	11/04/18	ND	ND	ND	ND	14.3	ND	ND	ND	19.0	ND	45.5	22.0	
	11/04/18	18/04/18	ND	5.5	6.9	ND	1.8	25.1	ND	ND	22.0	ND	< LOQ	25.4	
	18/04/18	25/04/18	-	-	-	-	-	-	-	-	-	-	-	1.2	
	25/04/18	02/05/18	ND	22.9	< LOQ	ND	ND	16.2	39.8	ND	ND	53.4	103.2	53.0	10.6
	02/05/18	09/05/18	-	-	-	-	-	-	-	-	-	-	-	1.8	
	09/05/18	16/05/18	7.9	13.7	7.2	ND	1.4	ND	27.4	10.8	ND	111.7	173.9	20.0	24.4
16/05/18	23/05/18	-	-	-	-	-	-	-	-	-	-	-	-	0.2	

	23/05/18	30/05/18	0.5	ND	ND	47.13	17.7	ND	19.6	< LOQ	ND	80.0	66.9	22.0	31.6
	30/05/18	06/06/18	ND	ND	ND	ND	3.9	ND	< LOQ	ND	ND	26.3	21.5	7.5	41.8
	06/06/18	13/06/18	ND	ND	ND	ND	ND	ND	ND	< LOQ	ND	ND	31.8	ND	66.2
	13/06/18	20/06/18	ND	ND	ND	ND	ND	ND	ND	13.7	ND	ND	< LOQ	ND	20.8
SUMMER	20/06/18	27/06/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	27/06/18	04/07/18	0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	9.7	ND	10.6
	04/07/18	11/07/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.4
	11/07/18	18/07/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	18/07/18	26/07/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.0
	25/07/18	01/08/18	-	-	-	-	-	-	-	-	-	-	-	-	0.8
	01/08/18	08/08/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	08/08/18	15/08/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	15/08/18	22/08/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	22/08/18	29/08/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	22.2
	29/08/18	05/09/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	05/09/18	12/09/18	-	-	-	-	-	-	-	-	-	-	-	-	1.6
	12/09/18	19/09/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	19/09/18	26/09/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11.2
AUTUMN	26/09/18	03/10/18	-	-	-	-	-	-	-	-	-	-	-	-	-
	03/10/18	10/10/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	14.0
	10/10/18	17/10/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	45.6
	17/10/18	24/10/18	-	-	-	-	-	-	-	-	-	-	-	-	0.2
	24/10/18	31/10/18	-	-	-	-	-	-	-	-	-	-	-	-	-

31/10/18	07/11/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	59.5	ND	ND	56.4
07/11/18	16/11/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	31.8
14/11/18	21/11/18	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
21/11/18	28/11/18	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.2	44.5	ND	ND	25.4

Table 2 : Concentrations of pesticides detected in rainwater in ng.L⁻¹, rainfall amount in mm, concentration minimum and maximum quantified during sampling period in ng.L⁻¹ and quantification frequency in % (ratio number of times detected /number of rain events) . ND : not detected; <LOQ : detected but below LOQ; "-" : no rainfall or sample volume collected was too small for analysis.

Sampling period			FUNGICIDES						HERBICIDES				INSECTICIDE	
			Fenpropidin		Epoiconazole		Metrafenone		S-metolachlor		Pendimethalin		Tau-fluvalinate 1,2	
Start	End		CF	OF	CF	OF	CF	OF	CF	OF	CF	OF	CF	OF
This study	22/05/2018	23/05/2018	0.23	0.50	ND	0.27	ND	ND	0.55	0.40	22.44	8.22	0.18	ND
	23/05/2018	24/05/2018	0.07	0.25	ND	ND	ND	0.09	0.34	0.31	6.19	6.04	0.17	0.16
	30/05/2018	31/05/2018	ND	<LOQ	ND	ND	ND	ND	0.54	1.08	11.61	1.21	0.12	0.04
	31/05/2018	01/06/2018	ND	ND	ND	ND	ND	ND	0.42	0.42	13.35	1.29	0.03	ND
AASQA ATMONA	22/05/2018	05/06/2018	ND LOD=0.15	ND LOD=0.15			NR		0.34 -1.32	0.17-1.32			NR	

Table 3: Range of pesticide concentrations detected in the air (ng.m^{-3}) in the conventional farming (CF) landscape window and organic farming landscape window (OF), measured weekly by AASQA ATMONA at the same sampling period, on the site selected in section 2.5. ND: not detected, NR: not researched, LOD: limit of detection.

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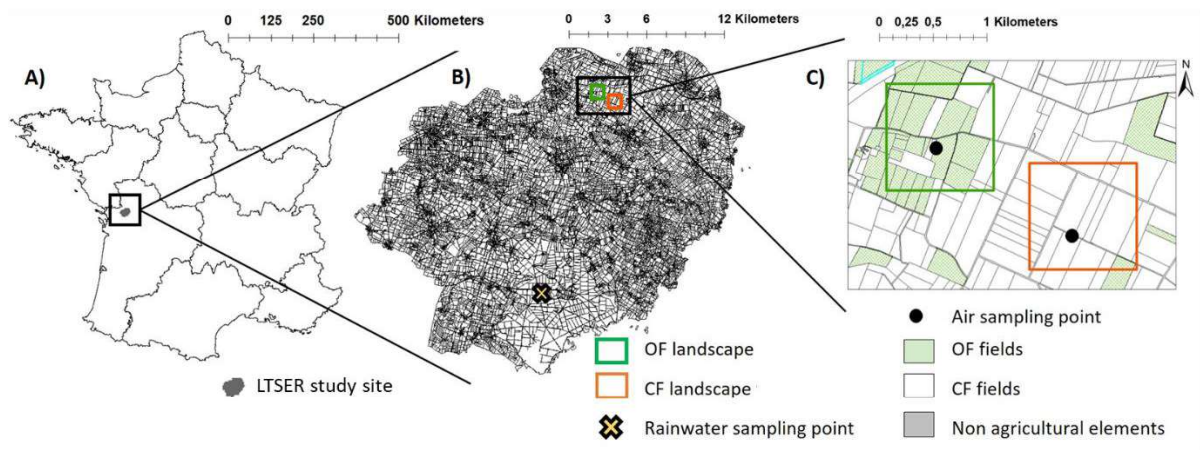


Figure 1: Spatially nested maps showing the location of A) the ZAPVS study site, B) the rainwater sampling point and the two 1 km² landscapes selected for air sampling (OF, CF) and C) the air sampling point in each landscape (black dots).

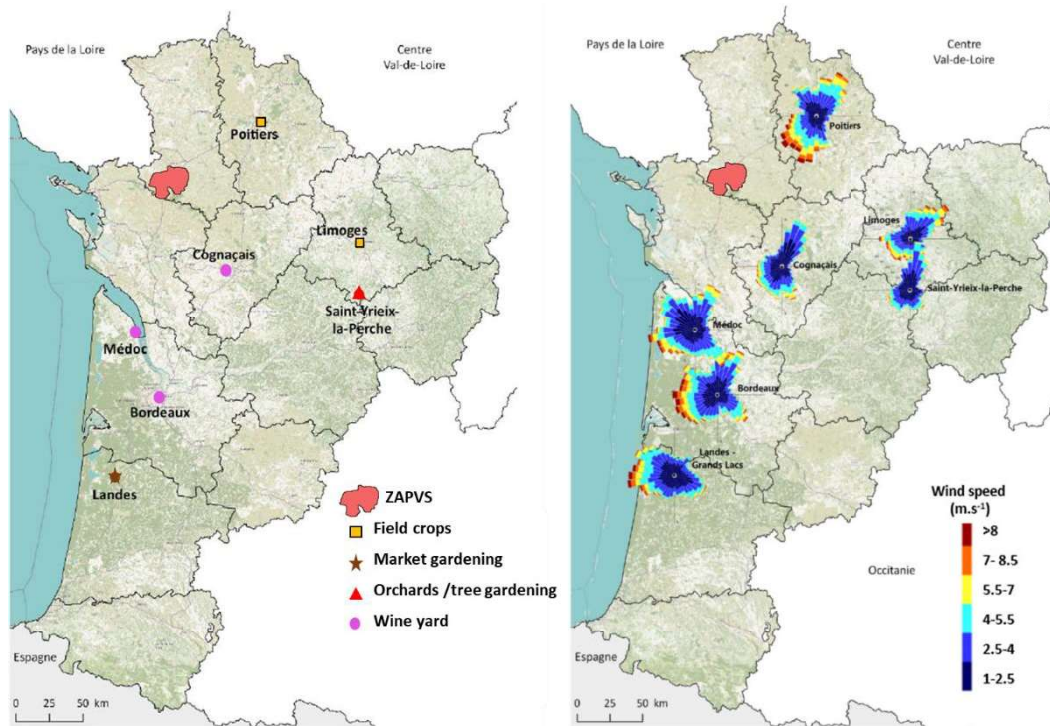


Figure 2: AASQA ATMONA map, location of the ZAPVS and the different monitoring sites (on the left), wind direction and speed (on the right). (ATMO nouvelle Aquitaine (2018))

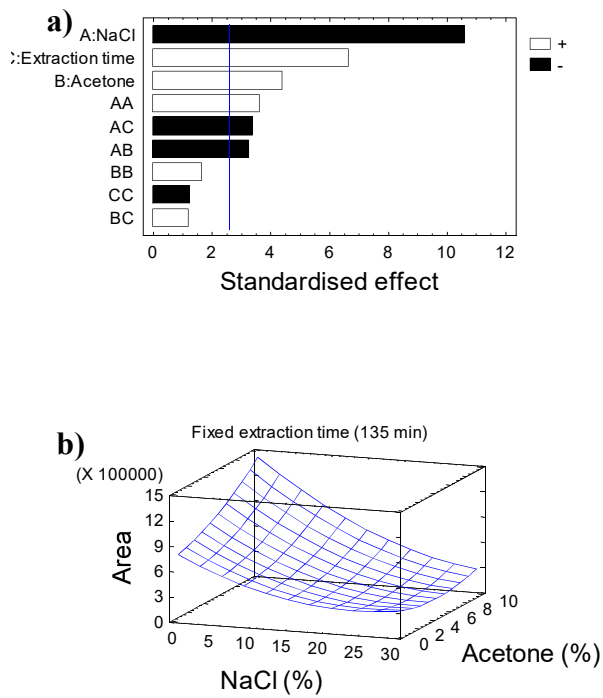


Figure 3: Pareto Chart (a) and response surface diagrams (b) obtained for bifenthrin. Pareto chart of the statistical analysis: the vertical line represents the Student's test quantile. (X-axis) Standardised effect. (Y-axis) Term of the second order polynomial regression. (A, B, C) for the linear terms, A, amount of NaCl in %, B amount of Acetone in % , and C extraction time in min. (AA, BB, CC) for the quadratic terms. (AB, AC, BC) for the cross-product terms.

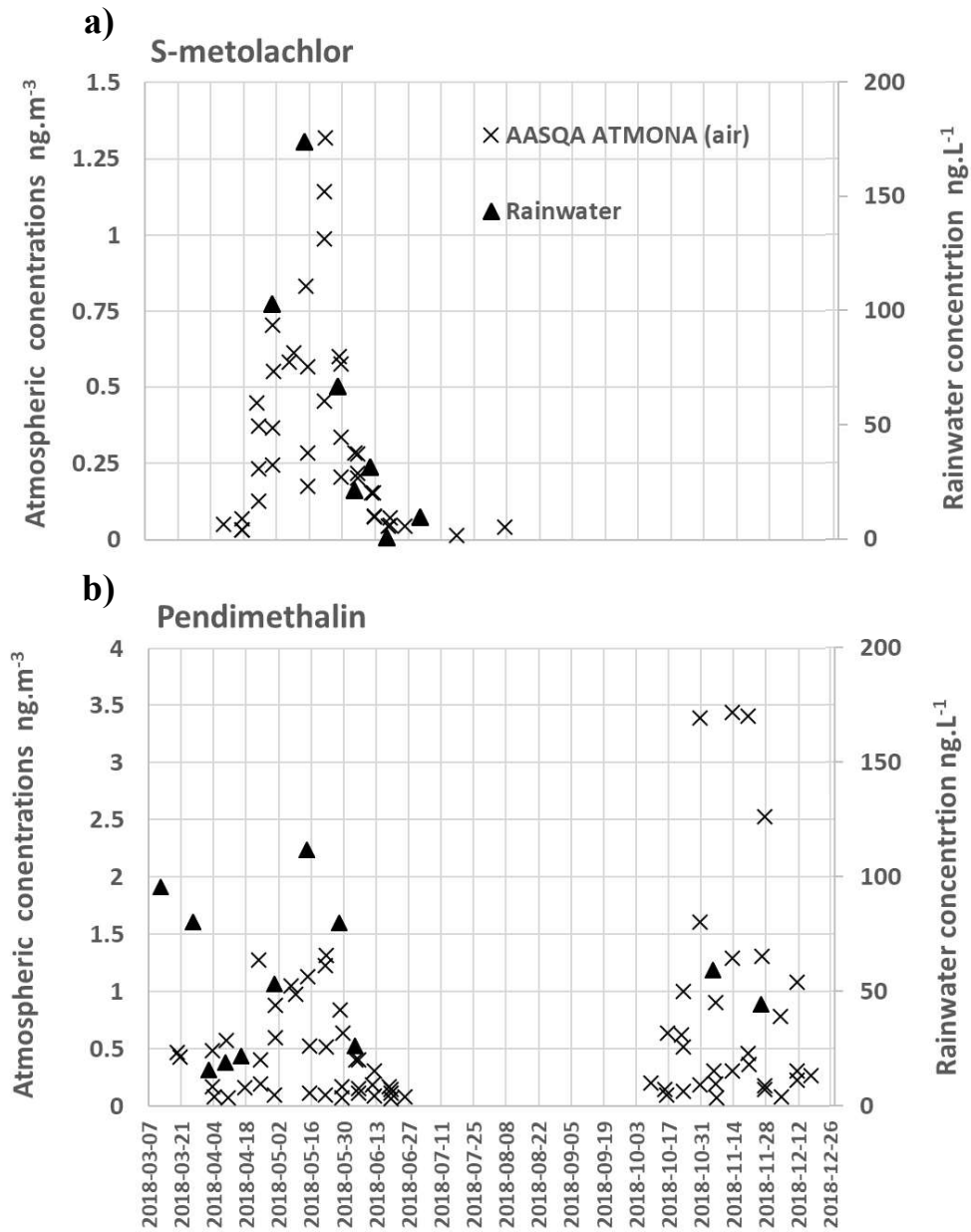


Figure 4: S-metolachlor (Figure a) and pendimethalin (Figure b) concentrations in the atmosphere (ng.m^{-3}) monitored by AASQA ATMONA (AASQA ATMONA air) and measured in rainwater in this study (Rainwater).

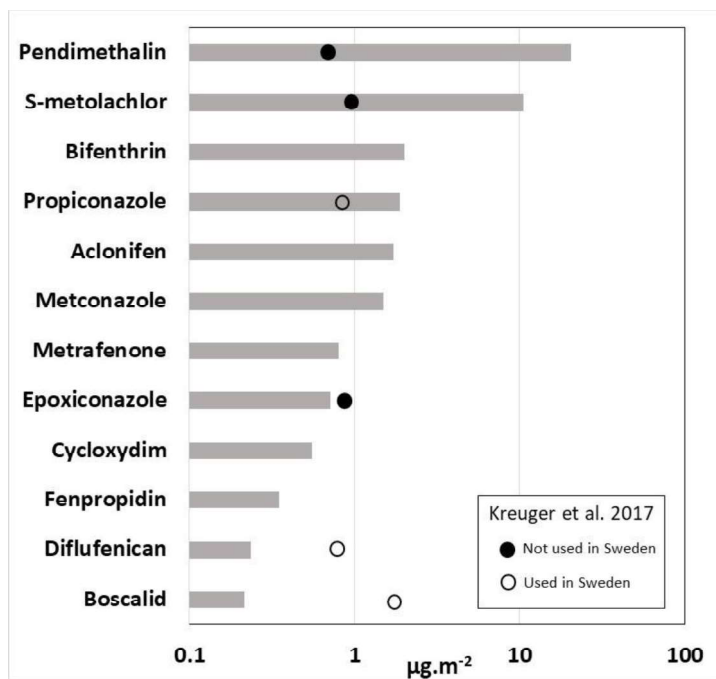


Figure 5: Cumulated wet deposition (grey bars) over all samples ($\mu\text{g}\cdot\text{m}^{-2}$) from March to November 2018 observed in this study and the dots refer to the average wet deposition per year from April to October in 2012 to 2015 observed by Kreuger et al. (2017) in Sweden . Used and not used compounds in Sweden refer to authorised and forbidden compounds.



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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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