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## Monitoring of Glyphosate, Glufosinate-ammonium, and (Aminomethyl)phosphonic acid in ambient air of Provence-Alpes-Côte-d'Azur Region, France

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1                   Monitoring of Glyphosate, Glufosinate-ammonium, and  
2                   (Aminomethyl)phosphonic acid in ambient air of Provence-Alpes-  
3                   Côte-d'Azur Region, France

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15

16 **Abstract**

17 Glyphosate, AMPA, its main metabolite, and Glufosinate-ammonium were monitored in  
18 ambient air samples collected for two years (2015-2016), at four sampling sites in Provence-  
19 Alpes-Côte-d'Azur Region (PACA, France) in different areas typologies (non-agricultural  
20 areas: city center, 'zero pesticide' policy, and industrial area but also agricultural sectors:  
21 mainly orchards and vineyards). Neither Glufosinate-ammonium nor AMPA were detected.  
22 Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice)  
23 to 23% (Cavaillon), according to the sampling site. Glyphosate concentration reached a  
24 maximum level of 1.04 ng m<sup>-3</sup> in the rural site of Cavaillon. This is despite the physicochemical  
25 characteristics of Glyphosate which are not favorable to its passage into the atmosphere. The  
26 absence of simultaneous detection of Glyphosate and AMPA suggests that drift during spraying  
27 operation is the main atmospheric source of Glyphosate and that resuspension from soil  
28 particles is minor. The present study offers one of the few report of Glyphosate, Glufosinate-  
29 ammonium, and AMPA in the air.

30 **Keywords**

31 Pesticides; Herbicides; Atmosphere; Transport

32 **Highlights**

- 33
- Neither Glufosinate-ammonium nor AMPA were detected.
  - Glyphosate was detected in rural and urban sampling sites at frequencies from 0%  
34 (Nice) to 23% (Cavaillon).
  - Glyphosate has reached a concentration exceeding 1 ng m<sup>-3</sup>.
  - The drift during spraying operation is the main atmospheric source of Glyphosate.
  - The expected dose of Glyphosate remains below of the chronic reference dose.
- 38

39

## 40 **1. Introduction**

41 Herbicides are chemical substances formulated to control or manipulate undesirable vegetation.  
42 They can be applied directly to the plant, applied to the soil, or sprayed onto the foliage.  
43 Herbicides may be applied before or after crop planting or may be used to control weeds in an  
44 already established crop. They are extensively used in farming but also in gardening,  
45 landscaping, turf management, roadways, and railways. In 2016, according to the most recent  
46 statistics on agriculture, forestry, and fisheries for the European Union (Eurostat, 2018), the  
47 annual quantity of herbicide sold in Europe amounted to close to 112,000 tons, i.e., around 32%  
48 of the total quantity of pesticide sold.

49 Among herbicides, Glyphosate (2-(phosphonomethylamino)acetic acid) and Glufosinate-  
50 ammonium (2-amino-4-[hydroxy(methyl)phosphoryl]butanoic acid) are both  
51 organophosphorus compounds with broad-spectrum systemic actions. Glyphosate is the non-  
52 selective herbicide the most sold worldwide (Benbrook, 2016). After spreading, Glyphosate is  
53 rapidly biotransformed in soils into (Aminomethyl)phosphonic acid (AMPA). Despite its high  
54 biodegradability and its strong adsorption on soil particles (i.e., weak leaching potential)  
55 (Nguyen et al., 2018), Glyphosate can contaminate water resources. Glufosinate-ammonium  
56 was presented by the European Commission as "one of the very few alternatives to Glyphosate"  
57 (European Commission, 2017). However, sales of Glufosinate-ammonium are much lower than  
58 that of Glyphosate (BNVD, 2017). As a result, because of both their physico-chemical  
59 properties and intensive use, these compounds were extensively monitored in soils and waters  
60 (Székács et al., 2015; Karanasios et al., 2018).

61 From a health point of view, Glyphosate and Glufosinate-ammonium are poorly absorbed both  
62 orally and via the dermal route and they are rapidly eliminated with no biotransformation and  
63 no accumulation in tissues (Gupta, 2018). More, several epidemiologic studies have concluded  
64 that there is no apparent association between Glyphosate and any solid tumors or lymphoid

65 malignancies overall (Acquavella et al., 2016; Andreotti et al., 2018). AMPA, the main  
66 metabolite of Glyphosate, is of no greater toxicological concern than its parent compound  
67 (JMPR, 2004).

68 On the other hand, the main environmental concern lies in the fact that some pesticides are  
69 persistent particularly in the atmosphere which make them possible to be transported over long  
70 distances (Socorro et al., 2015, 2016; Mattei et al., 2018 and references therein). Hence, the  
71 atmosphere is an important spread vector at local, regional, and global scales. Atmospheric  
72 pesticide contamination was observed in urban and rural areas with concentration levels from  
73 some picograms per cubic meter ( $\text{pg m}^{-3}$ ) to several nanograms per cubic meter ( $\text{ng m}^{-3}$ ) (Désert  
74 et al., 2018 and references therein). Unfortunately, atmospheric concentrations of Glyphosate  
75 and AMPA are poorly documented because very few studies have monitored them in the  
76 atmosphere, and none regarding Glufosinate-ammonium. Due to their low Henry's Law  
77 Constant and their low vapor pressure, their presence in the atmosphere seems to be more  
78 dependent on the drift of the finest droplets after spraying (Hewitt et al., 2009) or on the  
79 suspension of the soil particles on which they are adsorbed (Bento et al., 2017). In 2004,  
80 Glyphosate was searched in 59 atmospheric samples in Hauts-de-France Region (France), with  
81 a detection frequency of 14% and a maximum concentration of  $0.19 \text{ ng m}^{-3}$  (Prouvost and  
82 Declercq, 2005). In 2007-2008, Glyphosate and AMPA were sampled in the atmosphere of two  
83 agricultural areas (soybeans, rice, corn) of Mississippi and Iowa, USA (Chang et al., 2011).  
84 Atmospheric concentrations of Glyphosate reached  $9.1 \text{ ng m}^{-3}$  and  $5.4 \text{ ng m}^{-3}$  in Mississippi and  
85 Iowa, respectively, whereas atmospheric concentrations of AMPA reached  $0.49 \text{ ng m}^{-3}$  and  $0.97$   
86  $\text{ng m}^{-3}$  in Mississippi and Iowa, respectively. These data were supplemented by measurements  
87 in rainwater. Authors estimated that 97% of Glyphosate in the air would be removed by weekly  
88 rainfall greater than 30 mm. More, a study was carried out in Malaysia to determine Glyphosate  
89 atmospheric concentrations in a treated field (Morshed et al., 2011). They reached  $42.96 \text{ } \mu\text{g m}^{-3}$

90 <sup>3</sup> during spraying using a calibrated mist blower. It should be noted that a first modeling attempt  
91 of an estimated emission of Glyphosate to the atmosphere was done at a regional scale (Atmo  
92 Auvergne-Rhône-Alpes, 2017) but without any measurement to confirm the model output.  
93 In the present work, the results of a two year (2015-2016), field campaign (142 filters) are  
94 reported. It was dedicated to quantify Glyphosate, Glufosinate-ammonium, and AMPA in the  
95 ambient atmosphere of Provence-Alpes-Côte d’Azur (PACA, France) in different areas  
96 typologies (non-agricultural areas: city center, ‘zero pesticide’ policy, and industrial area but  
97 also agricultural sectors: mainly orchards and vineyards). Necessary laboratory extraction and  
98 analytical methods were developed. Atmospheric concentrations were compared to data  
99 obtained over the same period and at the same sampling sites for 50 current-use pesticides  
100 (Désert et al., 2018). The present study offers one of the few reports of Glyphosate, Glufosinate-  
101 ammonium, and AMPA in the air.

102

## 103 **2. Material and methods**

### 104 **2.1. Chemicals and reagents**

105 Glyphosate (99%), Glufosinate-ammonium (95%), and (Aminomethyl)phosphonic acid  
106 (AMPA, 99%) reference standards were purchased from Sigma-Aldrich. The main  
107 physicochemical properties, the agricultural uses and the legal situation of pesticides studies  
108 are summarized in Table 1.

109

110

111

112

113 Table 1. Physicochemical properties, agricultural uses, and legal situation.

Chemical name	CAS number	Molecular weight (g mol <sup>-1</sup> )	Vapor pressure (Pa, 25°C) <sup>a</sup>	Henry's law constant (Pa m <sup>3</sup> mol <sup>-1</sup> , 25°C) <sup>a</sup>	Solubility in water (g L <sup>-1</sup> , 20°C) <sup>a</sup>	Acceptable Daily Intake (mg kg bw <sup>-1</sup> day <sup>-1</sup> ) <sup>b</sup>	Principal agricultural uses <sup>c</sup>
Glyphosate	1071-83-6	169.1	1.3·10 <sup>-5</sup>	2.1·10 <sup>-7</sup>	10.5	0.3	General treatment, cereals, vegetable crops, orchards, vineyards, non-cropped areas
Glufosinate-ammonium	77182-82-2	198.2	3.1·10 <sup>-5</sup>	4.5·10 <sup>-9</sup>	500	0.02	General treatment, cereals, potatoes, vineyards, non-cropped areas
(Aminomethyl) phosphonic acid (AMPA)	1066-51-9	111.0	-	0.16	1,467	0.3	Transformation product

114 <sup>a</sup> PPDB: Pesticide Properties DataBase (Lewis et al., 2016). <sup>b</sup> APVMA, 2017.

115

116 9-Fluorenmethylchloroformate (FMOC-Cl, ≥ 99%) and isotope-labeled Glyphosate (2-<sup>13</sup>C, 99

117 atom % <sup>13</sup>C) from Sigma-Aldrich were used as derivatization reagent and internal standard (IS),

118 respectively. HPLC-grade dichloromethane (Sigma-Aldrich), ethylenediaminetetraacetic acid

119 (EDTA), sodium tetraborate decahydrate (Borax), ammonium formate, formic acid, ammonia

120 solution (35%), LC/MS-grade acetonitrile, and LC/MS-grade methanol (Fisher Scientific) were

121 used for extraction and chromatographic elution. Ultra-High Quality water (UHQ water, 18.2

122 MΩ cm<sup>-1</sup> at 25°C) was obtained by tap water passed through a Milli-Q water purification system

123 (Direct 8 MilliQ, Merck Millipore). Underivatized standards were dissolved in UHQ water and

124 the stock solutions of each compound at 0.5 g L<sup>-1</sup> for Glyphosate and Glufosinate-ammonium,

125 and 0.9 g L<sup>-1</sup> for AMPA were stored in a polypropylene bottle (PP) at 4°C.

126

## 127 2.2. Sampling and site characterization

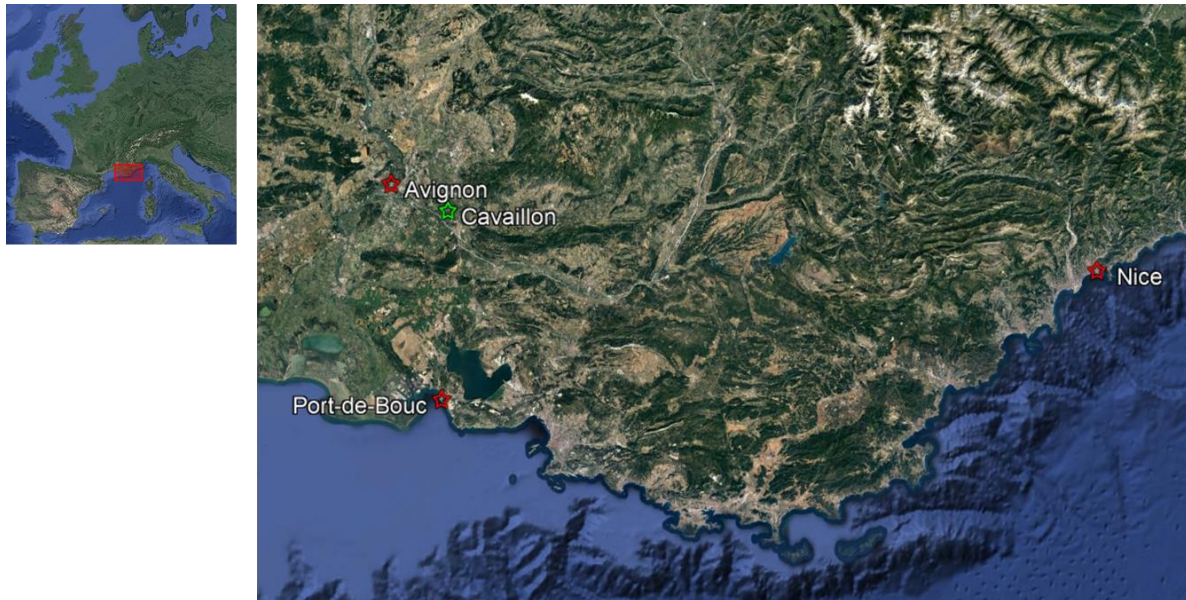
128 Sampling was undertaken at four sampling sites distributed throughout the Provence-Alpes-

129 Côte-d'Azur (PACA) region, France (Figure 1), from January 2015 to December 2016. The

130 description of sampling sites and sampling periods are summarized in Table 2. The three urban

131 sampling sites (i.e., Avignon, Nice, and Port-de-Bouc) were located in the city centers, whereas  
 132 the rural site of Cavaillon (hamlet of Les Vignères) was located in an intensive arboriculture  
 133 area.

134



135

136 **Fig 1.** Sampling sites (red: urban sites; green: rural site) distributed throughout the Provence-  
 137 Alpes-Côte-d'Azur (PACA) region, France.

138

139 **Table 2.** Description of sampling sites

Sampling site (French department)	Latitude	Longitude	Altitude	Typology	Land use description <sup>a</sup>	Total analysis number
Avignon (Vaucluse)	43.94976 N	4.80451 E	21 m	Urban	Complex cultivation patterns (33%), Vineyards (30%), Fruit trees and berry plantations (14%) Urban fabric (10%)	14
Cavaillon (Vaucluse)	43.88128 N	5.00611 E	60 m	Rural	Complex cultivation patterns (52%), Fruit trees and berry plantations (18%), Urban fabric (11%)	13
Nice (Alpes-Maritimes)	43.70207 N	7.28539 E	0 m	Urban	Urban fabric (47%), Forests (24%), Scrub and/or herbaceous vegetation associations (16%)	22
Port-de-Bouc (Bouches-du-Rhône)	43.40195 N	4.98197 E	1 m	Urban	Scrub and/or herbaceous vegetation associations (51%), Urban fabric with industrial area (27%), Forests (11%)	22

140 <sup>a</sup> Corine Land Cover nomenclature (zone of 10 km radius around the sampling site)

141



142 According to a gas/particle distribution model of semi-volatile organic compounds in the  
143 atmosphere, Glyphosate and Glufosinate-ammonium are expected to exist solely in the  
144 particulate-phase (AEROWIN program; Bidleman and Harner, 2000, Boethling et al., 2004).  
145 As a result, Glyphosate, Glufosinate-ammonium, and AMPA concentrations in the atmosphere  
146 are assumed to be equal to their particulate-phase concentrations.

147 Sampling was carried out using a high-volume sampler (Digitel Aerosol Sampler DHA-80)  
148 equipped with a PM-10 size selective inlet. Particulate samples (n = 142) were collected on 150  
149 mm diameter ashless quartz microfiber filter (ALBET LabScience). The sampling flow was 30  
150 m<sup>3</sup> h<sup>-1</sup> for 24 h. A total of 71 analyses were performed. Each analysis groups two filters, giving  
151 a total volume of filtered air around 1,400 m<sup>3</sup>.

152 Once collected, samples were stored and protected from light at -18°C until analysis. Moreover,  
153 in order to quantify the background contamination from sample handling and storage, field air  
154 blanks were done at each site. Typically, they consisted in a brief installation of a filter in the  
155 high-volume sampler without air pumping to simulate the sample handling. No contamination  
156 was detected, i.e., below the limit of detection.

157

### 158 **2.3. Sample extraction and derivatization**

159 *Extraction:* Extractions of samples and blanks were carried out using PolyTetraFluoroEthylene  
160 (PTFE) or PolyPropylene (PP) vessels to avoid any loss of studied compounds by wall  
161 adsorption. In a 70 mL PTFE centrifugation tube, two filters (i.e., one sample) were spiked with  
162 40 µL of IS solution (15.4 mg L<sup>-1</sup>). The sample was then extracted with 20 mL of UHQ water  
163 added by 2 mL of Borax (0.05 M) and 0.8 mL of EDTA (0.1 M) solutions using first a  
164 mechanical shaker (30 s), then an ultrasonic bath (10 min). Sample was finally centrifuged at  
165 12,000 rpm (12 min). A second extraction was performed with half volume of solutions

166 according to the same procedure. The supernatants of the two successive extractions were  
167 collected and filtered together through a polyethersulfone (PES) membrane of 0.45  $\mu\text{m}$  pore  
168 size under vacuum.

169 *FMOC (FluorenylMethylOxyCarbonyl) derivatization:* The filtrate was derivatized in 10 mL  
170 of acetonitrile with 2 mL of FMOC-Cl (50 g L<sup>-1</sup> in acetonitrile). The mixture was stirred, cap  
171 closed, for 90 min in the dark at room temperature. After derivatization, acetonitrile was  
172 evaporated under nitrogen flow using a concentration workstation (TurboVap II, Biotage) with  
173 pressure 1.1 bar and a water bath at 40°C. To remove unwanted by-products and FMOC excess,  
174 6 mL of dichloromethane were added at the residual aqueous solution then removed by settling.

175 *Purification and concentration:* Prior to purification and concentration on Solid Phase  
176 Extraction (SPE), the pH of the aqueous fraction was adjusted to pH 3 with formic acid 5%  
177 which corresponds to the optimum analyte retention. The extraction cartridge (OASIS HLB  
178 cartridge, 6 mL, 150 mg, Waters) was successively conditioned by 2 mL of methanol then 2  
179 mL of formic acid 0.1%. Impurities were eliminated by a selective washing step constituted by  
180 2 mL of formic acid 0.1% then 2 mL of UHQ water. Elution was achieved by 4 mL of  
181 [methanol/H<sub>2</sub>O (70/30) (v/v) + NH<sub>4</sub>OH 2%] solution. The extract was reduced to 1.5 mL by  
182 evaporating methanol using a concentration workstation and filtered through a PTFE membrane  
183 of 0.2  $\mu\text{m}$  pore size before analysis.

184

#### 185 **2.4. UPLC-MS/MS analysis**

186 Sample extracts were analyzed using an Ultra Performance Liquid Chromatographic (UPLC)  
187 system (Acquity, Waters) interfaced with a Quadrupole-Time-of-Flight Mass Spectrometer  
188 (Synapt G2 HDMS, Waters) equipped with an electrospray ion source (ESI). The mass  
189 spectrometer was used in its resolution mode, up to 18,000 FWHM (Full Width at Half

190 Maximum) at 400 Th and allowed extracted chromatograms with 0.01 Th mass accuracy. The  
191 chromatographic separations were carried out on an Acquity UPLC column BEH C18, 1.7  $\mu\text{m}$   
192 particle size, 100 mm  $\times$  2.1 mm i.d. (Waters, Milford, MA, USA), at 40°C. The mobile phases  
193 consisted in (A) UHQ Water + 5 mM ammonium formate and (B) acetonitrile (Optima®,  
194 LC/MS grade, Fisher Scientific). The gradient elution was performed at a flow rate of 0.6 mL  
195  $\text{min}^{-1}$  using 5% to 95% of (B) within 7.5 min and held at 95% of (B) for 1.5 min. The injection  
196 volume was 10  $\mu\text{L}$ . Analyses were carried out in negative ionization mode and optimum ESI  
197 conditions were found using a -0.85 kV capillary voltage, -15 V sampling cone voltage, 450°C  
198 desolvation temperature, 120°C source temperature, 20 L  $\text{h}^{-1}$ , and 1,200 L  $\text{h}^{-1}$  cone gas and  
199 desolvation gas flow rate respectively. Dwell times of 0.25 s  $\text{scan}^{-1}$  were chosen. Data  
200 acquisition and mass spectra treatments were provided by the MassLynx software (v.4.1,  
201 Waters). The negative ion electrospray of Total Ion Chromatogram (TIC), selected ion  
202 chromatograms, and ion spectra of Glyphosate-FMOC, AMPA-FMOC, and Glufosinate-  
203 ammonium-FMOC are available in Supplementary Information.

204

## 205 **2.5. Analytical performance of the method**

206 Method validation was carried out using spiked quartz filter as solid sorbent. The accuracy  
207 (including the recoveries) of the analytical method was integrated during calibration (i.e., each  
208 concentration levels were spiked on quartz filter and followed by the extraction, derivatization,  
209 and analytical protocol). Each concentration level (from 0.04 to 0.63  $\text{ng m}^{-3}$  for Glyphosate,  
210 from 0.17 to 2.67  $\text{ng m}^{-3}$  for Glufosinate-ammonium, and from 0.25 to 4.06  $\text{ng m}^{-3}$  for AMPA,  
211  $n = 6$ ) are triplicate. Calibration plots showed good linearity with correlation coefficients  $R^2 \geq$   
212 0.98 for Glyphosate,  $R^2 \geq 0.95$  for Glufosinate-ammonium, and  $R^2 \geq 0.99$  for AMPA.

213 The detection limit (LOD) and quantification limit (LOQ) were determined using the calibration  
214 graph residuals for each compound (ICH, 2005). The LOD and LOQ obtained using spiked

215 quartz filter, when air volumes of 1,400 m<sup>3</sup> were collected, are equal to 0.05 and 0.14 ng m<sup>-3</sup>  
216 for Glyphosate, 0.30 and 0.90 ng m<sup>-3</sup> for Glufosinate-ammonium, and 0.28 and 0.84 ng m<sup>-3</sup> for  
217 AMPA, respectively.

218

219 Table 3. Precipitation and atmospheric concentrations of Glyphosate, Glufosinate-ammonium, and AMPA in all sampling sites.

Date	Avignon				Cavaillon				Nice				Port-de-Bouc				
	Precipitation (mm)	Concentration (ng m <sup>-3</sup> )			Precipitation (mm)	Concentration (ng m <sup>-3</sup> )			Precipitation (mm)	Concentration (ng m <sup>-3</sup> )			Precipitation (mm)	Concentration (ng m <sup>-3</sup> )			
		GLY	GLU	AMPA		GLY	GLU	AMPA		GLY	GLU	AMPA		GLY	GLU	AMPA	
2015	01/21-23									20.2	-	-	-	28.8	-	-	-
	02/18-20									0	-	-	-	0	-	-	-
	03/10-12	0	-	-	-	0	-	-	-	0	-	-	-	0	-	-	-
	04/20-22	0.2	0.30	-	-	0.2	1.04	-	-	0	-	-	-	0.6	-	-	-
	05/18-20	0	-	-	-	0	0.62	-	-	0	-	-	-	0.2	-	-	-
	06/12-14	12.0	-	-	-					0.4	-	-	-	0	-	-	-
	07/23-25									0	-	-	-				
	08/24-26									11.0	-	-	-	5.6	-	-	-
	09/15-17									2.4	-	-	-	0	-	-	-
	10/09-11									0	-	-	-	0	-	-	-
	11/14-16													0	-	-	-
	12/04-06									20.6	-	-	-	2.8	-	-	-
2016	01/24-26									0	-	-	-	0	-	-	-
	02/25-27	0.2	-	-	-	0.2	-	-	-	0	-	-	-	0.8	-	-	-
	03/15-17	25.3	-	-	-	25.3	-	-	-	3.6	-	-	-	18.6	0.38	-	-
	04/25-27	0	-	-	-	0	-	-	-	0	-	-	-				
	05/27-29	0	-	-	-									0	-	-	-
	06/14-16	0.4	-	-	-	0.4	0.18	-	-	6.6	-	-	-	0	-	-	-
	07/15-17	0	-	-	-	0	-	-	-	0	-	-	-	0	-	-	-
	08/02-04	0	-	-	-	0	-	-	-	0	-	-	-	0	-	-	-
	09/04-06	0	-	-	-	0	-	-	-	0	-	-	-	0	-	-	-
	10/25-27	2.0	-	-	-	2.0	-	-	-	1.4	-	-	-	1.4	-	-	-
	11/20-22					24.1	-	-	-	28.3	-	-	-	20.9	-	-	-
	12/20-22	3.8	-	-	-	3.8	-	-	-	3.6	-	-	-	5.2	-	-	-

220 (-) means < Limit of Detection

## 221 **3. Results and discussion**

### 222 **3.1. Detection frequency and atmospheric concentrations**

#### 223 *Sales and application*

224 In 2015 and 2016, French sales of Glyphosate were 8,790 and 9,110 tons respectively. At the  
225 local scale, over the same period, the Glyphosate sales were stable in Alpes-Maritimes (Nice),  
226 i.e., 11.7 and 10.6 tons, and in Bouches-du-Rhône (Port-de-Bouc), i.e., 43.6 and 44.4 tons,  
227 respectively, whereas they were significantly reduced in Vaucluse (Avignon and Cavaillon),  
228 from 165.1 to 48.5 tons. The same pattern was observed for Glufosinate-ammonium for much  
229 smaller sold amounts, i.e., 255 and 185 kg in Alpes-Maritimes, 3.0 and 2.7 tons in Bouches-du-  
230 Rhône, and 3.5 and 1.0 tons in Vaucluse, in 2015 and 2016 respectively (BNVD, 2017).

231 In the areas under study, Glufosinate-ammonium is mainly used in agriculture (commercial  
232 formulation Basta® F1) while Glyphosate can be used for agricultural practice (e.g., Missile®  
233 360 and Clinic® Ace for the main formulations used) or in non-agricultural areas, i.e., public  
234 areas, roadways, amateur gardens... (e.g., Barclay® Gallup Super 360 Jardin and Glyfos®  
235 Jardin for the main formulations used) (BNVD, 2017). In France, in 2015 and 2016, non-  
236 agricultural uses of Glyphosate were estimated respectively at 18.6% and 16.1% of the total  
237 amount of sales.

238 The nature of soil and meteorological conditions (relative humidity (RH), temperature...) are  
239 important parameters for the weeding process. Indeed, as Glyphosate and Glufosinate-  
240 ammonium are systemic foliar and contact herbicides, their efficiencies are enhanced during  
241 humid ( $RH > 70\%$ ) and temperate ( $15-25^{\circ}\text{C}$ ) periods, without wind and rain causing pesticides  
242 dispersion by drift and leaching. They were mainly spread in late winter (February), during the  
243 spring and early summer periods (April to July), and to a lesser extent, during the fall period  
244 (October to December). However, since these active substances are not only used in agriculture

245 (but also by individuals), it is difficult to know the exact treatment schedule and to delimit the  
246 area of use.

#### 247 *Detection frequency and atmospheric concentrations*

248 Glyphosate was detected at a global frequency of 7% with frequencies ranging from 0% (Nice)  
249 to 23% (Cavaillon), according to the sampling site. These detection frequencies were of the  
250 same order of magnitude as those observed in the Hauts-de-France region (France), i.e., 14%  
251 (2004, Prouvost and Declercq, 2005). However, Glyphosate was observed with a higher  
252 frequency in the air of Mississippi and Iowa (USA), i.e., 94% and 67%, respectively (2007-  
253 2008, Chang et al., 2011). In this work, AMPA, the main Glyphosate degradation product, was  
254 never detected at any sampling sites. In the atmosphere, it was previously analyzed only in  
255 Mississippi and Iowa (USA), with detection frequencies of 78% and 58%, respectively (2007-  
256 2008, Chang et al., 2011). However, it should be noted that the LOD determined in the present  
257 study is too high to detect traces in some samples of Mississippi and Iowa. As AMPA is a bio-  
258 degradation product formed only in soils, its atmospheric concentrations could be only due to  
259 soils aeolian erosion (Bento et al., 2017). Since no simultaneous detection of Glyphosate and  
260 AMPA was observed in the present work, it can be assumed that the aeolian erosion was a  
261 pesticide atmospheric source of minor importance and thus, the atmospheric Glyphosate  
262 concentrations were mainly due to the drift during spraying (Hewitt et al., 2009).

263 As well as AMPA, Glufosinate-ammonium was never detected. Besides its low Henry's Law  
264 Constant and its low vapor pressure, two other hypotheses may be put forward to explain this  
265 result: its sales amount (i.e., its application) was far below of Glyphosate and its LOD was  
266 maybe too high to detect atmospheric concentrations. Anyway, to the best of our knowledge,  
267 no atmospheric monitoring is reported in the literature for this active substance and this work  
268 is the first effort to quantify it.

269 During the same period (2015-2016), 50 other active substances, including 21 herbicides, were  
270 monitored in the atmosphere on the sampling sites under study (Désert et al., 2018). Detection  
271 frequencies of herbicides, fungicides, and insecticides reached a maximum of 57% for  
272 Pendimethalin, 58% for Tebuconazole, and 98% for Lindane, respectively. Considering only  
273 herbicides, 12 active substances were never detected, and Glyphosate would be in 6/22  
274 position ranking behind Pendimethalin (57%), S-Metolachlor (23%), Diflufenican (16%),  
275 Chlorpropham (14%), and Prosulfocarb (9%), which makes its atmospheric detection frequency  
276 relatively important considering its physicochemical properties.

277 In an atmospheric concentrations point of view, Glyphosate concentration reached a maximum  
278 level of 1.04 ng m<sup>-3</sup> in Cavaillon. Until this study, the maximum peak concentration measured  
279 in France was only 0.19 ng m<sup>-3</sup> (2004, Prouvost and Declercq, 2005). These maximum values  
280 were much smaller than those measured in US agricultural areas where they can reach 9.1 ng  
281 m<sup>-3</sup> in Mississippi (2007, Chang et al., 2011) during the application period. However, these  
282 concentrations should be compared with the highest concentration (i.e., 42.96 µg m<sup>-3</sup>) measured  
283 in the atmosphere near a spray application (Morshed et al., 2011). In 2015 and 2016, among  
284 herbicides searched on the sampling sites under study, only Pendimethalin was quantified at a  
285 higher concentration, i.e., 1.924 ng m<sup>-3</sup> in Cavaillon.

286

### 287 **3.2. Spatial and temporal detections of Glyphosate**

288 According to sampling sites and years, spatial and temporal detection frequencies varied from  
289 0% (e.g., Nice) to 66% (i.e., Cavaillon in 2015). If some of these results may be explained by  
290 the context of sources (e.g., rural vs. urban), it is not always easy to correlate the detections and  
291 the environment of the sampling sites.

#### 292 *Spatial distribution*

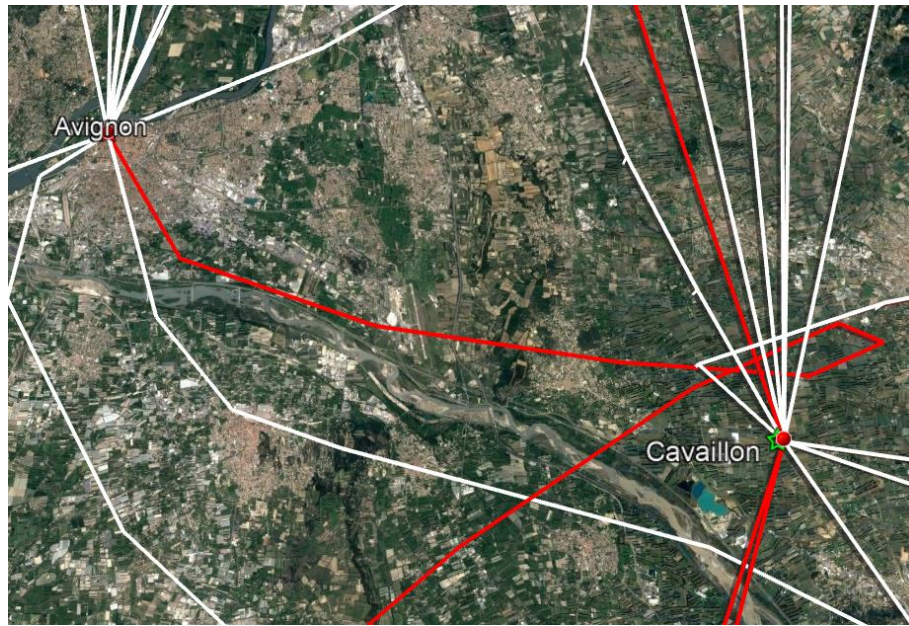


293 In Nice, sampling was performed in a wooded square in city center, near a cemetery (~550 m  
294 South-West), urban parks (~400 m East), and port (~500 m South). Nice was the only site where  
295 Glyphosate has never been detected (0/22 analysis). The explanation probably lies in the fact  
296 that, since 2009, Nice has adopted a 'zero pesticide' policy for the maintenance of green spaces,  
297 cemeteries, and roads.

298 On the other hand, with a detection frequency of 23% (3/13 analysis), Cavaillon is the sampling  
299 site where the atmosphere is the most contaminated by Glyphosate. In addition, the highest  
300 concentrations, until  $1.04 \text{ ng m}^{-3}$  in April 2015 were measured on this site. Back-trajectories  
301 calculated using the NOAA HYSPLYT model (Figure 4) indicate two regional sources: from  
302 North (May 2015) and South-West (April 2015 and June 2016). Samples of Cavaillon were  
303 collected in a hamlet named "Les Vignères", a rural site located in an intensive arboriculture  
304 area (the nearest orchard is less than 200 m from the sampler). According to the French National  
305 Institute for Agricultural Research (Reboud et al., 2017), mechanical weeding is not always  
306 possible in established orchards if it has not been thought upstream, which leads to use of  
307 herbicides and especially Glyphosate. The amounts of active substance applied per hectare and  
308 per year range from 62 to  $3,600 \text{ g ha}^{-1} \text{ yr}^{-1}$ . Moreover, these results were consistent with the  
309 monitoring of 59 other active substances during the 2012-2017 period (Désert et al., 2018),  
310 which have already shown important values both in detection frequency and in atmospheric  
311 concentration.

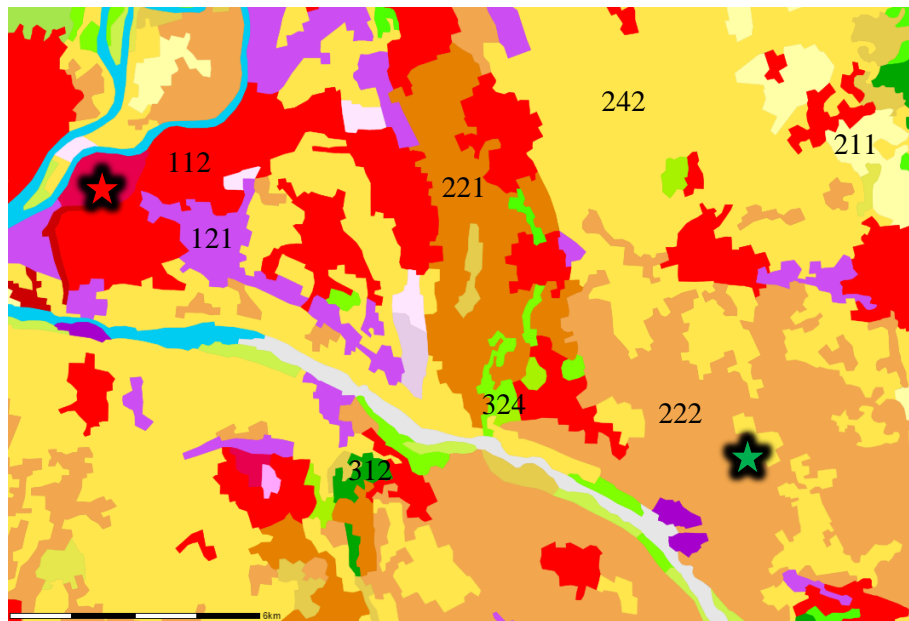
312 The sampling site of Avignon is located in the city center, near a public garden (~200 m North  
313 and North-West) and train station (~900 m South). From an agricultural point of view, there is  
314 also arable lands (~600 m North), orchards (~2 km North-East), and vineyards (~5 km North-  
315 West). Glyphosate was detected only once in April 2015 (1/14 analysis, 7%). Back-trajectories  
316 (Figure 4) suggest a South-East source with an air mass passing especially over the orchards  
317 surrounding the sampling site of Cavaillon.

318



319

a-



320

b-

321 **Fig. 4.** Geographical environment of Avignon and Cavaillon: a- Calculated back-trajectories  
322 (NOAA HYSPLIT model – GDAS meteorological data) during sampling (red line: detection  
323 of Glyphosate, white line: < LOD). b- Corine Land Cover nomenclature: 112/121-Urban fabric,  
324 211-Arable land, 221-Vineyards, 222-Fruit trees and berry plantations, 242-Heterogeneous  
325 agricultural areas, 312-Forests, 324-Scrub and/or herbaceous vegetation associations.

326

327 The sampling site of Port-de-Bouc is located at the harbor near the train station (~600 m North)  
328 and less than 2 km from an industrial complex (refinery, petrochemical facilities...). As in  
329 Avignon, Glyphosate was detected only once in March 2016 (1/22 analysis, 5%). However, the  
330 origin of the air mass coming from the East does not indicate specific areas where Glyphosate  
331 is intensively used.

332 These results highlight a higher detection frequency of Glyphosate in rural areas than in urban  
333 areas, i.e., 87% (3/13 analysis) against 13% (2/58 analysis), respectively. If rural and urban sites  
334 correspond rather to agricultural and non-agricultural applications, respectively, this is  
335 consistent with French sales with non-agricultural applications estimated at 18.6% in 2015 and  
336 16.1% in 2016.

### 337 *Temporal distribution*

338 All detections were made between March and June which is consistent with the main phase of  
339 Glyphosate spreading in late winter and during spring and early summer periods. In Mississippi,  
340 Glyphosate is detected throughout 2007 and 2008 but maximum concentration occurred in May  
341 during the application period and at a lesser extent in July and August. In Iowa, maximum  
342 concentrations of Glyphosate occurred in mid-June and mid-July (2007) and from late May to  
343 early June (2008), according to meteorological conditions (Chang et al., 2011). In contrast to  
344 these results, in 2003-2004, measurements in Caudry, a suburban area in Hauts-de-France  
345 Region (France), show only detections in the summer period between July and September  
346 (Prouvost and Declercq, 2005).

347 It should be noted that of the three sampling sites where Glyphosate has been detected (i.e.,  
348 Avignon, Cavaillon, and Port-de-Bouc), there is no reproducible detection pattern from 2015  
349 to 2016.

350

### 351 **3.3. Influence of meteorological conditions**

352 The meteorological data collected at the four sampling sites allow observing the influence of  
353 precipitation, temperature, and wind speed on the Glyphosate concentrations. However, it is  
354 necessary to be cautious because only 5 out of 71 samples contained Glyphosate. No literature  
355 data are available on the influence of temperature and wind speed. However, the weeding  
356 efficiency of Glyphosate is enhanced during humid ( $RH > 70\%$ ) and temperate ( $15-25^{\circ}\text{C}$ )  
357 periods, without wind and rain to avoid drift and leaching.

358 The 5 detections of Glyphosate were registered when mean daily temperatures ranged between  
359  $9.7^{\circ}\text{C}$  (Port-de-Bouc, March 2016) and  $21.0^{\circ}\text{C}$  (Cavaillon, June 2016), which is consistent with  
360 the temperatures commonly measured at the spreading period.

361 In France, it is forbidden to treat as soon as the wind speed reaches an intensity greater than  
362 about  $19 \text{ km h}^{-1}$  (Index Acta Phytosanitaire, 2018). During the days when Glyphosate was  
363 detected, the wind speed exceeded this value 33% of the time (hourly measurement), reaching  
364 up to a maximum of more than  $40 \text{ km h}^{-1}$  in Port-de-Bouc. These wind speeds can lead to greater  
365 resuspension and then long-range transport by aerial drift which will cause injury to nontarget  
366 plants. The probability of drift injury occurring increased when winds are gusty or when wind  
367 speed will allow spray drift to occur (Franz et al., 1997).

368 Due to its high solubility in water, Glyphosate is expected to be removed by rainfall. More, its  
369 detection in precipitation is probably due to its association with particulate matter (Anderson et  
370 al., 2005). In previous work (Chang et al., 2011), it was estimated that 87 to 92% of Glyphosate  
371 in the air would be removed by weekly rainfall lower than 30 mm and 97% by weekly rainfall  
372 greater than 30 mm. Only the sampling collected in Port-de-Bouc in March 2016 showed  
373 Glyphosate detection during a rainy period (precipitation 18.6 mm), suggesting that the  
374 measured concentration ( $0.38 \text{ ng m}^{-3}$ ) was potentially higher before the rain even.

375

#### 376 **4. Conclusion**

377 This work is one of the few monitoring studies in the atmosphere of Glyphosate, AMPA, its  
378 main metabolite, and Glufosinate-ammonium. Neither Glufosinate-ammonium nor AMPA  
379 were detected. However, at the same sampling sites, during the same period, detection  
380 frequency and maximum concentration of Glyphosate were sometimes higher than those found  
381 for other pesticides, especially herbicides. This is despite the physicochemical characteristics  
382 of Glyphosate which are not favorable to its passage into the atmosphere.

383 The absence of simultaneous detection of Glyphosate and AMPA suggests that drift during  
384 spraying operation is the main atmospheric source of Glyphosate and that resuspension from  
385 soil particles is minor.

386 However, in the worst-case scenario ( $1.04 \text{ ng m}^{-3}$ ), the expected dose of Glyphosate for an  
387 average consumer (70 kg body weight) respiring at a rate of  $1.5 \text{ m}^3 \text{ h}^{-1}$  during light exercise is  
388  $0.54 \text{ ng kg}^{-1} \text{ day}^{-1}$ . In these conditions, this value remains well below of the chronic reference  
389 dose for Glyphosate of  $1.75 \text{ mg kg}^{-1} \text{ day}^{-1}$  (US EPA, 2009).

390 Finally, the implementation of an extensive air monitoring network for Glyphosate control is  
391 needed to collect more data in order to be able to model the concentrations in the atmosphere.

392

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398

399 **Competing financial interests**

400 The authors declare no competing financial interests.

401

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