



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

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## Abstract

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

## Keywords

Pesticides; Herbicides; Atmosphere; Transport

## Highlights

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

## 1. Introduction

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

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

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

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

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

<sup>3</sup> during spraying using a calibrated mist blower. It should be noted that a first modeling attempt of an estimated emission of Glyphosate to the atmosphere was done at a regional scale (Atmo Auvergne-Rhône-Alpes, 2017) but without any measurement to confirm the model output.

In the present work, the results of a two year (2015-2016), field campaign (142 filters) are reported. It was dedicated to quantify Glyphosate, Glufosinate-ammonium, and AMPA in the ambient atmosphere of Provence-Alpes-Côte d’Azur (PACA, France) in different areas typologies (non-agricultural areas: city center, ‘zero pesticide’ policy, and industrial area but also agricultural sectors: mainly orchards and vineyards). Necessary laboratory extraction and analytical methods were developed. Atmospheric concentrations were compared to data obtained over the same period and at the same sampling sites for 50 current-use pesticides (Désert et al., 2018). The present study offers one of the few reports of Glyphosate, Glufosinate-ammonium, and AMPA in the air.

## **2. Material and methods**

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

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

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

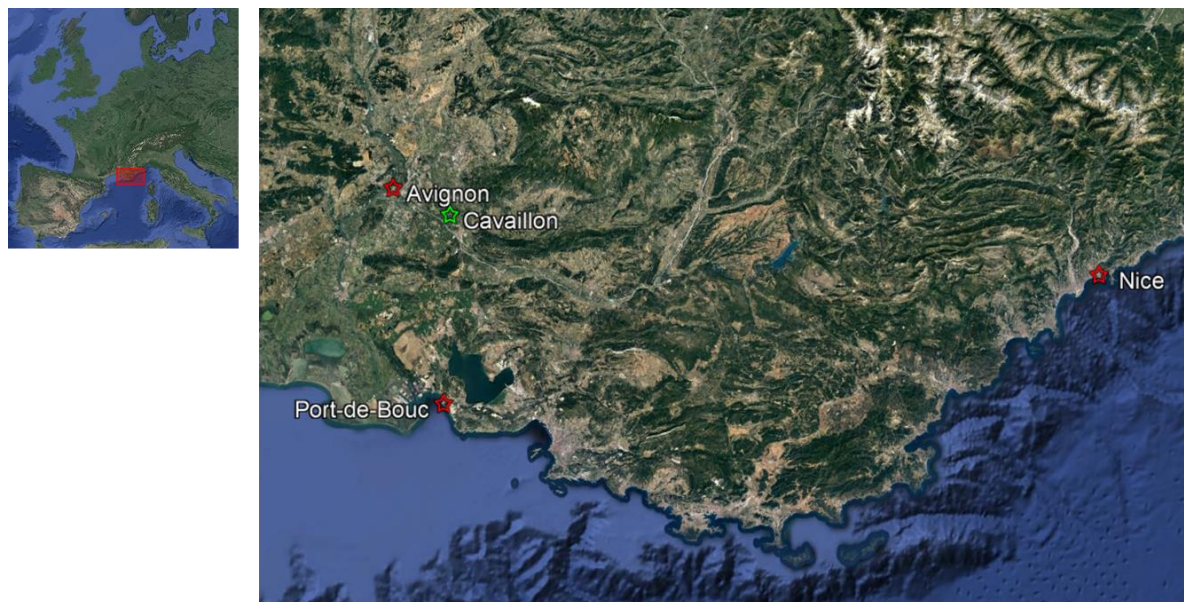
<sup>a</sup> PPDB: Pesticide Properties DataBase (Lewis et al., 2016). <sup>b</sup> APVMA, 2017.

9-Fluorenmethylchloroformate (Fmoc-Cl, ≥ 99%) and isotope-labeled Glyphosate (2-<sup>13</sup>C, 99 atom % <sup>13</sup>C) from Sigma-Aldrich were used as derivatization reagent and internal standard (IS), respectively. HPLC-grade dichloromethane (Sigma-Aldrich), ethylenediaminetetraacetic acid (EDTA), sodium tetraborate decahydrate (Borax), ammonium formate, formic acid, ammonia solution (35%), LC/MS-grade acetonitrile, and LC/MS-grade methanol (Fisher Scientific) were used for extraction and chromatographic elution. Ultra-High Quality water (UHQ water, 18.2 MΩ cm<sup>-1</sup> at 25°C) was obtained by tap water passed through a Milli-Q water purification system (Direct 8 MilliQ, Merck Millipore). Underivatized standards were dissolved in UHQ water and the stock solutions of each compound at 0.5 g L<sup>-1</sup> for Glyphosate and Glufosinate-ammonium, and 0.9 g L<sup>-1</sup> for AMPA were stored in a polypropylene bottle (PP) at 4°C.

## 2.2. Sampling and site characterization

Sampling was undertaken at four sampling sites distributed throughout the Provence-Alpes-Côte-d'Azur (PACA) region, France (Figure 1), from January 2015 to December 2016. The description of sampling sites and sampling periods are summarized in Table 2. The three urban

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



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

**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

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



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

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

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

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

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

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

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

*Purification and concentration:* Prior to purification and concentration on Solid Phase Extraction (SPE), the pH of the aqueous fraction was adjusted to pH 3 with formic acid 5% which corresponds to the optimum analyte retention. The extraction cartridge (OASIS HLB cartridge, 6 mL, 150 mg, Waters) was successively conditioned by 2 mL of methanol then 2 mL of formic acid 0.1%. Impurities were eliminated by a selective washing step constituted by 2 mL of formic acid 0.1% then 2 mL of UHQ water. Elution was achieved by 4 mL of [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 evaporating methanol using a concentration workstation and filtered through a PTFE membrane of 0.2  $\mu\text{m}$  pore size before analysis.

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

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

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

## 2.5. Analytical performance of the method

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

The detection limit (LOD) and quantification limit (LOQ) were determined using the calibration 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> )			Precipitation (mm)	Concentration (ng m <sup>-3</sup> )		
		GLY	GLU	AMPA		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

### 3. Results and discussion

#### 3.1. Detection frequency and atmospheric concentrations

##### *Sales and application*

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

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

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

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

#### *Detection frequency and atmospheric concentrations*

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

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

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

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

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

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

#### *Spatial distribution*

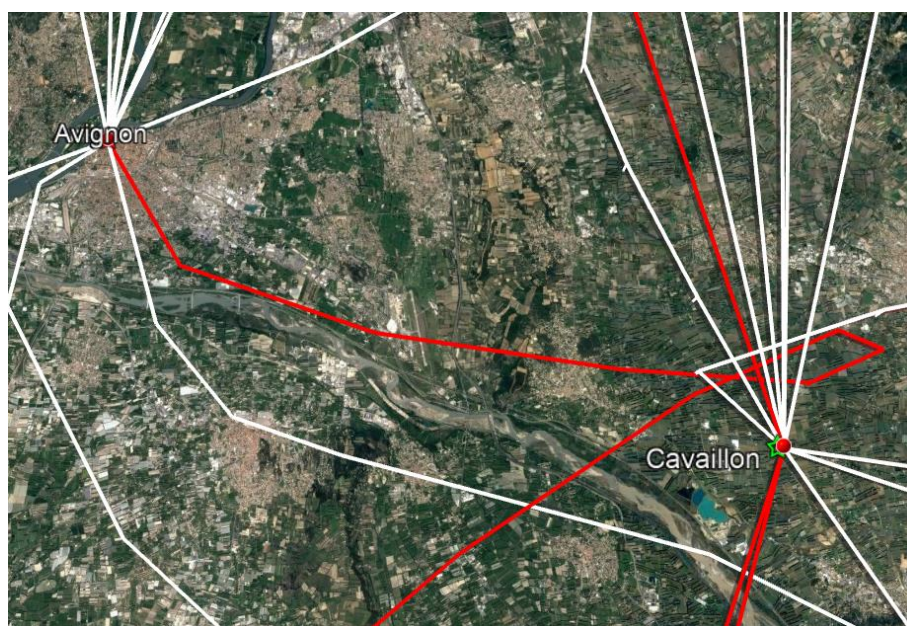


293 In Nice, sampling was performed in a wooded square in city center, near a cemetery (~550 m  
294 South-West), urban parks (~400 m East), and port (~500 m South). Nice was the only site where  
295 Glyphosate has never been detected (0/22 analysis). The explanation probably lies in the fact  
296 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.

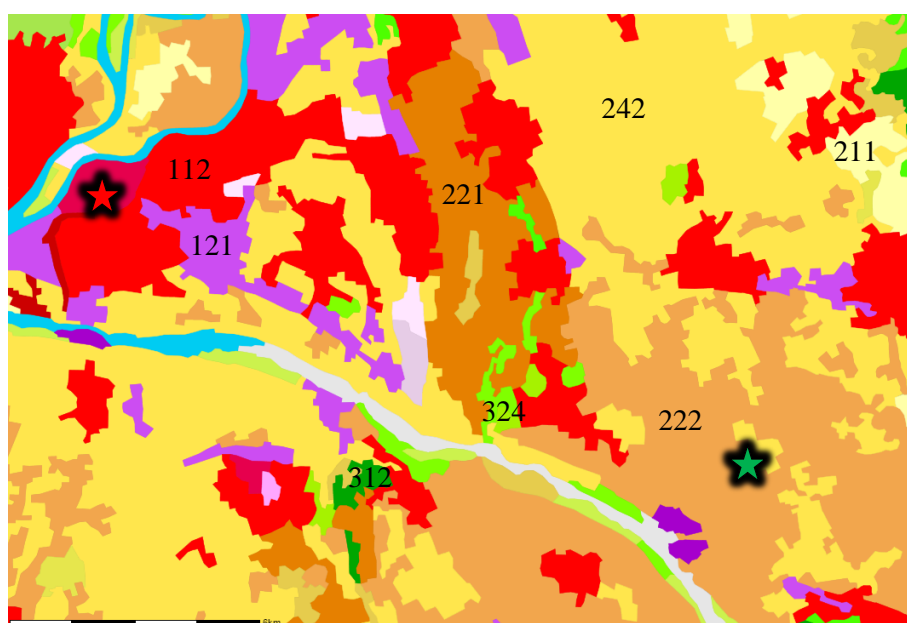
312 The sampling site of Avignon is located in the city center, near a public garden (~200 m North  
313 and North-West) and train station (~900 m South). From an agricultural point of view, there is  
314 also arable lands (~600 m North), orchards (~2 km North-East), and vineyards (~5 km North-  
315 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

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

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

#### *Temporal distribution*

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

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

### 3.3. Influence of meteorological conditions

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

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

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

Due to its high solubility in water, Glyphosate is expected to be removed by rainfall. More, its detection in precipitation is probably due to its association with particulate matter (Anderson et al., 2005). In previous work (Chang et al., 2011), it was estimated that 87 to 92% of Glyphosate in the air would be removed by weekly rainfall lower than 30 mm and 97% by weekly rainfall greater than 30 mm. Only the sampling collected in Port-de-Bouc in March 2016 showed Glyphosate detection during a rainy period (precipitation 18.6 mm), suggesting that the 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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410 [fce1-43fd-a109-8ec6423929b4/download/6444.pdf](https://open.alberta.ca/dataset/a4381736-cd17-4be1-b8ed-16aee8073be9/resource/5744d27f-fce1-43fd-a109-8ec6423929b4/download/6444.pdf)

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