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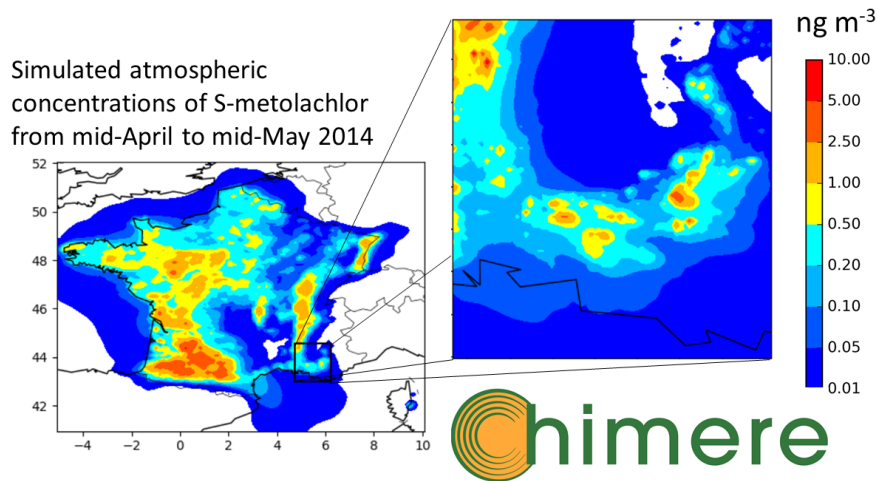


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Graphical Abstract

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Simulating the impact of volatilization on atmospheric concentrations of pesticides with the 3D chemistry-transport model CHIMERE: method development and application to S-metolachlor and folpet

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Abstract

A method to simulate the atmospheric concentrations of pesticides was implemented in the air quality model CHIMERE. The method is based on a module to simulate the volatilization of pesticides from soils and plants and on the spatiotemporal distribution of pesticide applications. Pesticide applications are spatially distributed according to the quantities of pesticides sold per municipality in France (recorded in the French BNVD-S database) and are temporally distributed according to the application periods determined with enquiries.

The model was applied to S-metolachlor (an herbicide used mainly on maize) and folpet (a fungicide mostly used to treat mildew). In the first stage of the study, the pesticide emissions simulated by CHIMERE are compared to the results of the Volt'Air model. In the second stage of the study, measured concentrations of S-metolachlor and folpet from mid-April to the end of June are compared to the simulation results at the French and PACA (Southeastern region of France) scales.

The model can reproduce the spatial distribution of S-metolachlor concentrations (spatial correlation over France of 0.79). The concentrations of both pesticides are simulated with the good order of magnitude (bias for S-metolachlor ranges from -50 to 50% for most stations during the application period).

Keywords: Pesticide, Air quality, Modelling

1. Introduction

Pesticides are chemical products widely used in agriculture for pest management and therefore to prevent yield losses. Numerous pesticides have however been detected in the atmosphere (e.g. studies of Moussaoui et al. (2012); Coscollà et al. (2017) or Désert et al. (2018)) due to losses by spray drift during the application of pesticides and volatilization from soil and plants in post-application.

Although gaseous pesticides are degraded by both direct and indirect photochemical reactions, including light, (O_3), hydroxyl (OH) and nitrate (NO_3) radicals, their atmospheric lifetime can reach several days. Moreover, condensation of gaseous pesticides onto atmospheric particles may in some cases protect the compounds from degradation (Socorro et al., 2016; Mattei et al., 2018, 2019c,a,b). The atmospheric medium and long-range transport of pesticides is therefore possible and has been highlighted by several studies (Muir et al., 2004; Pokhrel et al., 2018; Huang et al., 2019).

Due to the ubiquity of pesticides and their potential harmful effect, it is necessary to develop tools in order to understand and evaluate their transport and evolution in the atmosphere. Modelling pesticide concentrations at the regional or national scale would help in designing spatiotemporal sampling strategies set up to monitor atmospheric contamination by pesticides or in determining population exposure as a basis for health and environmental impact studies. Air quality models such as the CHIMERE model (Mailler et al., 2017), have been developed to simulate the formation and transport of main pollutants (such as ozone and particulate matter) by representing the physicochemical processes involved in their evolution (such as gas-phase chemistry of radicals and major compounds, particle formation, gas/particle partitioning, deposition). This type of model can be applied to the simulation of pesticide concentrations by simulating the atmospheric transport and degradation of these compounds. However, the use of chemical transport models to simulate pesticide concentrations in the atmosphere is scarce. Most of the Modelling studies on pesticides are focused on the local transport of spray-drift over short distances in order to assess the exposure of non-target ecosystems such as surface waters (Raupach et al., 2001; Tsai et al., 2005; Zhang et al., 2018). Some studies focused on gaseous atmospheric dispersion and deposition of pesticides (Asman et al., 2003; Jacobs et al., 2007; Bedos et al., 2013; van den Berg et al., 2016). A few models have been developed to investigate the long-range transport of pesticides. Zhang et al. (2008) used the Canadian model for environmental transport of organochlorine pesticides (CanMETOP) (Ma et al., 2003) and the multicompartiment environmental diagnosis and assessment (MEDIA) model (Koziol and Pudykiewicz, 2001) to provide evidence of the intercontinental transport of lindane. Li et al. (2011a,b) developed a Modelling system based on chemistry transport Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2005) and the Pesticide Emission Model (PEM) (Scholtz et al., 2002). They applied it to the transport of toxaphene from the heavily contaminated soils in the southern United States and Mexico to several water bodies (the Atlantic Ocean, the Gulf of Mexico, and the Great Lakes). The authors compared the simulated concentrations to measurements at two stations in Louisiana and Michigan and found a good agreement (simulated and measured average concentrations agree within a factor 2).

50 The objective of this study is to implement pesticides within the chemical
51 transport model CHIMERE in order to simulate the spatiotemporal distribu-
52 tion of current used pesticides in the atmosphere at a regional and national
53 scale. The model is tested and applied for 2 pesticides: S-metolachlor (a her-
54 bicide used in France mostly on maize at the early stage of the crop growth)
55 and folpet (a fungicide mostly used to treat mildew in vineyards), both be-
56 ing frequently detected in the atmosphere (AtmoFrance, 2019). S-metolachlor
57 and folpet are used in this study as compounds representative of pesticides
58 emitted by volatilization from soil and plant surfaces, respectively. First, the
59 emissions by volatilization estimated by CHIMERE are compared to those cal-
60 culated with the pesticide version of the model Volt’Air developed to predict
61 pesticide volatilization at the field scale and tested against volatilization flux
62 measurements for different herbicides and fungicides applied on bare soil and
63 wheat crops (Bedos et al., 2009; Garcia et al., 2014; Lichiheb et al., 2016).
64 The contribution of emission by spray drift during application to atmospheric
65 concentration was assumed negligible given the resolution of the model but its
66 deposition on the different surfaces of the mesh which can therefore contribute
67 to the subsequent volatilization was considered. Then, the simulated results
68 are compared to concentrations measured over France in 2014 with a focus on
69 France southeastern PACA (Provence-Alpes-Côte d’Azur) region.

70 2. Method

71 The CHIMERE model has been modified to be able to simulate the concen-
72 trations of pesticides. The concentrations of pesticides are simulated over two
73 domains: France at a resolution of $0.15^\circ \times 0.1^\circ$ (around 120 km^2) and the PACA
74 region at a resolution of $0.02^\circ \times 0.02^\circ$ (around 3.5 km^2).

75 The results of the France simulation are used as boundary condition for the
76 PACA (the concentrations of air masses entering the PACA domain are taken
77 from the France simulation). CHIMERE was first run over an European domain
78 (with a resolution of $0.4^\circ \times 0.25^\circ$) in order to simulate the concentrations of the
79 main atmospheric pollutants (that may intervene in the evolution of pesticides)
80 and to be used as boundary conditions of the France simulation.

81 The model development is presented in the Method section. The emissions
82 over the PACA region simulated with CHIMERE are compared with the emis-
83 sions estimated with the Volt’Air model. Emission calculations with both mod-
84 els are presented briefly in Sections 2.2.1 and 2.2.2.

85 Finally, the model results are compared to measurements available from
86 mid April to the beginning of July 2014. This period was selected based on the
87 availability of databases at the time of this study (see section 2.1.3) and the
88 periods of application of pesticides (see section 2.2.3).

89 First, the general performance of the model were analyzed by comparing
90 the results of national simulation to all the measurements available during the
91 simulation period in France. Second, the analysis was focused on the regional
92 PACA simulation.

93 2.1. Overview

94 2.1.1. General description

95 The approach used in this study is illustrated by Fig. 1.

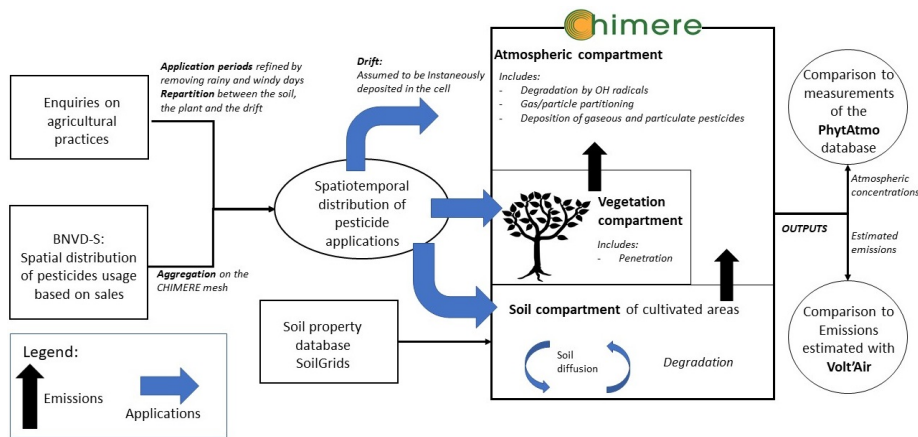


Figure 1: Scheme of the pesticide Modelling approach used in this study.

96 Couvidat and Bessagnet (2021) developed a revised version of the CHIMERE
 97 2017 β version (Couvidat et al., 2018) of the model to take into account the ex-
 98 changes of semivolatile organic compounds (SVOC) between the atmosphere
 99 and the soil and vegetation compartment (with exchanges accounting for both
 100 the volatilization and the deposition). The soil/atmosphere exchange module
 101 from Couvidat and Bessagnet (2021) uses a resistance scheme and parameter-
 102 izations to consider the multiphase partitioning as well as the diffusion in the
 103 soil. This version was extended by implementing pesticides. In that order, a
 104 parameterization accounting for the volatilization of the pesticide layer covering
 105 the plants was implemented by following Lichiheb et al. (2016).

106 The model used in this study accounts for:

- 107 • The chemical evolution of compounds in the atmosphere by considering
 108 the gas-phase degradation of pesticides by OH radical and the partitioning
 109 of semivolatile pesticides between the gas and the particle phase.
- 110 • The soil/atmosphere and vegetation/atmosphere exchanges that can lead
 111 to the deposition of pesticides (sorption of pesticide by the soil or the
 112 vegetation) or their emissions (by volatilization). The exchanges are con-
 113 sidered for both the treated crops (on which the pesticides are applied)
 114 and the other surfaces (in that case, accumulated pesticides in the com-
 115 partments can be re-emitted).
- 116 • The evolution of pesticides inside the soil by considering the multi-phase
 117 partitioning inside the compartment (gaseous, solid, and liquid), the degra-
 118 dation of pesticides within the soil by using the compound half-life time
 119 and the vertical diffusion.

120 The impact of spray drift was not considered in the model as its contribution
 121 is expected to be very local (close to the treated crop) compared to the scale
 122 of the CHIMERE (above 1 km). However, the deposition of the spray drift
 123 onto the different surfaces of the mesh (and its potential re-emissions due to
 124 volatilization) was considered.

125 In order to simulate properly the emissions of pesticide by volatilization,
 126 the spatiotemporal distribution of pesticide application have to be known. The

127 French BNVD-S database uses the mandatory register on pesticide sales to esti-
128 mate the spatialized usage of pesticides for the year considered, this database is
129 presented in section 2.1.3. Enquiries on the agricultural practices used by farm-
130 ers in PACA were carried out by contacting experts of the different agricultural
131 sectors of the region to obtain information in terms of types of sprayer used and
132 timing of application. The enquiry methodology is presented in Section 2.2.3.
133 For the purpose of the Modelling exercise, the agricultural practices identified
134 for PACA were used for the whole country.

135 The spatiotemporal distribution of pesticide usage is used within CHIMERE
136 to estimate the amount of pesticides emitted in the atmosphere.

137 2.1.2. Substance selection and properties

138 Two substances were simulated in this study: S-metolachlor and folpet.
139 These two substances were selected because they correspond mostly to one type
140 of volatilization (from the soil for S-metolachlor and from the plant for folpet)
141 and to one type of culture (mostly applied on maize crops for S-metolachlor
142 and on the vineyards for folpet). Moreover, these two substances are among the
143 pesticides frequently detected in the air over the PACA region (Désert et al.,
144 2018).

145 S-metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl)
146 acetamide] is a selective chloroacetamide herbicide widely used for pre- and
147 postemergence weed control for a variety of crops including maize, soybean,
148 sunflower, and sorghum (Alletto et al., 2013).

149 Folpet [N-(trichloromethylthio)phthalimide] is a phthalimide protective fungi-
150 cide used for broad spectrum control of fungal pathogens. It is widely used in
151 vineyard against mildews or excoriosis for example (Index Acta Phytosanitaire,
152 2018).

153 The properties of the two substances used in this study are summarized in
154 Table 1. Most of the data are taken from the Pesticide Properties DataBase
155 (PPDB) database centralizing the properties of pesticides to estimate the en-
156 vironmental risks associated to these molecules (PPDB, 2020). For Volt’Air
157 model, K_{oc} values are required as input, whereas in CHIMERE, this adsorption
158 coefficient is derived from the K_{ow} value (Couvidat and Bessagnet, 2021). In
159 Volt’Air, values of 0.206 and $0.304 \text{ m}^3 \text{ kg}^{-1}$ were chosen for S-metolachlor and
160 folpet, respectively. This information was available in the PPDB database for
161 folpet but not for S-metolachlor. The K_{oc} used for S-metolachlor is the average
162 value given by Alletto et al. (2013). The half-life inside the soil (DT_{50} -soil) is
163 used to simulate their degradation inside the soil. In the atmosphere, the sec-
164 ond order kinetic rate parameter with OH radicals (k_{OH}) in gas phase is used
165 as follow: for folpet, k_{OH} was estimated according to theoretical calculations
166 from AOPWIN software (Atmospheric Oxidation Program for MicrosoftWin-
167 dows (Meylan and Howard, 1993)); for S-metolachlor, k_{OH} was based on Chao
168 et al. (2018) who estimated a value of $6.83 \times 10^{-11} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$ close
169 to the value estimated with AOPWIN of $5.59 \times 10^{-11} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$.

170 Large uncertainties exist however on the determination of several parame-
171 ters. The estimation of saturation vapor pressure (or similarly of the Henry’s
172 law constant) is rather uncertain as discussed by Leistra (2011) and using quan-
173 titative structure–property relationship (QSPR) for example may lead to error
174 up to a factor 10 (Beck et al., 2000). Various studies reported DT_{50} -soil be-
175 tween 4 and 141 days for S-metolachlor indicating that this parameter is also

176 quite variable. (Grey et al., 2007; Bedmar et al., 2017; Wolejko et al., 2017;
 177 Marín-Benito et al., 2018; Fernandez et al., 2020).

Properties	S-metolachlor	Folpet
P_i^0 (Pa)	3.7×10^{-3}	2.1×10^{-5}
Solubility (mg/L)	480	0.8
Henry (mol/L/atm)	46 300	13 600
$\log(K_{ow})$	3.05	3.02
DT ₅₀ -soil (days)	51.8	1.6
k_{OH} (molecules ⁻¹ cm ³ s ⁻¹)	6.83×10^{-11}	1.57×10^{-11}

Table 1: Substance properties used in this study for S-metolachlor and folpet

178 2.1.3. Input databases

179 Three types of databases are necessary to simulate the volatilization of pes-
 180 ticides:

- 181 • Hourly meteorological data necessary for the emission calculation (such as
 182 the temperature, the wind velocity) were taken from the European Centre
 183 for Medium-Range Weather Forecast (ECMWF) model. As CHIMERE
 184 do not solve the soil thermal and hydric evolution (contrary to Volt’Air
 185 which is based on global radiation), the soil temperature and volumetric
 186 water content of ECMWF were also used in CHIMERE. It has to be noted
 187 that the low vertical resolution of the soil data (between 0 and 7 cm) and
 188 that the model calculates the average soil moisture and temperature over
 189 the whole cell. These parameters may not be representative of the type
 190 of soil on which pesticides are applied.
- 191 • The soil properties needed by CHIMERE (organic carbon content, bulk
 192 density) are taken from the SoilGrids database (Batjes et al., 2020). This
 193 database provides soil property maps for the world produced using ma-
 194 chine learning at 250 m resolution. SoilGrids uses global models that are
 195 calibrated using all available input observations and globally available en-
 196 vironmental covariates. Data are available at 6 standard depths but only
 197 data at the surface (for depths between 0 and 5 cm) were used. Additional
 198 parameters needed by the model Volt’Air (soil texture and van Genuchten
 199 parameters) are taken from the combination of the spatial distribution of
 200 the soil types provided by the European Soil Data Center (ESDC) in the
 201 form of a soil map (European Soil DataBase, scale 1:1,000,000) (Pana-
 202 gos et al., 2012) with the dominant soil type in agricultural areas of each
 203 Small Agricultural regions (SAR) selected by overlaying and intersecting
 204 the soil map with the CORINE Land Cover and SAR maps. Soil prop-
 205 erties of these soil types were provided with the Harmonized World Soil
 206 Database by the Food and Agriculture Organization of the United Nations
 207 (FAO et al., 2012).
- 208 • The spatialized usage of pesticides is based on the French BNVD-S (“Banque
 209 Nationale des Ventes de produits phytopharmaceutiques par les Distribu-
 210 teurs agréés - Spatialisée”) database (Carles et al., 2015) which was only
 211 available for year 2014 at the time of the study. The usage of S-metolachlor

212 and folpet over France is illustrated by Fig. 2. In this database, the spa-
213 tialization of the pesticide sales is based on sales to professionals declared
214 by each seller and aggregated at the national level (all sellers combined)
215 according to the buyer's ZIP code. This base, updated annually, was
216 initiated in 2013. In order to spatialize the sales, the contents are disag-
217 gregated at the level of each of the land use blocks making up the postal
218 code. The information can then be re-aggregated according to the spatial
219 extent considered. Disaggregation is based on a high-resolution land use
220 map (LPIS) that integrates the declarations made by farmers each year
221 to receive support from the Common Agricultural Policy (CAP) of the
222 European Union. All the plots on a farm are allocated to a single ZIP
223 code, that of the farm's head office, estimated by the municipality with
224 the maximum surface area of the farm. The agricultural areas that are not
225 subject to CAP declarations (mainly vineyards, market gardening, etc.)
226 are reconstructed by combining agricultural statistics with the CORINE
227 Land Cover database. The disaggregation of sales is done in each of the
228 polygons constituting the postal code considered. Each product sold will
229 only be allocated to the areas for which it is registered, taking into ac-
230 count the differences in registered doses in the distribution factors (the
231 same product can be authorized for different areas mapped at different
232 doses). Due to the methodology, small quantities tend to be distributed
233 spatially over large areas leading to very low application dose per hectare,
234 sometimes not consistent with agricultural practices. In some rare cases,
235 the opposite trend could occur (large quantities applied on small areas).
236 To correct this feature, the surface on which pesticides were applied were
237 corrected by assuming a dose of 1.9 kg ha^{-1} for S-metolachlor and 1.2
238 kg ha^{-1} for folpet corresponding to an average value based on available
239 registered doses for various commercial products for the considered ac-
240 tive ingredient and enquiries. Treated surfaces were then recalculated to
241 match the total quantities used in the given area.

242 *2.2. Emission calculation*

243 *2.2.1. Volt'Air and SurfAtm-Pesticides*

244 The model used here to predict pesticide emission for comparison with
245 CHIMERE at the PACA region scale is issued from the coupling of the Volt'Air
246 model (Bedos et al., 2009; Garcia et al., 2014) which simulates the emission
247 by volatilization from bare soil and SurfAtm-Pesticides model (Lichiheb et al.,
248 2016) which predicts the emission by volatilization from a crop canopy.

249 Briefly, Volt'Air is a process-based model organized in modules that calculate
250 the energy budget at the soil surface, the vertical transfer of energy (using
251 Fourier's law), of water (using Richards equation), and of solutes in the soil
252 including the diffusion of gaseous compounds in the air-filled pore space. The
253 soil profile is divided into a user-defined number of layers. The computation of
254 transfer fluxes of heat and water are not coupled. Either the van Genuchten-
255 Mualem water retention and hydraulic conductivity models or the Clapp and
256 Hornberger models can be used to describe water dynamics functions in the soil.
257 In this study, the van Genuchten water retention and hydraulic conductivity
258 models haven been selected. Pesticide volatilization to the air is calculated
259 by the local advection approach (see Eq. 1) coupled with the physicochemical

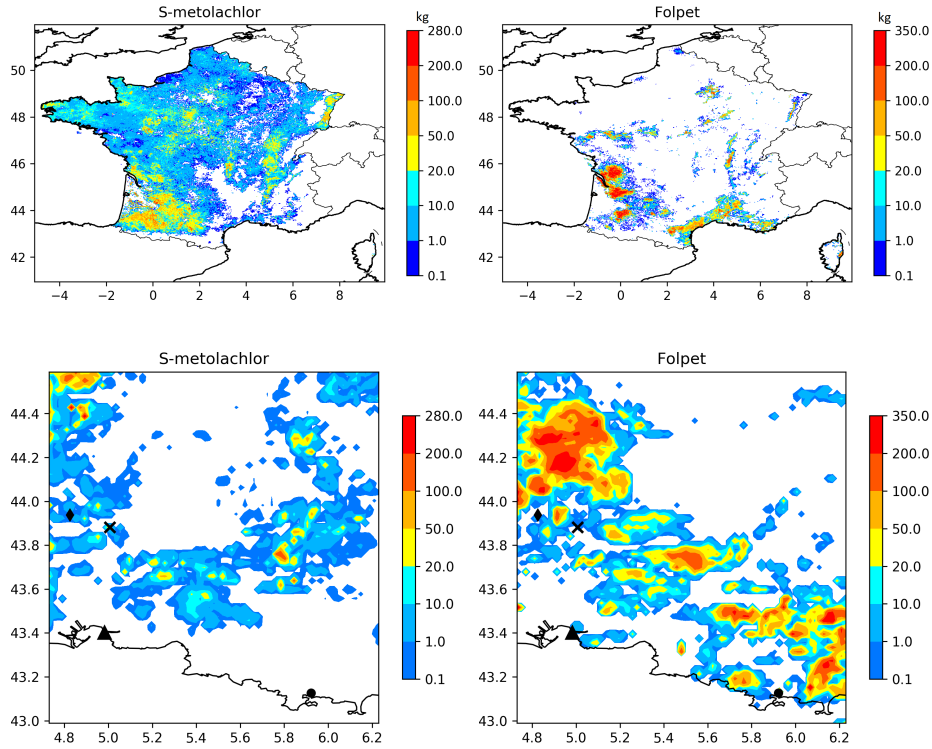


Figure 2: Pesticide usage over France (in kg) for year 2014 from the BNVD-S database over France (top, aggregated at a resolution of $0.01^\circ \times 0.01^\circ$) and over the PACA region (bottom) for S-metolachlor (left) and folpet (right). The cross, diamond symbols, triangle and circle symbols represent the location of the Cavailon, Avignon, Port-de-Bouc and Toulon stations used in this study (see section 2.4).

260 equilibrium Jury's model (Jury et al., 1983) describing the pesticide adsorption
 261 between the gas/water based on the Henry's law and water/soil phases based
 262 on the adsorption coefficient K_d calculated as the product of the soil organic
 263 fraction and the K_{oc} value of the compound, assuming to be instantaneous for
 264 an ideal solution (see Eq. 2). Additional adsorption from the gas phase to the
 265 soil matrix occurring under dry soil conditions can also be calculated provided
 266 data on the specific adsorption coefficient. This option has not been used in this
 267 study due to the lack of information. Under such conditions, an extrapolation of
 268 the water retention model to the dry domain has been implemented by Garcia
 269 et al. (2014) following Schneider and Goss (2012). Volt'Air can be run over
 270 several weeks at the field scale with a timestep ranging from a few minutes to
 271 few hours (with a calculated internal time-step for transfer calculation of the
 272 order of a few seconds). The capacity of Volt'Air to describe the temperature
 273 and surface humidity conditions in a bare soil has been evaluated (Garcia et al.,
 274 2011) validating the physicochemical parameterizations used in the model.

$$F_{volat,soil} = \kappa u^* a_i C \left(\frac{0.3x}{z_0} \right)^{b_i} \quad (1)$$

275 with $F_{volat,soil}$ the volatilization flux ($\mu\text{g m}^{-2}\text{s}^{-1}$), u^* the friction velocity (in

276 m s⁻¹) κ the Von Karman constant (=0.4), a_i and b_i two coefficients of the
 277 advection model (dimensionless), C the atmospheric concentration ($\mu\text{g m}^{-3}$), x
 278 the fetch (m) and z_0 the roughness length (m).

$$C_T = \rho_s C_s + \alpha_w C_{aq} + \alpha_a C_g \quad (2)$$

279 with C_T the total concentration of the pesticide in the soil compartment, C_s ,
 280 C_g and C_{aq} , the concentrations in the solid phase, in the gaseous phase and
 281 in the aqueous phases respectively, $\rho_{s,ref}$ the soil density, α_w and α_a the soil
 282 volumetric water content (m^3m^{-3}) and the air content in the soil pore (m^3m^{-3})
 283 respectively.

284 The SurfAtm-Pesticides model is a mechanistic model that includes one
 285 vegetation layer and one soil compartment (Personne et al., 2009; Lichiheb
 286 et al., 2016). The model is based on the transfer resistances concept (aero-
 287 dynamic, boundary layer and soil resistances) to simulate heat, water vapor and
 288 chemical compound fluxes between the biogenic surfaces and the atmosphere.
 289 The energy balance and the pesticide exchange models are coupled through the
 290 surface temperature of leaves. Regarding pesticide volatilization, the description
 291 of the dissipation processes of pesticides applied on the leaf surface is based on
 292 a compartmental approach on the base of experimental study performed under
 293 controlled conditions using laboratory volatilization chamber (Lichiheb et al.,
 294 2015). Briefly, the total pesticide quantity in the different leaf compartments,
 295 Q_{tot} ($\mu\text{g m}^{-2}$) is given by the following equation (Lichiheb et al. (2016)):

$$Q_{tot} = Q_{s;nad} + Q_{s;ad} + Q_l \quad (3)$$

296 with Q_l the quantity of pesticide accumulated in the leaf tissue ($\mu\text{g m}^{-2}$), $Q_{s;nad}$
 297 the quantity of pesticide non-adsorbed on the cuticle surface and $Q_{s;ad}$ the quan-
 298 tity of pesticide adsorbed on the cuticle surface ($\mu\text{g m}^{-2}$). It is assumed that
 299 only the mass fraction in the non-adsorbed phase is available for volatilization.
 300 Pesticide adsorption on the cuticle and further penetration are calculated thanks
 301 to relationships derived from experimental results and physico-chemical proper-
 302 ties of the compounds. Volatilization flux ($\mu\text{g m}^{-2}\text{s}^{-1}$) is given by the following
 303 equation:

$$F_{volat,leaf} = -\frac{1}{R_b}(C_{top} - C_{s,eff}) \quad (4)$$

304 with R_b the canopy boundary layer resistance (s m^{-1}), C_{top} the concentrations
 305 ($\mu\text{g m}^{-3}$) in the air close to the top of the canopy (calculated as a function of
 306 the pesticide concentration in the air at the reference level, the aerodynamic
 307 resistance above the canopy and $C_{s,ref}$) and $C_{s,eff}$ the concentration in the
 308 air just above the leaf (calculated as a function of the vapour pressure of the
 309 compound at saturation and the amount of pesticide available for volatilisation
 310 $Q_{s;nad}$). The effect of pesticide formulation on volatilization and leaf penetration
 311 can be taken into account following an empirical approach. This model has
 312 been developed to calculate pesticide volatilization after an application on a
 313 well-developed homogeneous crop. In this study, we used this model for the
 314 application under vineyard conditions as no models are available up to now to
 315 describe pesticide volatilization from vineyard.

316 2.2.2. CHIMERE

317 The emissions calculated with CHIMERE are based on Couvidat and Bessag-
 318 net (2021) where a soil/atmosphere SVOC exchange module was implemented.

319 This exchange module was used to determine the volatilization from the soil.
 320 In this module, processes of sorption and desorption of organic vapors by the
 321 soil as well as the diffusion of organic compounds inside the soil are considered
 322 through a discretization of the soil into 13 layers. The thickness of the first layer
 323 is computed as a function of the chemical properties of the compound in order
 324 to correspond to a characteristic time of diffusion equal to 1 s. The thickness of
 325 the other layers are calculated to cover a depth of 20 cm. A complete descrip-
 326 tion of the air/atmosphere exchange module is provided in the Supplementary
 327 Materials.

328 In this module, the methodology of Jacobs and van Pul (1996) considering
 329 the equilibrium between the different phases of the soil, is used to express the
 330 total concentration C_{tot} of the pesticides similarly to Volt'Air (Eq. 2) but by
 331 adding C_{doc} , the concentrations in the dissolved organic matter.

$$C_T = \rho_s C_s + \alpha_w (C_{aq} + C_{doc}) + \alpha_a C_g \quad (5)$$

332 The equilibrium between the different phases are based on the Henry's law
 333 and the organic carbon/water partitioning coefficient K_{oc} . K_{oc} (in $\text{m}^3 \text{kg}^{-1}$) is
 334 calculated with the following formula based on Karikhoff (1981):

$$K_{oc} = 0.000411 \frac{K_{ow}}{\rho_{s,ref}} \quad (6)$$

335 with $\rho_{s,ref}$ the reference density equal to 1300 kg m^{-3} .

336 The vertical flux of organic compounds (F_{trans} in $\mu\text{g m}^{-2}\text{s}^{-1}$) takes into ac-
 337 count both the diffusion of organic compounds inside the soil and the convective
 338 flux due to water transport. It is computed as:

$$F_{trans} = D_e \frac{\partial C_T}{\partial z} - V_e C_T \quad (7)$$

339 with D_e the effective diffusion coefficient (in m^2s^{-1} , computed as a function
 340 of the gas and liquid tortuosities, the diffusion coefficients in the air and in
 341 water) and V_e the effective velocity (in m s^{-1} , calculated as a function of the
 342 precipitation rate).

343 The exchange flux of SVOC at the soil-atmosphere interface $F_{volat,soil}$ (in
 344 $\mu\text{g m}^{-2}\text{s}^{-1}$) is calculated with a resistance scheme:

$$F_{volat,soil} = \frac{C_{a,s} - C_g}{R_b} \quad (8)$$

345 with $C_{a,s}$ the air concentration above the quasi-laminar layer (in $\mu\text{g m}^{-3}$), R_b
 346 the quasi-laminar layer resistance (in s m^{-1}). R_b is calculated for a surface
 347 roughness of 0.5 cm for S-metolachlor (corresponding to an application on bare
 348 soils) and of 25 cm for folpet (corresponding to an application on vineyard soils,
 349 fixed at one tenth of the tree height).

350 Volatilization of pesticides from the film covering plants are computed with
 351 the same parameterization as Volt'Air (see Eq. 4). However, the leaf temper-
 352 ature was calculated with MEGAN parameterizations for crops (Müller et al.,
 353 2008).

354 *2.2.3. Determination of cultural practice based on inquiries*

355 44 local experts from extension services, cooperatives, or technical institutes
356 from the different agricultural sectors in the PACA region were surveyed to
357 define the main farm management strategies in relation to pesticide use, includ-
358 ing timing of application and type of spray equipment. All the results of the
359 inquiries were reported by Carra and Ruelle (2018).

360 The inquiries indicate that S-metolachlor is applied from mid April to mid
361 May with most applications during the morning (between 8h and 12h) or in
362 the evening (between 17h and 21h). For folpet, applications take place during
363 May and June, mostly during the morning (between 8h and 12h). As these
364 periods are quite large, they were refined by removing periods when farmers
365 are not likely to apply pesticides: periods when the wind velocity exceeds 19
366 km/h (farmers cannot legally applied pesticides on these conditions in France)
367 and rainy days were removed from the possible periods for applications (more
368 information on the refinement is given in the supplementary materials).

369 Hulin et al. (2021) provided information on the repartition between the soil,
370 the plant, and the air of sprayed pesticides as a function of the type of equipment
371 used. By combining this information to the results of the inquiries on the type
372 of equipment used, it was estimated that 80% of S-metolachlor quantities are
373 sprayed to the soil, 60% and 10% of folpet are sprayed to the plant and to the
374 soil, respectively. The remaining fractions correspond to the drift.

375 *2.3. 3D simulations*

376 *2.3.1. Representing pesticide in CHIMERE*

377 S-metolachlor and folpet were implemented into CHIMERE by taking into
378 their gas-phase degradation by OH and their gas-particle partitioning. The gas-
379 phase degradation by OH radicals is simulated by using the k_{OH} kinetic constant
380 shown in Table 1. Due to the molecular of the considered pesticides, gas-phase
381 degradation by O_3 is expected to be negligible. Due to the lack of data, the
382 effect of photolysis, gas-phase degradation by NO_3 radicals and heterogeneous
383 reactions, was not taken into account in CHIMERE.

384 Following Couvidat et al. (2018), the gas-particle partitioning of organic
385 compounds is calculated with the Secondary Organic Aerosol Processor (SOAP)
386 thermodynamic model (Couvidat and Sartelet, 2015) that takes into account
387 the absorption of organic compounds into the aqueous and organic phases of
388 the aerosols based on Raoult's law. It takes into account the non-ideality of the
389 aerosol (influence on the partitioning of interactions between organics, inorganic
390 ions and water). The thermodynamic properties (saturation vapor pressures,
391 Henry's law constants) and the molecular structures of the pesticides are nec-
392 essary input for SOAP. The molecular composition of the organic aerosol (nec-
393 essary to calculate the interactions with the considered pesticides) is simulated
394 with the Hydrophylic/Hydrophobic Organics (H^2O) secondary organic aerosol
395 mechanism. The partitioning of inorganic compounds and their influence on
396 the liquid water content of aerosols is based on ISORROPIA (Fountoukis and
397 Nenes, 2007).

398 CHIMERE uses a sectional approach that separates particles into 10 diam-
399 eters bins covering a range from 10 nm to 10 μm . Dry and wet deposition of
400 particles is taken into account as a function of the mean diameter of the bin.

401 In addition to considering the volatilization from crops of pesticides, the
402 model considers air/soil exchanges of pesticides (by using Eq. 8) for soil types.

403 These exchanges can lead to the deposition of gas-phase pesticides (by sorption
404 onto surfaces with low concentrations of pesticides) or the re-volatilisation of
405 previously deposited pesticides. Moreover, sorption of organics by the vegeta-
406 tion compartment is taken into account (Couvidat and Bessagnet, 2021).

407 The atmospheric concentrations simulated by CHIMERE does not account
408 for the drift contributed due to its coarse resolution. Due to the short lifetime
409 of drift droplets, very high resolution (of a few meters) would be necessary to
410 simulate properly the concentrations in the vicinity of agricultural fields with
411 significant applications. However, re-volatilization of drifted pesticides is taking
412 into account as the drift is assumed to be deposited instantaneously onto the
413 different surface types of the cell.

414 *2.3.2. Configuration of simulations*

415 CHIMERE uses as inputs anthropogenic emissions from an inventory, me-
416 teorological data, and results from a global model to constrain the models as
417 the boundaries of the European domain. Anthropogenic emissions of gases and
418 particles were taken from the EMEP inventory (Vestreng, 2003) for year 2014.
419 Meteorology was obtained from the operational analysis of the Integrated Fore-
420 casting System (IFS) model of the European Centre for Medium-Range Weather
421 Forecasts (ECMWF). Boundary conditions of the European domain are based
422 on a climatology of MACC simulation results.

423 Concentrations of S-metolachlor and folpet are simulated from 2014-04-15
424 (beginning of the application period for S-metolachlor) to 2014-07-01 (end of
425 the application period for folpet).

426 *2.4. Comparison to measurements*

427 Simulations results are compared to measurements from the French Regional
428 Networks for Air Quality Monitoring that measure the atmospheric concentra-
429 tions of pesticides in gas and particulate fractions. These field measurements
430 are compiled in the PhytAtmo database which aggregates about 7,000 samples
431 at 176 sites throughout mainland France and overseas for 321 active substances
432 sought (AtmoFrance, 2019).

433 The overall mean uncertainty (i.e., sampling, extraction, and analysis) asso-
434 ciated with the measured concentration was estimated at 10-15% for low-volume
435 samples (e.g., Partisol), and at 20-25% for high-volume samples (e.g., Digital
436 Aerosol Sampler DHA-80), regardless of the sampling medium or the cut-off
437 diameter (i.e., Total Suspended Particulates (TSP), Particulate Matter PM10,
438 and PM2.5 inlets) used. Both particulate and gaseous fractions were extracted
439 and analyzed by gas chromatography coupled to tandem mass spectrometry
440 (GC-MS/MS), for folpet and S-metolachlor.

441 The concentrations measured in PACA in 2014 and the description of sam-
442 pling sites were summarized in Désert et al. (2018). Briefly, sampling (considered
443 necessary for the study purpose) was undertaken at four sites located through-
444 out the PACA region (i.e., Avignon, Cavaillon, Toulon, and Port-de-Bouc).
445 Cavaillon (hamlet of Les Vignères) is located in an intensive arboriculture area.
446 Avignon, Toulon and Port-de-Bouc are urban stations. Vineyards and other
447 cultivated areas are however present in a radius of 10 km around the Toulon
448 and Avignon stations. Additional information on the station vicinity is provided
449 in Table S1 in the Supplementary materials.

450 The locations of the stations in the PACA domain are shown in Fig. 2 to-
451 gether with the application of S-metolachlor and folpet in the domain. The other
452 french stations used in this study are shown in the Supplementary materials
453 (Fig. S5). During the period of interest, 24 and 29 stations in France measured
454 S-metolachlor and folpet, respectively. 4 of these stations are in the PACA
455 region. In 2014, S-metolachlor was only detected on the Cavaillon and Avi-
456 gnon stations, it was chosen to focus the comparison of the PACA simulations
457 on these two stations. The BNVD-S shows that applications of S-metolachlor
458 and Folpet occurred only in the vicinity of the Cavaillon and Avignon stations.
459 Large application of Folpet occurred in the vicinity of the Toulon station and
460 in the North of the Cavaillon and Avignon stations.

461 One difficulty of the comparison is that the measurements do not cover en-
462 tirely the period of interest (beginning with the period of applications). In
463 PACA, measurements were done during two 8-day periods starting from May
464 21st and from June 25th. At the National level, different measurement proto-
465 cols may be used. For some regions, 7-day samplings were done instead of 2-day
466 samplings. For the purpose of the model to measurement comparison, concen-
467 trations of the model were averaged on the sampling duration (over 7 days or 2
468 days depending on the sampling procedure).

469 3. Results and discussions

470 3.1. Comparison of emissions simulated by Volt'Air and CHIMERE

471 In order to provide information on the capacity of the two models to simulate
472 emissions, a comparison of emissions simulated by both models is done in two
473 steps: first, a comparison of both estimations with measured volatilization rates
474 of S-metolachlor (no data set could be found for folpet volatilization); then, a
475 comparison of the model emission estimations of S-metolachlor and folpet by
476 volatilization over the domain covering the PACA region.

477 In order to estimate the capacity of models to reproduce the evolution of
478 emission, a comparison of simulated volatilization fluxes to experiments carried
479 out by Bedos et al. (2017). Details on the scenario built on the experimental data
480 set together with both model results are available in the supplemental materials
481 (section 2). Briefly, both models could reproduce the order of magnitude of the
482 observed volatilization losses three days after application, with however some
483 discrepancies, e.g., on the diurnal cycle as predicted by Volt'Air in relation to
484 the overall pedoclimatic conditions. CHIMERE reproduces well the temporal
485 evolution of emissions as well the level of emissions (underestimation by 1%),
486 while Volt'Air underestimates emissions the volatilization flux on the first day
487 and overestimates emissions the following days.

488 Regarding emissions calculated at the PACA scale by combining the data
489 from the BNVD-S database, the meteorological conditions and the repartition
490 rules described in section 2.2.3, these emissions were computed from the start
491 of application period (starting from April 15th for S-metolachlor and from May
492 1st for folpet) to July 1st.

493 Fig. 3 shows the daily emissions computed with CHIMERE and Volt'Air over
494 the PACA domain. During the application period, the two models simulated
495 similar temporal trends of emissions for the two compounds (correlation between
496 the two models of 0.97 for S-metolachlor and of 0.90 for folpet). The root mean

497 square error (normalized by the average emissions of the two models) between
498 the two models is 18% for S-metolachlor and 30% for folpet.

499 The emissions of S-metolachlor simulated with CHIMERE are close to those
500 simulated by Volt'Air during the application period (307 kg simulated with
501 CHIMERE against 379 kg simulated with Volt'Air). However, for S-metolachlor,
502 significant differences were found between CHIMERE and Volt'Air after the
503 application period (after May 16th). Emissions estimated with CHIMERE de-
504 creased rapidly in the first days following the application period while emissions
505 estimated with Volt'Air remain at a high level. From May 16th to July 15th,
506 the emissions simulated by Volt'Air are higher by a factor close to 3 (257 kg
507 simulated with CHIMERE against 858 kg simulated with Volt'Air).

508 From April 15th to July 1st, 6.2%, and 13.5% of the applied S-metolachlor
509 has been lost to the atmosphere by volatilization in the CHIMERE and Volt'Air
510 simulations, respectively. For comparison, Bedos et al. (2017) found after 3
511 days after application 2.8% of cumulated S-metolachlor volatilisation losses.
512 As mentioned by these authors, other studies reported 6.5% of the nominal
513 application found to be lost after 21 days after application on a freshly tilled
514 soil (Rice et al., 2002). Prueger et al. (2017) found volatilization losses 5 days
515 after application ranging from 5 to 63% depending on the year considered (based
516 on a 13 consecutive years of experiments).

517 The differences between the two models are due to differences in the dis-
518 cretization of soil layers as confirmed by tests carried out with Chimere with
519 the same discretization as Volt'Air. Under such conditions, CHIMERE would
520 lead to emissions lower than Volt'Air by a factor 3 on the whole simulation
521 period (from April 15th to July 1st) but with a similar temporal evolution
522 (temporal correlation of 0.93). Indeed, while CHIMERE estimates the depth of
523 the first layer as a function of the compound properties in order to correspond
524 to a characteristic time of diffusion equal to 1 s that would be necessary for a
525 proper numerical resolution of diffusion (leading to a value of around 0.001 cm
526 for S-metolachlor), the first layer of Volt'Air is set to 1 cm in order to avoid
527 any numerical problems in the soil water transfers during potential intense rain
528 events (whereas for CHIMERE soil humidity conditions are taken directly from
529 ECMWF). This comparison raises the issue of the validation of long-term cal-
530 culated emissions. While CHIMERE manages to properly reproduce short-term
531 emissions (see section 2.3 in Supplementary materials), the calculation of long-
532 term emissions is probably more uncertain in connection with an uncertainty
533 on the quantity of compounds still available for volatilization, quantity affected
534 by degradation, the variability of which was noted according to the conditions,
535 as well as the transfers of the compound in the soil. To our knowledge, no
536 experimental dataset exist to carry out this comparison.

537 For folpet, the two models show similar trends but with higher emissions
538 for Volt'Air and a strong peak of emissions at the beginning of June. Emis-
539 sions rapidly decrease after the application period. After July 10th, the daily
540 emissions computed by the two models are lower than 20 kg day^{-1} . During the
541 application period, CHIMERE and Volt'Air-pesticides estimated that 3847 kg
542 and 5940 kg of folpet were emitted in the atmosphere, respectively, representing
543 7% and 11% of folpet applications.

544 The normalized emissions (normalized by the crops surface treated with
545 pesticides) simulated with CHIMERE and Volt'Air are shown in Fig. 4. For
546 both pesticides, stronger emissions are simulated by both models in the west-

ern part of the domain. However, the spatial gradient is different between the two models with stronger normalized emissions in the western part simulated by Volt'Air. While the maps simulated with CHIMERE are spatially smooth, Volt'Air can simulate pixels with normalized emissions. While in CHIMERE the normalized emissions do not depend on the size of parcels with applications (due to the resistance scheme) and depend only on meteorological parameters, emissions by volatilization from the soil are calculated by Volt'Air with an advection scheme depending on the size. This feature may also depends on the soil texture database used by Volt'Air.

Maps of emissions (per surface of cells cumulated over the application periods for each compounds) are shown in Fig. S4 in Supplementary materials.

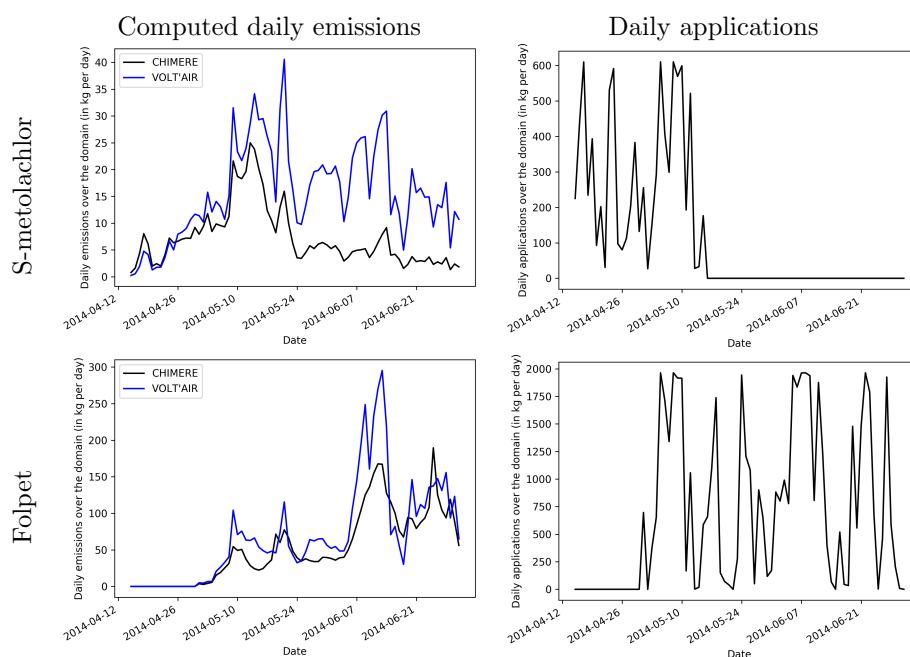


Figure 3: Computed daily emissions and daily applications (without the drifted fraction) over the PACA region (in kg/day) computed with the CHIMERE and Volt'Air.

The emissions of S-metolachlor and folpet simulated with CHIMERE are shown in Fig. 5 for the France and PACA domains. This figure shows that emissions of S-metolachlor in PACA are low compare to the emissions in other regions (simulated emissions are particularly strong in southwestern France in relation to maize acreage). Local emissions are however simulated in some areas of the PACA domain (in the Northwestern part of the domain and in some areas in the center). On the contrary, strong folpet emissions are simulated in southeastern France. In the PACA domain, an area at the Northwest of the domain have particularly high emissions. The corresponding concentrations are in shown in Fig. 6.

3.2. Simulation and spatial comparison to measurements on France

Fig. 7 shows the comparison between the temporal averaged concentrations of S-metolachlor and folpet simulated by CHIMERE against the concentrations

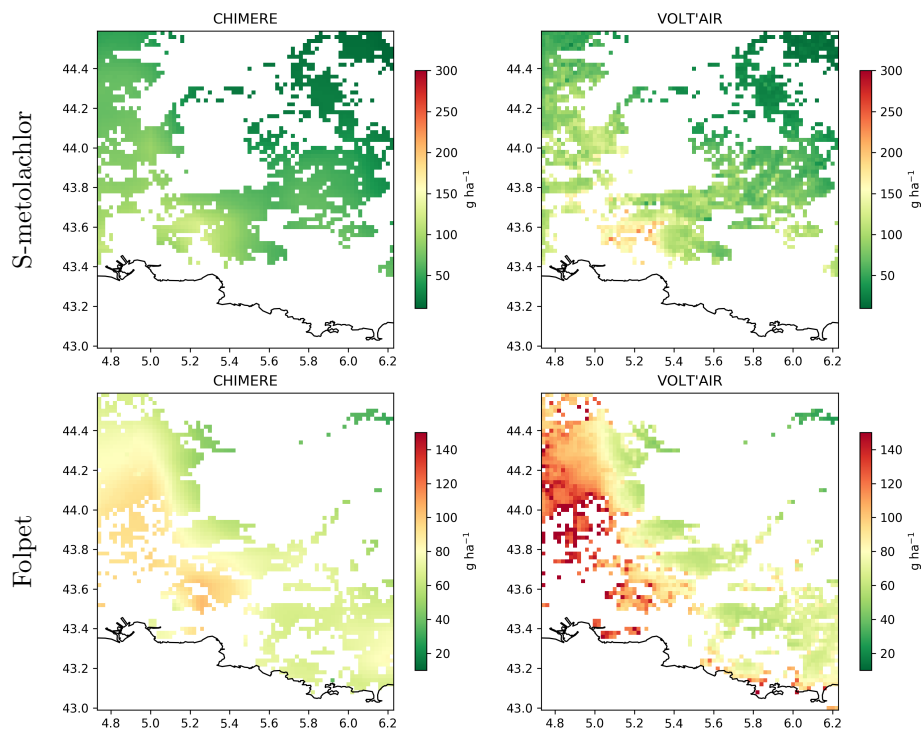


Figure 4: Maps of volatilized amounts (in g ha^{-1}) per hectare of crops using pesticides for S-metolachlor (top) and folpet (bottom) during the application period simulated by CHIMERE (left) and Volt'Air (right).

571 measured for all the stations over France. For S-metolachlor, as substantial
 572 emissions can remain long after the application, the comparison was done for
 573 two periods: during the application period and after the application period.

574 The comparison for S-metolachlor during the application period shows that
 575 the spatial distribution of concentrations is well reproduced by the model. High
 576 spatial correlations are obtained for the concentrations simulated during (0.77)
 577 and after the application period (0.79) after excluding the Ohnenheim and Stras-
 578 bourg station in northeastern France, for which very high concentrations were
 579 measured: around 14 ng m^{-3} for Ohnenheim during the application period (sim-
 580 ulated concentration for CHIMERE is around 0.19 ng m^{-3}), around 8 ng m^{-3}
 581 for Ohnenheim after the application period (simulated concentrations around
 582 0.52 ng m^{-3}) and around 2 ng m^{-3} for Strasbourg after the application pe-
 583 riod (simulated concentration around 0.26 ng m^{-3}). This underestimation for
 584 the Northeastern region could be due to missing applications estimated from the
 585 BNVD-S database or to missing concentrations coming from Germany (as the
 586 two stations are close to the german border). These two stations are removed
 587 for the computation of the different statistics.

588 During the application period, a mean normalized bias (MNB) of only 0.3%
 589 is obtained with the CHIMERE simulation. However, the bias obtained with the
 590 CHIMERE simulation during the application period are between from -60% to
 591 90%. For the one month period after the application period, the calculated MNB
 592 is around -49%. This feature seems to indicate that the decrease of emissions

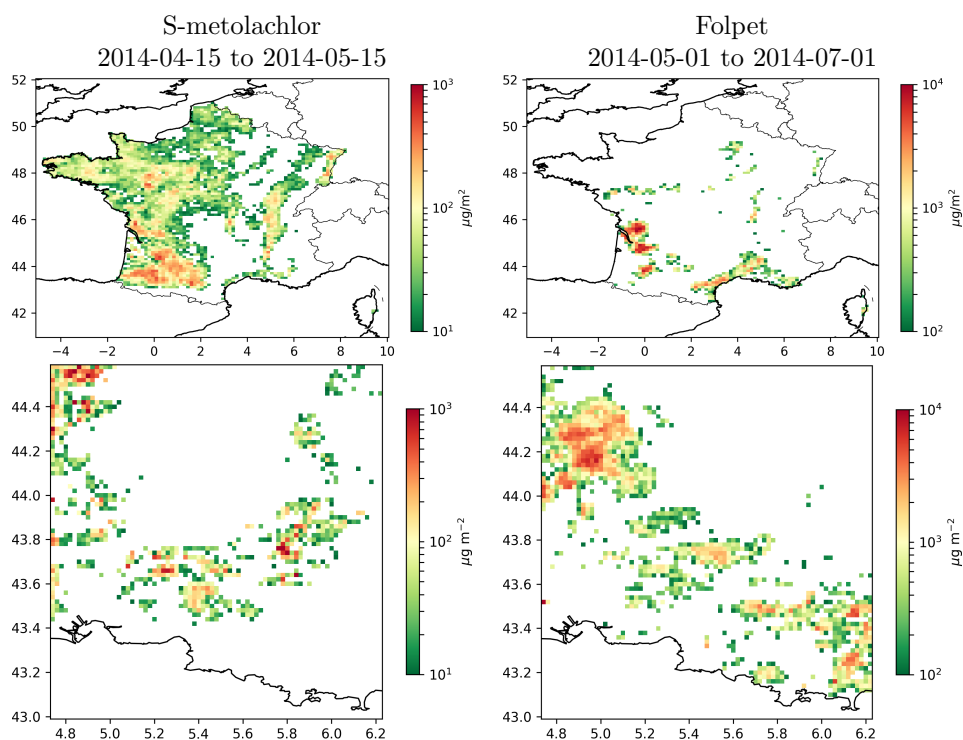


Figure 5: Simulated emissions over France (top) and over the PACA region (bottom) by CHIMERE (in $\mu\text{g}/\text{m}^2$) of S-metolachlor (left) and folpet (right) during the periods of application.

593 after the applications may be too strong. Several reasons could explain this
 594 feature (such as the underestimation of the DT_{50} -soil or an underestimation of
 595 the effect of temperature on volatilization). One possibility is that calculated
 596 emissions may be too precocious for some regions. While the selected period
 597 for application is quite large, the repartition of applications within this period
 598 may lead to precocious application.

599 For folpet, this compound was only detected by 10 out of 29 stations. For the
 600 stations where folpet was detected, the model simulates concentrations ranging
 601 from 0.03 ng m^{-3} to 2.9 ng m^{-3} against averaged measured concentrations rang-
 602 ing from 0.05 to 3.2 ng m^{-3} with a spatial correlation of 0.52. For the 12 stations
 603 where the folpet concentrations could not be detected, the model simulates aver-
 604 aged concentrations under 0.6 ng m^{-3} (upper value of the quantification limit).
 605 For the remaining 7 stations, the model gives high folpet concentrations that
 606 exceeds 1 ng m^{-3} for 5 of these stations (Auch: 3.3 ng m^{-3} , Kintzheim: 1.9
 607 ng m^{-3} , Lyon: 1.2 ng m^{-3} , Reims: 2.6 ng m^{-3} , and Sigolsheim: 3.3 ng m^{-3}).
 608 For some stations (such as Kintzheim and Sigolsheim), the presence of folpet in
 609 the simulation could be due to the lack of refinement of the application period:
 610 applications are distributed over the application period (whereas they are prob-
 611 ably limited in time) while folpet was measured for limited periods which may
 612 not correspond to the real application period. For the Reims and Auch stations,
 613 where weekly measurements were performed, strong concentrations (around 4
 614 ng m^{-3}) were measured onto a single week after the selected application period

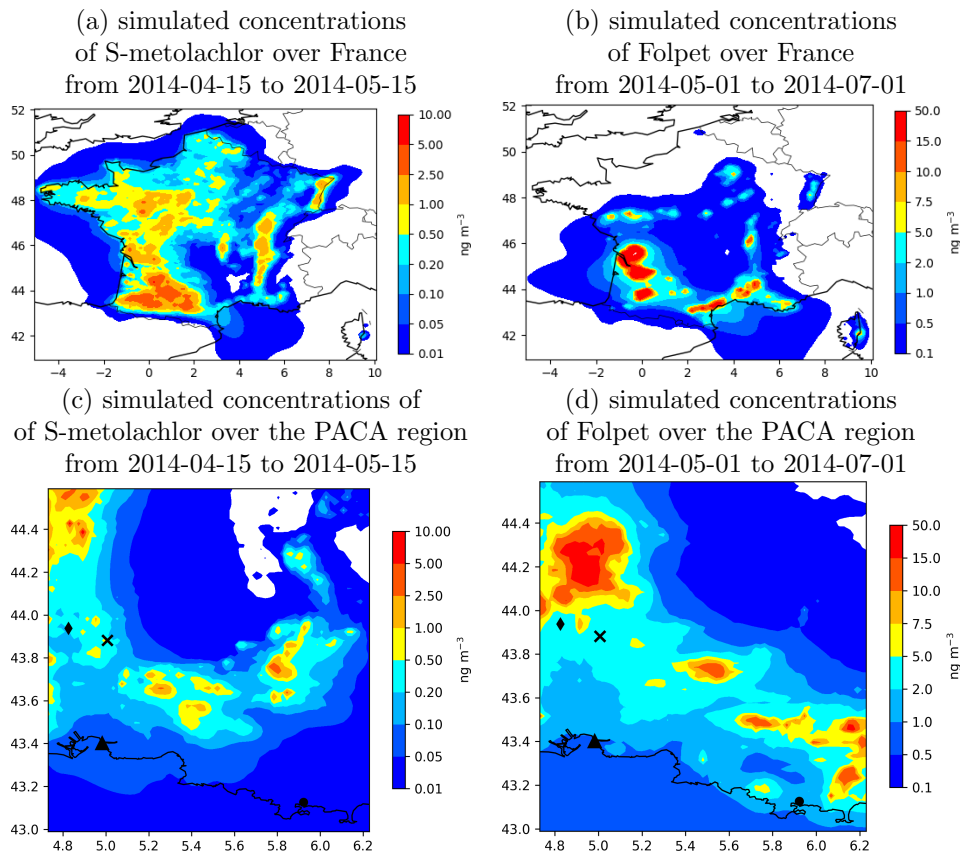


Figure 6: Simulated average concentrations over France (top) and over PACA (bottom) by CHIMERE (in ng m^{-3}) of S-metolachlor (left) and folpet (right) during the periods of application. The cross, diamond symbols, triangle and circle symbols represent the location of the Cavaillon, Avignon, Port-de-Bouc and Toulon stations (see section 2.4).

615 (week of July 15th). Folpet emissions may therefore be sporadic and difficult
 616 to temporalize appropriately. Better results may be difficult to obtain without
 617 knowing precisely the periods of application.

618 3.3. Focus on the PACA region

619 The Fig. 6c shows the concentrations of S-metolachlor and folpet simulated
 620 on the PACA domain. It appears that while S-metolachlor is one of the most
 621 present pesticide (in terms of detection limit exceedance) in the PACA region,
 622 the model simulates (due to the low applications given by the BNVD-S, see Fig.
 623 2) low concentrations of S-metolachlor compared to the high concentrations
 624 in western France and in the Rhone valley (valley at the north of the PACA
 625 region). Due to the high level of S-metolachlor emissions outside PACA, the
 626 long-range transport of pesticides may influence the amount of S-metolachlor
 627 simulated inside the domain. According to the simulation results, from April
 628 15th to May 15th 2014, 57% and 11% of S-metolachlor concentrations at the
 629 Avignon (at 7 kilometers from the domain western border) and Cavaillon (at
 630 22 kilometers from the domain western border) stations, respectively, originates

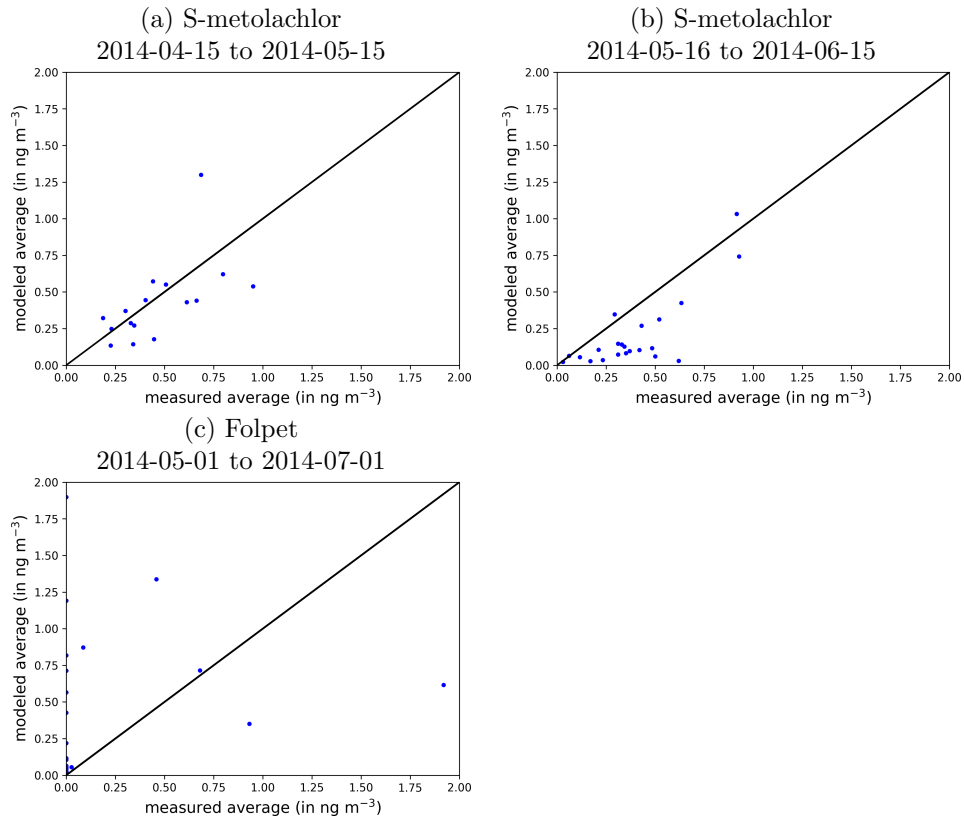


Figure 7: Comparison of averaged measured and modeled concentrations for S-metolachlor during the application period (a) during one month after the application period (b) and folpet during the application period (c).

631 from outside the PACA domain. On the contrary, strong concentrations of folpet
 632 are simulated in the northwestern part of the PACA domain with concentrations
 633 exceeding 10 ng m^{-3} during the application period.

634 Fig. 8 shows the comparison of the model results for the Avignon and
 635 Cavaillon stations. Unfortunately, for S-metolachlor, the first measurements
 636 begin after the application period (May 21st). However, as the concentrations
 637 are measured outside the expected application period, it seems probable that
 638 the concentrations come solely from the volatilization and not from the drift.
 639 It was therefore not possible to evaluate the ability of the model to simulate
 640 concentrations in PACA during the application period. Averaged S-metolachlor
 641 concentrations simulated are close to the measurements (0.058 ng m^{-3} in mea-
 642 surements against 0.059 ng m^{-3} in simulations for Avignon and 0.11 ng m^{-3}
 643 in measurements against 0.17 ng m^{-3} in simulations for Cavaillon). The model
 644 succeeds in explaining the strongest concentrations at Cavaillon that are due
 645 to emissions in the vicinity of the stations. For the two stations, the peak at
 646 the beginning of the comparison (corresponding to concentrations measured be-
 647 tween May 21st and May 23rd; simulated concentrations around 0.10 ng m^{-3}
 648 for Avignon and around 0.34 ng m^{-3} for Cavaillon) is not present in the ob-
 649 servations. Outside of this peak, the model seems to reproduce the temporal

650 evolution.

651 S-metolachlor concentrations were also measured at the Port-de-Bouc and
652 Toulon stations. At the Toulon station, concentrations below 0.01 ng m^{-3}
653 are obtained with CHIMERE. As the detection limit is equal to 0.012 ng m^{-3}
654 for S-metolachlor (Désert et al., 2018), these simulations results are coherent
655 with non-detection of the pesticide. At the Port-de-Bouc station, S-metolachlor
656 was detected once (from May 28th to May 29th) with a concentrations of
657 0.03 ng m^{-3} , while a concentration of 0.023 ng m^{-3} was estimated. How-
658 ever, CHIMERE estimated that the concentrations can exceed a second time
659 the detection limit of 0.012 ng m^{-3} (simulated concentration of 0.018 ng m^{-3}).

660 For folpet, the model may slightly underestimate the concentrations. Con-
661 centrations around 2.9 ng m^{-3} are measured at the Avignon and Cavaillon
662 stations while the simulated concentrations (on the same period than the sam-
663 plings) are around 1.9 and 1.7 ng m^{-3} , respectively. The underestimations is
664 stronger for the Port-de-Bouc (0.5 ng m^{-3} in simulations against 2.9 ng m^{-3}
665 in measurements) and Toulon (1.0 ng m^{-3} in simulations against 2.2 ng m^{-3}
666 in measurements) stations. However, the model simulates concentrations dur-
667 ing the period (and not averaged on the sampling periods) close to the mea-
668 sured concentrations. Simulated concentrations during the application period
669 are around 2.9 ng m^{-3} , 3.3 ng m^{-3} , and 2.3 ng m^{-3} at the Cavaillon, Avignon,
670 and Toulon, respectively. It may therefore be possible that the underestimation
671 on these stations are mainly due to difficulties to temporalize the application
672 appropriately. This hypothesis may be supported by Fig. 8 that shows that
673 the model is not able to explain the strong concentration peak (from May 24th
674 to May 25th) observed at both the Avignon and Cavaillon stations (around 7
675 and 9 ng m^{-3} in measurements). It seems unlikely that the low concentrations
676 simulated at Port-de-Bouc can be explained by the temporalization alone as the
677 average concentrations during the application period at Port-de-Bouc is only of
678 0.9 ng m^{-3} . The lower simulated concentrations at Port-de-Bouc are due to low
679 emissions in the vicinity of the station.

680 A measurement carried out at the beginning and before the expected appli-
681 cation period shows that S-metolachlor can be detected at the beginning of April
682 before April 15th. This could be explained by applications on other crops than
683 maize (such as sunflower, generally sowed earlier), even if these applications are
684 expected to be minor in the region (Carra and Ruelle, 2018). The first detection
685 of folpet happens in coherence with the beginning of the expected application
686 period but folpet was also detected in August while the model would simulate
687 negligible concentrations at this time. S-metolachlor was detected in August at
688 the Cavaillon station (with concentrations between 0.1 and 0.2 ng m^{-3}) but not
689 at other stations. Concentrations simulated by CHIMERE at the beginning of
690 August are around 0.04 ng m^{-3} at the Cavaillon station. This could be due to
691 an underestimation by the model of long-term volatilization of S-metolachlor
692 (for example due to an underestimation of the DT_{50} -soil).

693 *3.4. Proposed procedure for the Modelling of atmospheric concentrations of pes-* 694 *ticides*

695 Based on the results of this study, the following procedure is recommended
696 to improve simulation of the atmospheric concentrations of pesticides due to
697 volatilization:

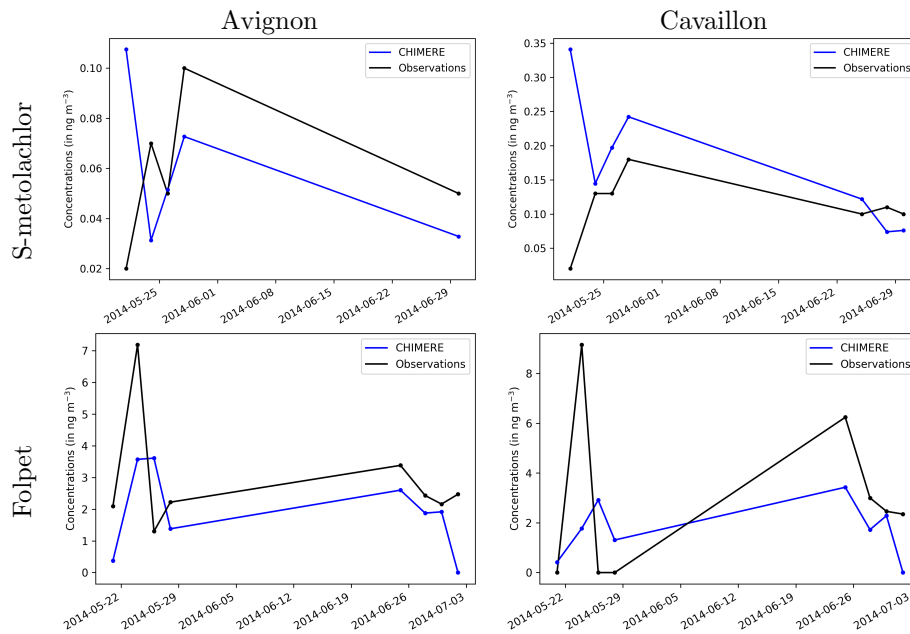


Figure 8: Temporal evolution (in ng m^{-3}) of simulated and measured concentrations of S-metolachlor and folpet at the Avignon and Cavaillon stations.

- 698 1. Improve spatio-temporal pesticide application:
- 699 (a) Use a database of the spatialized usage of pesticides. In France, the
- 700 BNVD-S database based on the sales of pesticides provides the most
- 701 complete source of information to this date. This tool is indispens-
- 702 able when we are looking to spatialize the behaviour of pesticides in
- 703 the environment, such as their emission into the atmosphere as in
- 704 this study. It is essential that this tool can be deployed over several
- 705 years in order to continue the modelling work for more recent years.
- 706 However, another issue is that pesticide may be distributed over agri-
- 707 cultural areas where pesticide is not applied in reality, in relation to
- 708 hypothesis that have to be made to identify potential treated crops
- 709 leading thus to uncertainties and requiring a re-evaluation of the the
- 710 surface onto which pesticides are applied to conserve realistic doses
- 711 and locations. This re-evaluation may not be straightforward be-
- 712 cause of the range of potential application doses (e.g., estimated to
- 713 be from 1 to 2.5 kg ha^{-1} for S-metolachlor and from 0.225 to 1.5 kg
- 714 ha^{-1} for folpet).
- 715 (b) Estimate application periods as precisely as possible. In our case, for
- 716 the purpose of the Modelling exercise, application periods specific
- 717 of the PACA region were used and were refined according to wind
- 718 velocities and precipitations. However, it appears that more refined
- 719 application periods may be necessary and that the application pe-
- 720 riods may vary significantly from one region to another. Enquiries
- 721 with farmers could provide precise information but may be difficult
- 722 to obtain at the scale of a region or a country. One possible option
- 723 could be to use parameterizations on plant growth or fungi/insect

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appearance as a function of meteorological data to constrain probable application periods. For example for the case fungicides applied to treat Mildew on grapevine, the methodologies of Calonnec et al. (2008); González-Fernández et al. (2019) or Lagomarsino Oneto et al. (2020) could be used.

2. Improve pesticide emission calculation

- (a) The volatilization process of pesticides from the treated surface (soil or plant) depends on a number of factors, related to the properties of the substances (which may be uncertain), to the application techniques but also to the surface conditions (van den Berg et al., 1999; Schneider et al., 2013; Taylor et al., 2020). With regard to applications on bare soil, as is the case with S-metolachlor, the temperature of the soil surface can follow a very marked diurnal cycle, with maximums of the order of 50°C under certain conditions. In general, models calculating the energy balance of soil surfaces manage to describe these temperature variations at the plot scale relatively well (Luo et al., 1992; Grant et al., 1995; Garcia et al., 2011). The water status of the soil is more complex to describe in conditions of strong drying of the soil (Schneider and Goss, 2012), which may be the case at the surface (yet these conditions may be favourable to the adsorption of compounds on the soil and thus limit, at least punctually, volatilization). A challenge is to describe these surface conditions for the landscape element within the mesh that is going to be concerned, in this case, an agricultural plot. Another driver of volatilization is the factors governing the adsorption of compounds on the soil organic matter, which depend on the adsorption coefficients (highly variable) and the organic content of the soil. The test carried out on the data set acquired on the volatilization of S-metolachlor presented in Supplementary materials showed the sensitivity of the models to this factor. However, having access to this data on the landscape elements of interest within the grid cell is also complicated. Similar questions on surface conditions may also arise with regard to applications on plant cover (leaf temperature and wetness). Additional challenges consist in dealing with the effect of formulation on the compound behaviour: for example Lichiheb et al. (2016) demonstrated that the formulation the penetration of the compound with the leaf.
- (b) For each pesticide, compare the modeled emission fluxes to multiple flux measurements carried out into different conditions. Doing this could be use to evaluate the model performance in simulating the pesticide volatilization and (if necessary) to constrain some parameters of the model for the studied compounds that may be very uncertain (such as K_{oc} , DT_{50} -soil, or the Henry's law constant) or to integrate the difficulties to simulate properly physicochemical variables close to the interface. As shown by the comparison of emissions between CHIMERE and Volt'Air, it may be important to validate the capacity of model to reproduce not only the short-term but also the long-term evolution of emissions as specific phenomena may intervene. However, it has to be highlighted that such long term datasets are not available up to now. Even in the short term period, in addition to the the variability of the volatilization fluxes under various pedoclimatic

774 conditions as discussed by Prueger et al. (2017), the determination
775 of volatilization fluxes are also uncertain (Loubet et al., 2010; Yates
776 et al., 2016; Alfieri et al., 2017). Under these conditions, calibration
777 of the models may be challenging.

778 3. Compare the results of the model with measurements in terms of concen-
779 trations in the air. The validation of the model by comparing to mea-
780 surements is a necessary step to evaluate the model performance and the
781 quality of the results. In France, 80 pesticides were measured at 50 sites
782 during a national campaign from June 2018 to June 2019 (Marlière et al.,
783 2019). This campaign provides a unique data set of atmospheric concen-
784 trations of pesticides that could be use to evaluate the model. This
785 comparison was not carried out in our study as only the years 2014 and
786 2015 were available in the BNVD-S database for years (at the time of
787 study). However, the comparison to measurements is challenging as mea-
788 surements of pesticides may be local (depending of the representativeness
789 of the station compared to the background contamination), sporadic or
790 missing and concentrations may be below the quantification limit (specific
791 of the compound and the analytical method).

792 As this methodology only accounts for the contribution due to volatilization
793 (due to the expected short lifetime of drift droplets in the atmosphere compared
794 to the coarse resolution of the model), it may be necessary to simulate with
795 separate methods the contribution of the drift to pesticide concentrations for
796 studies on the exposition of residents close to agricultural fields. Local dispersion
797 model could be applied for this purpose (Costanzini et al., 2018). Even for local
798 studies, accounting for volatilization may be necessary. Exposure to pesticide
799 droplets can result in exposure to very high instantaneous concentrations of
800 pesticides. On the contrary, pesticide volatilization may results in the exposure
801 to small but ubiquitous concentrations.

802 4. Conclusions

803 A methodology was developed to simulate the atmospheric concentrations of
804 pesticides and implemented in the air quality model CHIMERE. This method
805 is based on a module to simulate the volatilization of pesticides from crops
806 (either from the soil or from the pesticide layer covering the plant). After their
807 volatilization, the transport, chemical degradation, gas-particle partitioning and
808 deposition of the pesticides is simulated. This method rests on the capacity to
809 spatialize and temporalize the applications of pesticides. The French BNVD-S
810 database (based on records of pesticide sales) was used to provide information
811 on the spatial distribution of pesticide applications. The application periods
812 of pesticides was determined based on inquiries among experts from the PACA
813 French region and were refined by removing windy and rainy winds.

814 Concentrations of two pesticides were simulated on France with a focus on
815 the PACA region: S-metolachlor, a herbicide used mainly mainly on crop crops
816 at a early stage of the plant growth and folpet a fungicide used mainly to treat
817 mildew in vineyards. The two compounds were selected because they are among
818 the pesticides frequently detected in the PACA region, because they are mostly
819 used on one type of crops and because they are representative of two types
820 of emissions: volatilization from the bare soil in the case of S-metolachlor and

821 volatilization from the layer of pesticides covering plants. Emissions simulated
822 by CHIMERE were compared to the emissions simulated by the Volt'Air model.
823 The simulated concentrations are compared to measurements.

824 The comparison of emissions show that the calculation of pesticide emis-
825 sions may be uncertain (particularly for the evolution of long-term emissions).
826 Volatilization from the soil is driven by processes happening in the first cen-
827 timeters of the soil. The soil moisture and temperature were taken from the
828 results of the IFS meteorological model. However, as the first soil layer covers a
829 depth down to 15 cm and as the model may not be representative of agricultural
830 fields, the choice of using the IFS simulation results could lead to an underesti-
831 mation of pesticide volatilization. Additionally, regarding emission calculations
832 with the Volt'Air model, the results could be improved using a model designed
833 especially for vineyard application as the structure in row may impact the en-
834 ergy budget and in consequences the surface conditions and the volatilization
835 rate. The physicochemical soil properties may be also a source of uncertainty.
836 The SoilGrids database was used to provide data on the soil organic carbon
837 content (a key parameter for the volatilization from the soil). In this database,
838 constructed by machine learning, the first layer covers a depth of 5 cm while
839 the other databases cover a depth of 15 cm but it may still be too coarse to
840 represent the processes at the Soil/Atmosphere interface. However, the repre-
841 sentativeness of such a database for agricultural fields could be questioned. The
842 volatilization of pesticides is also computed using the physicochemical properties
843 of the compounds alone (for example volatilization from plants are computed
844 as a function of the saturation vapor pressure). This may not be appropriate
845 if the co-formulants present in the products act on the pesticide volatilization.
846 As it is difficult to deal with all these issues, we recommend that comparison to
847 measurements of pesticide volatilization fluxes are performed in order to con-
848 strain some parameters of the model and therefore integrating by this way the
849 error due to all these uncertainties.

850 Estimating the spatiotemporal distribution of pesticide application is also
851 a major source of uncertainties. While the BNVD-S seems to provide relevant
852 information on the spatial distribution of pesticide applications for Modelling
853 atmospheric concentrations of pesticides, the temporal distribution remains a
854 key issue. In this study, we chose to determine application periods as repre-
855 sentative as possible of the PACA region. As a result, the application periods
856 probably lack in precision or may not be representative of the other regions.
857 The comparison to measurements seems to indicate that in some cases, the ap-
858 plication period could be lengthier. Interrogating directly farmers could provide
859 the necessary information but such a method would be difficult to generalize at
860 the scale of region or a country.

861 Nonetheless, the comparison of the first model results to measurements seems
862 to indicate that the model is able to reproduce the order of magnitude of con-
863 centrations and can even capture the spatial distribution of S-metolachlor con-
864 centrations over France (with a spatial correlation of 0.79). The comparison to
865 measurements was however limited as the measurements do not cover all the
866 period of interest.

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