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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 module to simulate the volatilization of pesticides from soils and plants was implemented in the air quality model CHIMERE in order to simulate spatiotemporal distribution of pesticide atmospheric concentrations. 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 and folpet. In the first stage of the study, pesticide emissions simulated by the CHIMERE and Volt'Air models are compared. In the second stage, 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) with a bias ranging from -50 to 50% for most stations during the application period. The simulation of folpet concentrations remains challenging with a lack of correlation between model results and measurements, that could possibly be due to a lack of precision in the temporalization of applications.

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 Mousaoui et al., 2012; Coscollá et al., 2017; 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 photochemical reactions, including degradation by light, ozone (O₃), hydroxyl (OH) and nitrate (NO₃) 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, 2019a, 2019b, 2019c). The atmospheric medium and long-range transport of pesticides is therefore possible and has been highlighted by numerous studies especially for organochlorine compounds (e.g. Qu et al., 2015; Vorkamp and Rigét, 2014; Gong et al., 2015; Pokhrel et al., 2018; Huang et al., 2019; Hermanson et al., 2021). Due to the ubiquity of pesticides and their potential harmful effect on human health and non-targeted ecosystems, 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

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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 exposition 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 (Kozioł and Pudykiewicz, 2001) to provide evidence of the intercontinental transport of lindane. Li et al. (2011a, 2011b) 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).

The objective of this study is to implement pesticides within the chemical transport model CHIMERE in order to simulate the spatio-temporal distribution of current-use pesticides in the atmosphere at a regional and national scale. The model is tested and applied for 2 pesticides: S-metolachlor (S enantiomer of metolachlor, a herbicide used in France mostly on maize at the early stage of the crop growth) and folpet (a fungicide mostly used to treat mildew in vineyards), both being frequently detected in the atmosphere (AtmoFrance, 2019) and being identified by ANSES (2020) as compounds to be monitored in the air in the future due to their potential risk on the population. S-metolachlor and folpet are used in this study as compounds representative of pesticides emitted by volatilization from soil and plant surfaces, respectively. First, the emissions by volatilization estimated by CHIMERE are compared to those calculated with the pesticide version of the model Volt'Air developed to predict pesticide volatilization at the field scale and tested against volatilization flux measurements for different herbicides and fungicides applied on bare soil and wheat crops (Bedos et al., 2009; Garcia et al., 2014; Lichiheb et al., 2016). The contribution of emission by spray-drift during application to atmospheric concentration was assumed negligible given the resolution of the model but its deposition on the different surfaces of the grid which can therefore contribute to the subsequent volatilization was considered. Then, the simulated results are compared to concentrations measured over France in 2014 with a focus on France southeastern PACA (Provence-Alpes-Côte d'Azur) region.

This study focused on parent pesticides. While the degradation of the parent pesticide was accounted for, the formation of transformation products was not considered as it requires specific information (reaction kinetics, formation mechanisms, physico-chemical properties of transformation products) and specific measurements (atmospheric concentrations of transformation products). Moreover, satisfying simulation of parent pesticides is a pre-requisite to the study of transformation formation.

2. Method

The CHIMERE model has been modified to be able to simulate the concentrations of pesticides. Simulations were performed over two domains: France at a resolution of $0.15^\circ \times 0.1^\circ$ (around 120 km^2) and the PACA region at a resolution of $0.02^\circ \times 0.02^\circ$ (around 3.5 km^2).

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

The model development is presented below in the Method section. The emissions over the PACA region simulated with CHIMERE are compared with the emissions estimated with the Volt'Air model. Emission calculations with both models are presented briefly in Sections 2.2.1 and 2.2.2.

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

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

2.1. Overview

2.1.1. General description

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

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

The model used in this study accounts for:

- The chemical evolution of compounds in the atmosphere by considering the gas-phase degradation of pesticides (only the degradation by OH radical was used for the pesticides considered in this study, however the model can account for photolysis and degradation by O_3 and NO_3 radicals if data are available) and the partitioning of semivolatile pesticides between the gas and the particle phase.
- Wet deposition (both by in-cloud and below-cloud scavenging) of gases (based on Henry's law constants) and wet and dry deposition of particles are based on CHIMERE 2017 β parameterizations.
- The soil/atmosphere and vegetation/atmosphere exchanges that can lead to the deposition of pesticides (sorption of pesticide by the soil or the vegetation) or their emissions (by volatilization). The exchanges are considered for both the treated crops (on which the pesticides are applied) and the other surfaces (in that case, accumulated pesticides in the compartments can be re-emitted).
- The evolution of pesticides inside the soil by considering the multiphase partitioning inside the compartment (gaseous, solid, and liquid), the degradation of pesticides within the soil by using the compound half-life time and the vertical diffusion. Uptake of pesticides by roots was not taken into account.

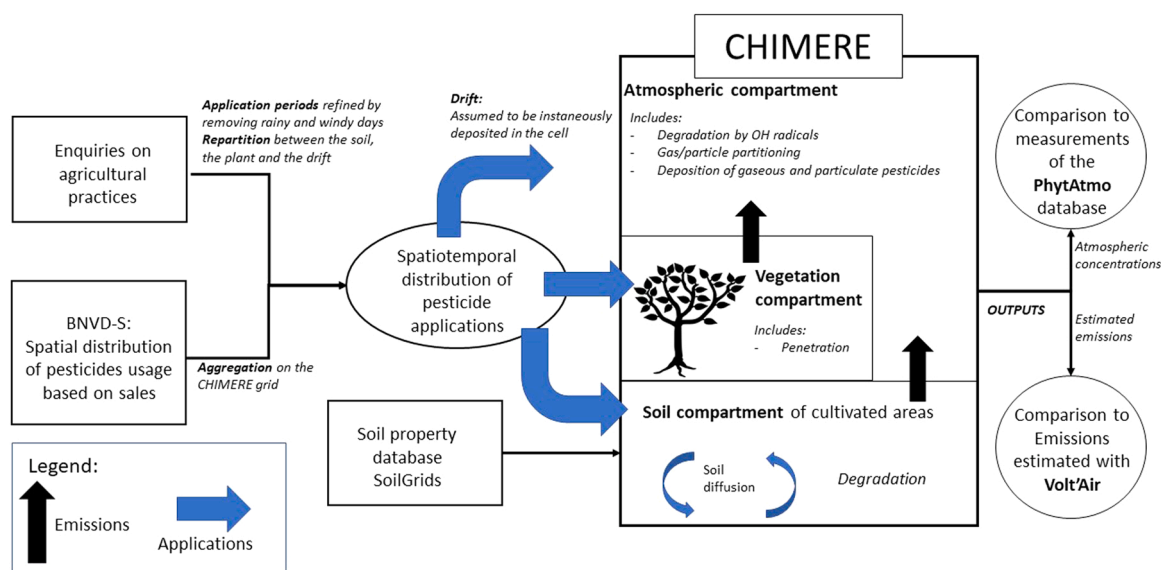


Fig. 1. Scheme of the pesticide Modelling approach used in this study.

Whereas spray-drift may contribute to the exposure of residents, it was not considered in the model as its contribution is expected to be very local compared to the scale of the CHIMERE model (above 1 km, more adapted to evaluate the exposition at the regional scale). Realistic atmospheric concentrations of spray-drift at the local scale cannot, therefore, be computed with this kind of model. However, an indirect impact of spray-drift was taken into account as the deposition of the spray-drift onto the different surfaces of the grid (and its potential re-emissions due to volatilization computed with the air/ecosystem exchange module of CHIMERE) were considered.

In order to simulate properly the emissions of pesticide by volatilization, the spatiotemporal distribution of pesticide application must be known. The French BNVD-S database uses the mandatory register on pesticide sales to estimate the spatialized usage of pesticides for the year considered, this database is presented in Section 2.1.3. Enquiries on the agricultural practices used by farmers in PACA were carried out by contacting experts of the different agricultural sectors of the region to obtain information in terms of types of sprayer used and timing of application. The enquiry methodology is presented in Section 2.2.3. For the purpose of the Modelling exercise, the agricultural practices identified for PACA were used for the whole country.

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

2.1.2. Substance selection and properties

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

S-metolachlor, the S enantiomer of metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl) acetamide], is a selective chloroacetamide herbicide widely used for pre- and post-emergence weed control for a variety of crops including maize, soybean, sunflower, and sorghum (Alletto et al., 2013). The usage of racemic metolachlor is prohibited and only S-metolachlor was used in France since the early 2000 s. However, a fraction of R-metolachlor in products is possible.

Folpet [N-(trichloromethylthio)phthalimide] is a phthalimide

protective fungicide used for broad spectrum control of fungal pathogens. It is widely used in vineyards against mildews or excoresis for example (Index Acta Phytosanitaire, 2018).

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

Large uncertainties exist however on the determination of several parameters. The estimation of saturation vapour pressure (or similarly of the Henry's law constant) is rather uncertain as discussed by Leistra (2011) and using quantitative structure-property relationship (QSPR) for example may lead to error up to a factor 10 (Beck et al., 2000). Various studies reported $DT_{50-soil}$ between 4 and 141 days for S-metolachlor indicating that this parameter is also quite variable (Grey et al., 2007; Bedmar et al., 2017; Wolejko et al., 2017; Marín-Benito et al.,

Table 1

Substance properties used in this study for S-metolachlor and folpet. The provided values for the saturation vapour pressure, the Henry's law constant and the solubility correspond to a Temperature of 298 K.

Properties	S-metolachlor	Folpet
Saturation vapour pressure (Pa)	3.7×10^{-3}	2.1×10^{-5}
Solubility (mg/L)	480	0.8
Henry's law constant (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}

2018; Fernandez et al., 2020).

2.1.3. Input databases

Three types of databases are necessary to simulate the volatilization of pesticides:

- Hourly meteorological data necessary for the emission calculation (such as the temperature, the wind velocity) were taken from the European Centre for Medium-Range Weather Forecast (ECMWF) model. As CHIMERE do not solve the soil thermal and hydric evolution (contrary to Volt’Air which is based on global radiation), the soil temperature and volumetric water content of ECMWF were also used in CHIMERE. It has to be noted that the low vertical resolution of the soil data (between 0 and 7 cm) and that the model calculates the average soil moisture and temperature over the whole cell. These parameters may not be representative of the type of soil on which pesticides are applied.
- The soil properties needed by CHIMERE (organic carbon content, bulk density) are taken from the SoilGrids database (Batjes et al., 2020). This database provides soil property maps for the world produced using machine learning at 250 m resolution. SoilGrids uses global models that are calibrated using all available input observations and globally available environmental covariates. Data are available at 6 standard depths but only data at the surface (for depths between 0 and 5 cm) were used. Additional parameters needed by the model Volt’Air (soil texture and van Genuchten-Mualem parameters) are taken from the combination of the spatial distribution of the soil types provided by the European Soil Data Center (ESDC) in the form of a soil map (European Soil DataBase, scale 1:1,000,000)

(Panagos et al., 2012) with the dominant soil type in agricultural areas of each Small Agricultural regions (SAR) selected by overlaying and intersecting the soil map with the CORINE Land Cover and SAR maps. Soil properties of these soil types were provided with the Harmonized World Soil Database by the Food and Agriculture Organization of the United Nations (FAO, IIASA, ISRIC, ISSCAS, JRC, 2012).

- The spatialized usage of pesticides is based on the French BNVD-S (“Banque Nationale des Ventes de produits phytopharmaceutiques par les Distributeurs agréés - Spatialisée”) database (Carles et al., 2015) which was only available for year 2014 at the time of the study. The usage of S-metolachlor and folpet over France is illustrated by Fig. 2. In this database, the spatialization of the pesticide sales is based on sales to professionals declared by each seller and aggregated at the national level (all sellers combined) according to the buyer’s postal code. This base, updated annually, was initiated in 2013. In order to spatialize the sales, the contents are disaggregated at the level of each of the land use blocks making up the postal code. The information can then be re-aggregated according to the spatial extent considered. Disaggregation is based on a high-resolution land use map (LPIS) that integrates the declarations made by farmers each year to receive support from the Common Agricultural Policy (CAP) of the European Union. All the plots on a farm are allocated to a single postal code, that of the farm’s head office, estimated by the municipality with the maximum surface area of the farm. The agricultural areas that are not subject to CAP declarations (mainly vineyards, market gardening, etc.) are reconstructed by combining agricultural statistics with the CORINE Land Cover database. The disaggregation of sales is done in each of the polygons constituting

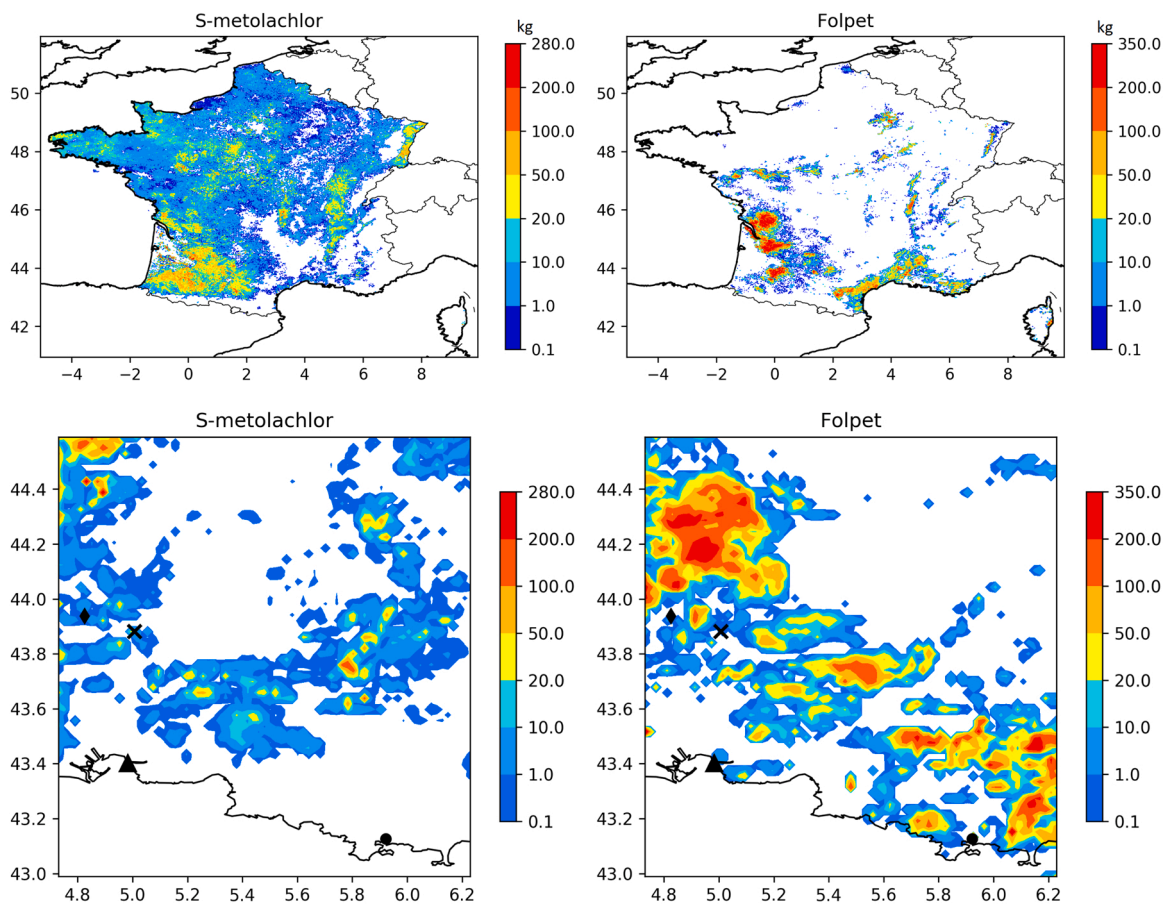


Fig. 2. Pesticide usage over France (in kg) for year 2014 from the BNVD-S database over France (top, aggregated at a resolution of $0.01^\circ \times 0.01^\circ$) and over the PACA region (bottom) for S-metolachlor (left) and folpet (right). The cross, diamond symbols, triangle and circle symbols represent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

the postal code considered. Each product sold will only be allocated to the areas for which it is registered, taking into account the differences in registered doses in the distribution factors (the same product can be authorized for different areas mapped at different doses). Due to the methodology, small quantities tend to be distributed spatially over large areas leading to very low application dose per hectare, sometimes not consistent with agricultural practices. In some rare cases, the opposite trend could occur (large quantities applied on small areas). To correct this feature, the surface on which pesticides were applied were corrected by assuming a dose of 1.9 kg ha^{-1} for S-metolachlor and 1.2 kg ha^{-1} for folpet corresponding to an average value based on available registered doses for various commercial products for the considered active ingredient and enquiries. Treated surfaces were then recalculated to match the total quantities used in the given area.

2.2. Emission calculation

2.2.1. Volt'Air and SurfAtm-Pesticides

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

Briefly, Volt'Air is a process-based model organized in modules that calculate the energy budget at the soil surface, the vertical transfer of energy (using Fourier's law), of water (using Richards equation), and of solutes in the soil including the diffusion of gaseous compounds in the air-filled pore space. The soil profile is divided into a user-defined number of layers. The computation of transfer fluxes of heat and water are not coupled. Either the van Genuchten-Mualem water retention and hydraulic conductivity models or the Clapp and Hornberger models can be used to describe water dynamics functions in the soil. In this study, the van Genuchten-Mualem water retention and hydraulic conductivity models have been selected. Pesticide volatilization to the air is calculated by the local advection approach (see Eq. 1) coupled with the physicochemical equilibrium Jury's model (Jury et al., 1983) describing the pesticide adsorption between the gas/water based on the Henry's law and water/soil phases based on the adsorption coefficient K_d calculated as the product of the soil organic fraction and the K_{oc} value of the compound, assuming to be instantaneous for an ideal solution (see Eq. 2). Additional adsorption from the gas phase to the soil matrix occurring under dry soil conditions can also be calculated provided data on the specific adsorption coefficient. This option has not been used in this study due to the lack of information. Under such conditions, an extrapolation of the water retention model to the dry domain has been implemented by Garcia et al. (2014) following Schneider and Goss (2012). Volt'Air can be run over several weeks at the field scale with a timestep ranging from a few minutes to few hours (with a calculated internal time-step for transfer calculation of the order of a few seconds). The capacity of Volt'Air to describe the temperature and surface humidity conditions in a bare soil has been evaluated (Garcia et al., 2011) validating the physicochemical parameterizations used in the model.

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

with $F_{volat,soil}$ the volatilization flux ($\mu\text{g m}^{-2}\text{s}^{-1}$), u^* the friction velocity (in m s^{-1}) κ the Von Karman constant (= 0.4), a_i and b_i two coefficients of the advection model (dimensionless), C the atmospheric concentration ($\mu\text{g m}^{-3}$), x the fetch (m) and z_0 the roughness length (m).

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

with C_T the total concentration of the pesticide in the soil compartment, C_s , C_g and C_{aq} , the concentrations in the solid phase, in the gaseous phase

and in the aqueous phases respectively, ρ_s the soil density, α_w and α_a the soil volumetric water content (m^3m^{-3}) and the air content in the soil pore (m^3m^{-3}) respectively.

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

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

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

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

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

2.2.2. CHIMERE

The emissions calculated with CHIMERE are based on Couvidat and Bessagnet (2021) where a soil/atmosphere SVOC exchange module was implemented. This exchange module was used to determine the volatilization from the soil. In this module, processes of sorption and desorption of organic vapours by the soil as well as the diffusion of organic compounds inside the soil are considered through a discretization of the soil into 13 layers. The thickness of the first layer is computed as a function of the chemical properties of the compound in order to correspond to a characteristic time of diffusion equal to 1 s. The thickness of the other layers are calculated to cover a depth of 20 cm. A complete description of the air/atmosphere exchange module is provided in the Supplementary materials.

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

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

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

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

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

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

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

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

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

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

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

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

2.2.3. Determination of cultural practice based on inquiries

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

The inquiries indicate that S-metolachlor is applied from mid April to mid May with most applications during the morning (between 8 h and 12 h) or in the evening (between 17 h and 21 h). For folpet, applications take place during May and June, mostly during the morning (between 8 h and 12 h). As these periods are quite large, they were refined by removing periods when farmers are not likely to apply pesticides: periods when the wind velocity exceeds 19 km/h (farmers cannot legally apply pesticides on these conditions in France) and rainy days were removed from the possible periods for applications (more information on the refinement is given in the Supplementary materials). Hulin et al. (2021) provided information on the partition between the soil, the plant, and the air of sprayed pesticides as a function of the type of equipment used. By combining this information to the results of the inquiries on the type of equipment used, it was estimated that 80% of S-metolachlor quantities are sprayed to the soil, 60% and 10% of folpet are sprayed to the plant and to the soil, respectively. The remaining fractions correspond to the drift.

2.3. 3D simulations

2.3.1. Representing pesticide in CHIMERE

S-metolachlor and folpet were implemented into CHIMERE by taking into their gas-phase degradation by OH and their gas-particle partitioning. The gas-phase degradation by OH radicals is simulated by using the k_{OH} kinetic constant shown in Table 1. Due to the molecular

structure of the considered pesticides, gas-phase degradation by O_3 is expected to be negligible. Due to the lack of data, the effect of photolysis, gas-phase degradation by NO_3 radicals and heterogeneous reactions, was not taken into account in CHIMERE.

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

CHIMERE uses a sectional approach to represent the size distribution of particles. In this study, particles are separated into 10 size bins according to their size in order to cover a range from 10 nm to 10 μm . Dry and wet deposition of particles is taken into account as a function of the mean diameter of the bin.

In addition to considering the volatilization from crops of pesticides, the model considers air/soil exchanges of pesticides (by using Eq. 8) for soil types. These exchanges can lead to the deposition of gas-phase pesticides (by sorption onto surfaces with low concentrations of pesticides) or the re-volatilization of previously deposited pesticides. Moreover, sorption of organics by the vegetation compartment is taken into account (Couvidat and Bessagnet, 2021).

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

2.3.2. Configuration of simulations

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

Concentrations of S-metolachlor and folpet are simulated from 2014-04-15 (beginning of the application period for S-metolachlor) to 2014-07-01 (end of the application period for folpet). While measurements show the presence of both compounds up to August, simulations were stopped at the beginning of July as the model would only simulate very low concentrations of both pesticides due to very low emissions.

2.4. Comparison to measurements

Simulations results are compared to measurements from the French Regional Networks for Air Quality Monitoring that measure the atmospheric concentrations of pesticides in gas and particulate fractions. These field measurements are compiled in the PhytAtmo database which aggregates about 7000 samples at 176 sites throughout mainland France and overseas for 321 active substances sought (AtmoFrance, 2019).

The overall mean uncertainty (i.e., sampling, extraction, and analysis) associated with the measured concentration was estimated at 10–15% for low-volume samples (e.g., Thermo Partisol), and at 20–25% for high-volume samples (e.g., Digitel Aerosol Sampler DHA-80), regardless of the sampling medium or the cut-off diameter (i.e., Total Suspended Particulates (TSP), Particulate Matter PM₁₀, and PM_{2.5} inlets) used. Both particulate and gaseous fractions were extracted and analysed by gas chromatography coupled to tandem mass spectrometry (GC-MS/MS), for folpet and S-metolachlor. It should be noted that S-metolachlor cannot be distinguished from the R enantiomer of metolachlor by GC-MS/MS.

The concentrations measured in PACA in 2014 and the description of sampling sites were summarized in [Désert et al. \(2018\)](#). Briefly, sampling (considered necessary for the study purpose) was undertaken at four sites located throughout the PACA region (i.e., Avignon, Cavaillon, Toulon, and Port-de-Bouc). Cavaillon (hamlet of Les Vignéres) is located in an intensive arboriculture area. Avignon, Toulon and Port-de-Bouc are urban stations. Vineyards and other cultivated areas are however present in a radius of 10 km around the Toulon and Avignon stations. Additional information on the station vicinity is provided in [Table S1 in the Supplementary materials](#).

The locations of the stations in the PACA domain are shown in [Fig. 2](#) together with the application of S-metolachlor and folpet in the domain. The other french stations used in this study are shown in the [Supplementary materials \(Fig. S5\)](#). During the period of interest, 24 and 29 stations in France measured S-metolachlor and folpet, respectively. Four of these stations (Avignon, Cavaillon, Port-de-Bouc and Toulon) are located in the PACA region. In 2014, S-metolachlor was only detected on the Cavaillon and Avignon stations, it was chosen to focus the comparison of the PACA simulations on these two stations. The BNVD-S shows that applications of S-metolachlor and folpet occurred only in the vicinity of the Cavaillon and Avignon stations. Large application of folpet occurred in the vicinity of the Toulon station and in the North of the Cavaillon and Avignon stations.

One difficulty of the comparison is that the measurements do not cover entirely the period of interest (beginning with the period of applications). In PACA, measurements were done during two 8-day periods starting from May 21st and from June 25th. At the National level, different measurement protocols may be used. For some regions, 7-day samplings were done instead of 2-day samplings. For the purpose of the model to measurement comparison, concentrations of the model were averaged on the sampling duration (over 7 days or 2 days depending on the sampling procedure).

3. Results and discussions

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

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

In order to estimate the capacity of models to reproduce the evolution of emission, a comparison of simulated volatilization fluxes to experiments carried out by [Bedos et al. \(2017\)](#). Details on the scenario built on the experimental data set together with both model results are available in the [Supplemental materials \(Section 2\)](#). Briefly, both models could reproduce the order of magnitude of the observed volatilization losses three days after application, with however some discrepancies, e.g., on the diurnal cycle as predicted by Volt'Air in relation to the overall pedoclimatic conditions. CHIMERE reproduces well the temporal evolution of emissions as well the level of emissions (underestimation by 1%), while Volt'Air underestimates the volatilization flux on the first

day and overestimates emissions the following days.

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

[Fig. 3](#) shows the daily emissions computed with CHIMERE and Volt'Air over the PACA domain. During the application period, the two models simulated similar temporal trends of emissions for the two compounds (correlation between the two models of 0.97 for S-metolachlor and of 0.90 for folpet). The root mean square error (normalized by the average emissions of the two models) between the two models is 18% for S-metolachlor and 30% for folpet.

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

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

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

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

The normalized emissions (normalized by the crops surface treated with pesticides) simulated with CHIMERE and Volt'Air are shown in [Fig. 4](#). For both pesticides, stronger emissions are simulated by both

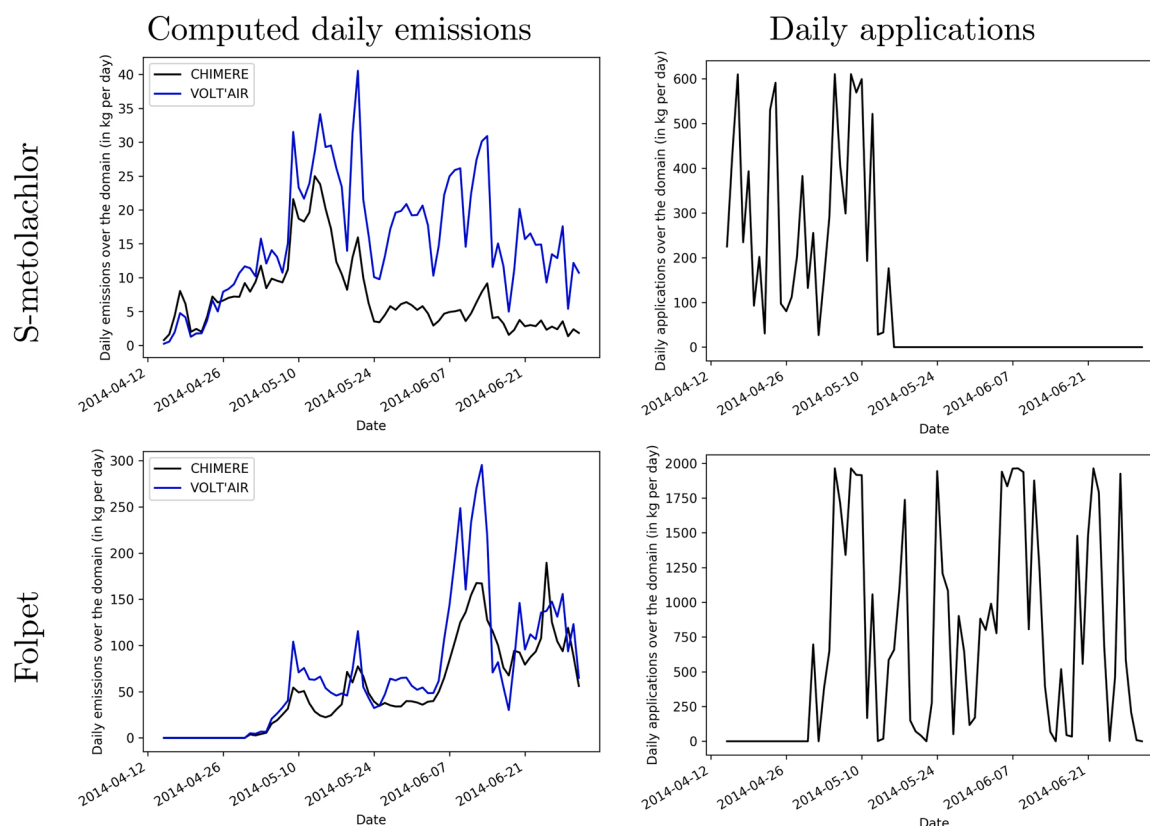


Fig. 3. Computed daily emissions and daily applications (without the drifted fraction) over the PACA region (in kg/day) computed with the CHIMERE and Volt'Air.

models in the western 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 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.

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 compared 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 centre). On the contrary, strong folpet emissions are simulated in southeastern France. In the PACA domain, an area at the Northwest of the domain has particularly high emissions. The corresponding concentrations are 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 measured for all the stations over France. For S-metolachlor, as substantial emissions can remain long after the application, the comparison was done for two periods: during the application period and after the application period.

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

During the application period, a mean normalized bias (MNB, average of the biases divided by the measured concentrations) of only 0.3% is obtained with the CHIMERE simulation. However, the bias obtained with the CHIMERE simulation during the application period are between -60% and 90% . For the one month period after the application period, the calculated MNB is around -49% . This feature seems to indicate that the decrease of emissions after the applications may be too strong. Several reasons could explain this feature (such as the underestimation of the DT_{50} -soil or an underestimation of the effect of temperature on volatilization). One possibility is that calculated emissions may be too premature for some regions. While the selected period for application is quite large, the repartition of applications within this period may lead to premature application.

For folpet, this compound was only detected by 10 out of 29 stations. For the stations where folpet was detected, the model simulates concentrations ranging from 0.03 ng m^{-3} to 2.9 ng m^{-3} against averaged measured concentrations ranging from 0.05 to 3.2 ng m^{-3} with a spatial

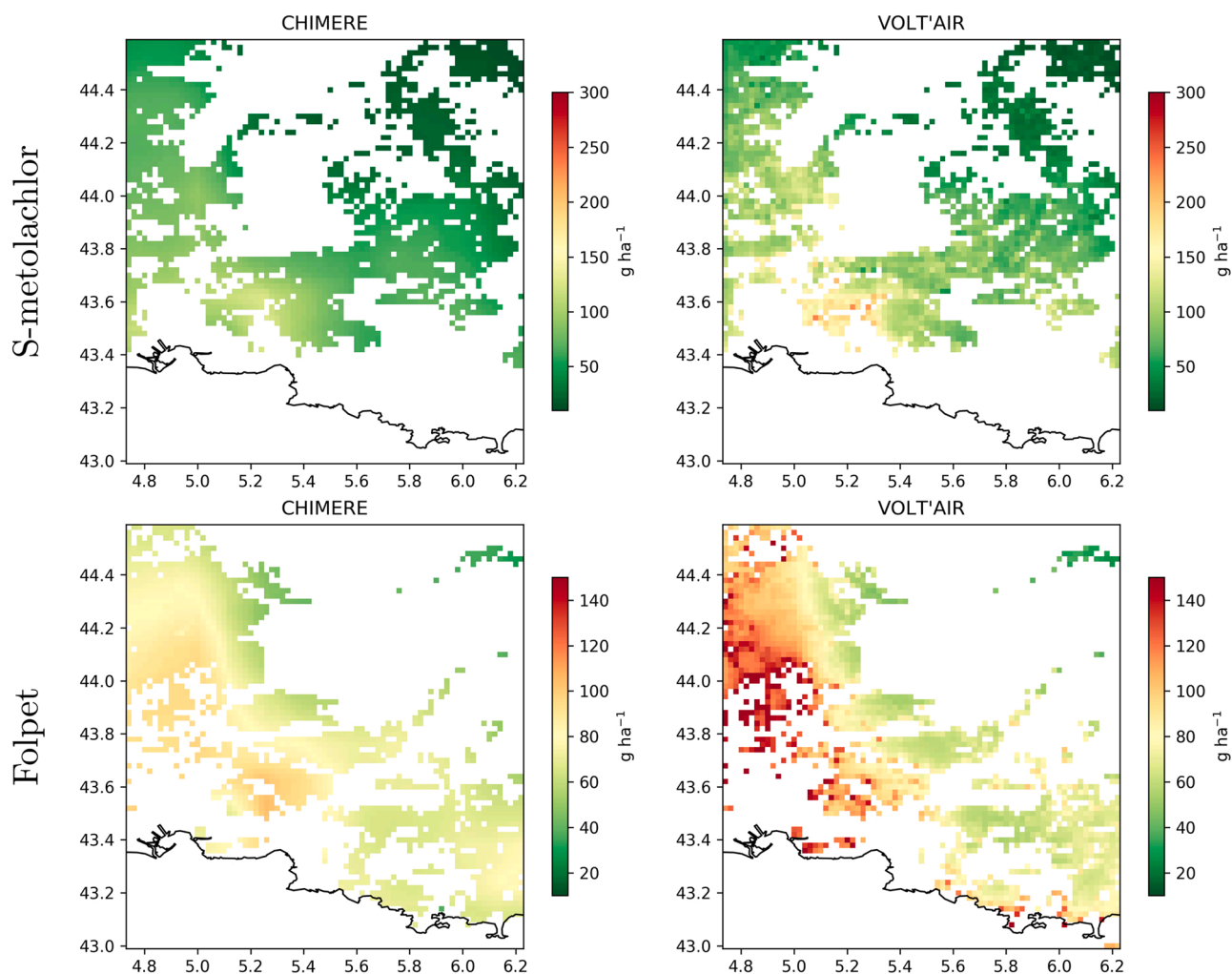


Fig. 4. Maps of volatilized amounts (in g ha^{-1}) per hectare of crops using pesticides for S-metolachlor (top) and folpet (bottom) during the application period simulated by CHIMERE (left) and Volt'Air (right).

correlation of 0.52. For the 12 stations where the folpet concentrations could not be detected, the model simulates averaged concentrations under 0.6 ng m^{-3} (upper value of the quantification limit). For the remaining 7 stations, the model gives high folpet concentrations that exceeds 1 ng m^{-3} for 5 of these stations (Auch: 3.3 ng m^{-3} , Kintzheim: 1.9 ng m^{-3} , Lyon: 1.2 ng m^{-3} , Reims: 2.6 ng m^{-3} , and Sigolsheim: 3.3 ng m^{-3}). For some stations (such as Kintzheim and Sigolsheim), the presence of folpet in the simulation could be due to the lack of refinement of the application period: applications are distributed over the application period (whereas they are probably limited in time) while folpet was measured for limited periods which may not correspond to the real application period. For the Reims and Auch stations, where weekly measurements were performed, strong concentrations (around 4 ng m^{-3}) were measured onto a single week after the selected application period (week of July 15th). Folpet emissions may therefore be sporadic and difficult to temporalize appropriately. Better results may be difficult to obtain without knowing precisely the periods of application.

3.3. Focus on the PACA region

Fig. 6c and d shows the concentrations of S-metolachlor and folpet simulated on the PACA domain. It appears that while S-metolachlor is one of the most present pesticide (in terms of detection limit exceedance) in the PACA region, the model simulates (due to the low

applications given by the BNVD-S, see Fig. 2) low concentrations of S-metolachlor compared to the high concentrations in western France and in the Rhone valley (valley at the north of the PACA region). Due to the high level of S-metolachlor emissions outside PACA, the long-range transport of pesticides may influence the amount of S-metolachlor simulated inside the domain. According to the simulation results, from April 15th to May 15th 2014, 57% and 11% of S-metolachlor concentrations at the Avignon (at 7 kilometres from the domain western border) and Cavaillon (at 22 kilometres from the domain western border) stations, respectively, originates from outside the PACA domain. On the contrary, strong concentrations of folpet are simulated in the northwestern part of the PACA domain with concentrations exceeding 10 ng m^{-3} during the application period.

Fig. 8 shows the comparison of the model results for the Avignon and Cavaillon stations. Unfortunately, for S-metolachlor, the first measurements begin after the application period (May 21st). However, as the concentrations are measured outside the expected application period, it seems probable that the concentrations come solely from the volatilization and not from the drift. It was therefore not possible to evaluate the ability of the model to simulate concentrations in PACA during the application period. Averaged S-metolachlor concentrations simulated are close to the measurements (0.058 ng m^{-3} in measurements against 0.059 ng m^{-3} in simulations for Avignon and 0.11 ng m^{-3} in measurements against 0.17 ng m^{-3} in simulations for Cavaillon). The model succeeds in explaining the strongest concentrations at Cavaillon that are

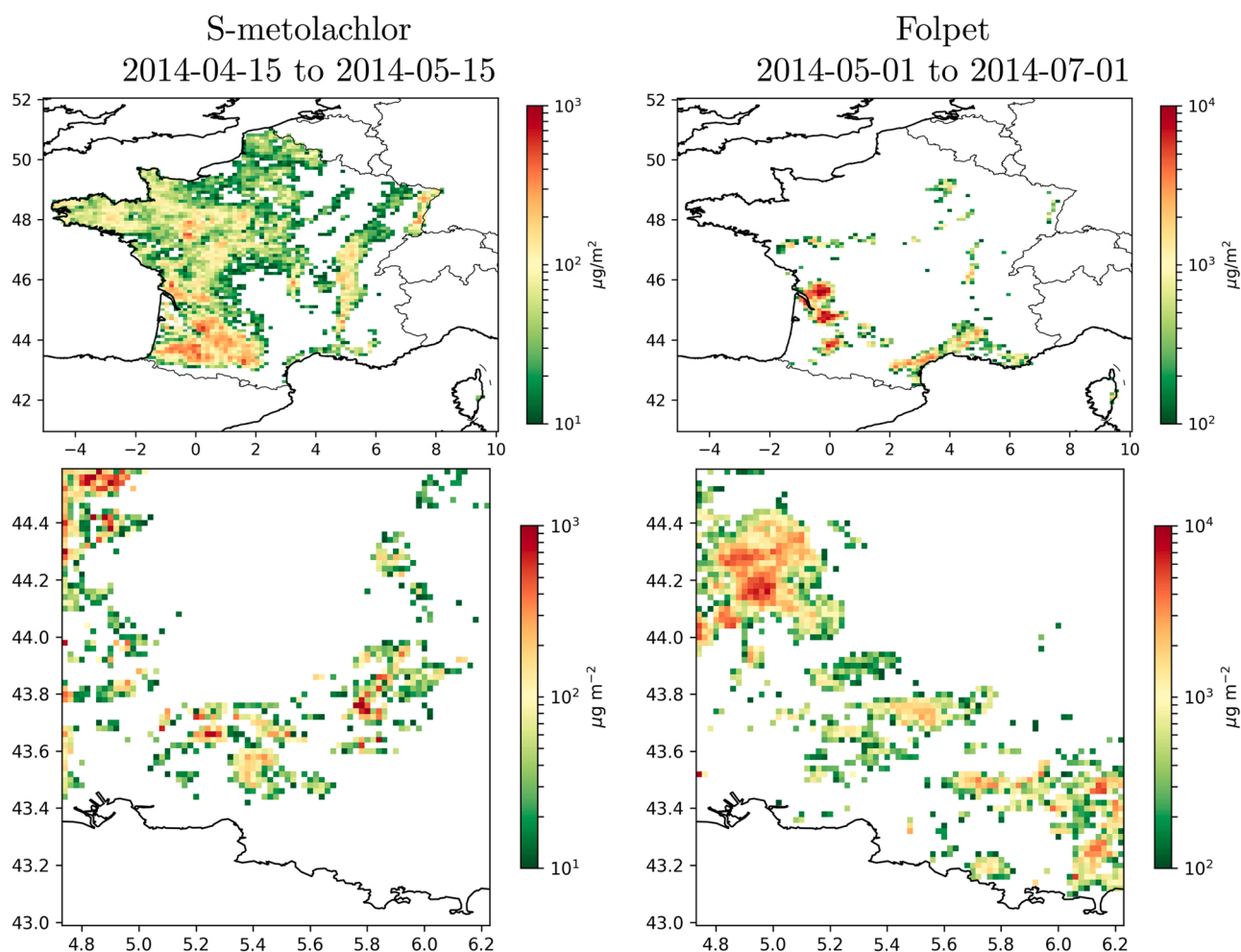


Fig. 5. Simulated emissions over France (top) and over the PACA region (bottom) by CHIMERE (in $\mu\text{g}/\text{m}^2$) of S-metolachlor (left) and folpet (right) during the periods of application.

due to emissions in the vicinity of the stations. For the two stations, the peak at the beginning of the comparison (corresponding to concentrations measured between May 21st and May 23rd; simulated concentrations around 0.10 ng m^{-3} for Avignon and around 0.34 ng m^{-3} for Cavaillon) is not present in the observations. Outside of this peak, the model seems to reproduce the temporal evolution.

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

For folpet, the model may slightly underestimate the concentrations. Concentrations around 2.9 ng m^{-3} are measured at the Avignon and Cavaillon stations while the simulated concentrations (on the same period than the samplings) are around 1.9 and 1.7 ng m^{-3} , respectively. The underestimation is stronger for the Port-de-Bouc (0.5 ng m^{-3} in simulations against 2.9 ng m^{-3} in measurements) and Toulon (1.0 ng m^{-3} in simulations against 2.2 ng m^{-3} in measurements) stations. However, the model simulates concentrations during the period (and not averaged on the sampling periods) close to the measured concentrations. Simulated concentrations during the application period are around 2.9 ng m^{-3} , 3.3 ng m^{-3} , and 2.3 ng m^{-3} at the Cavaillon,

Avignon, and Toulon, respectively. It may therefore be possible that the underestimation on these stations are mainly due to difficulties to temporalize the application appropriately. This hypothesis may be supported by Fig. 8 that shows that the model is not able to explain the strong concentration peak (from May 24th to May 25th) observed at both the Avignon and Cavaillon stations (around 7 and 9 ng m^{-3} in measurements). It seems unlikely that the low concentrations simulated at Port-de-Bouc can be explained by the temporalization alone as the average concentrations during the application period at Port-de-Bouc is only of 0.9 ng m^{-3} . The lower simulated concentrations at Port-de-Bouc are due to low emissions in the vicinity of the station.

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

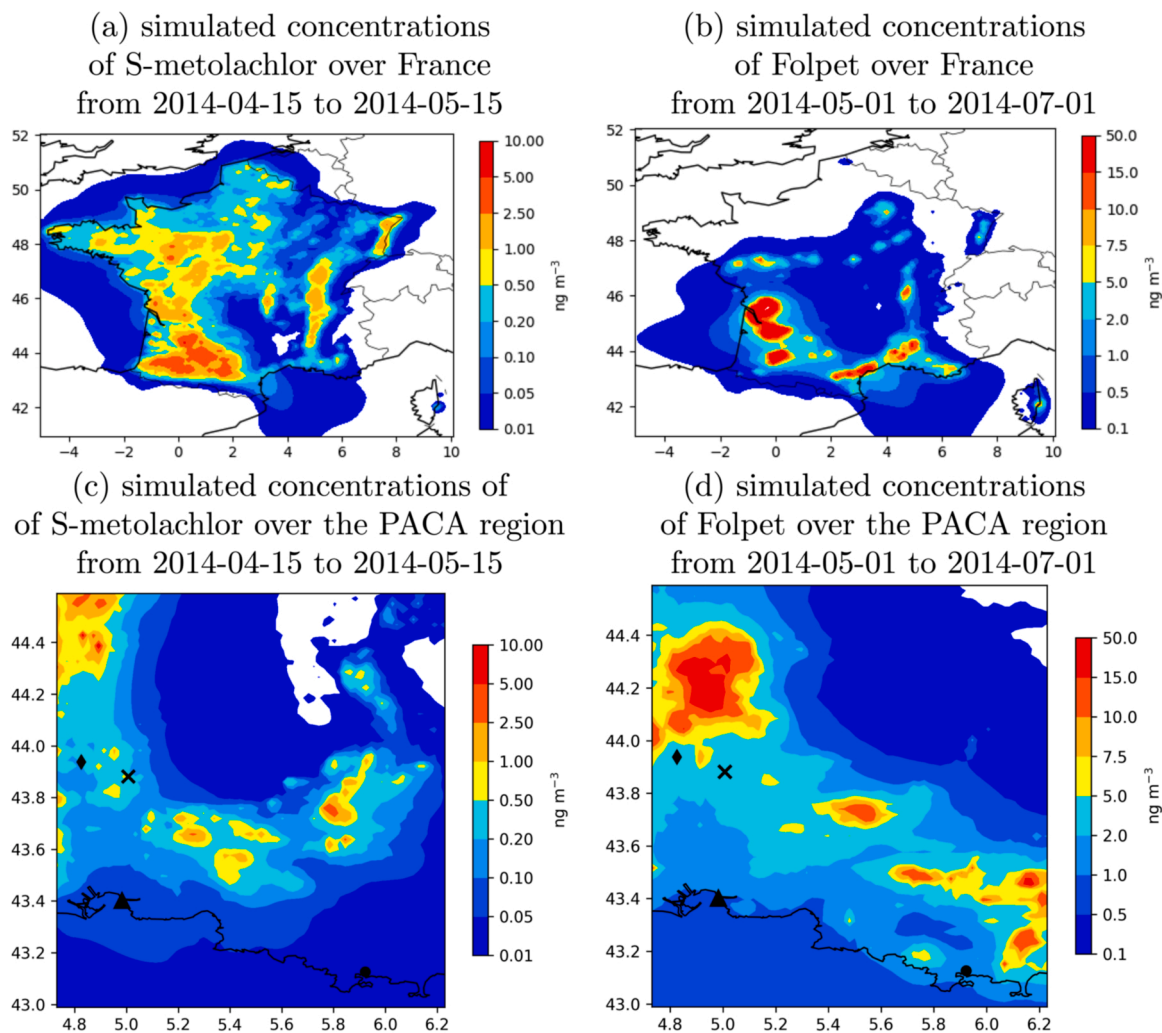


Fig. 6. Simulated average concentrations over France (top) and over PACA (bottom) by CHIMERE (in ng m^{-3}) of S-metolachlor (left) and folpet (right) during the periods of application. The cross, diamond symbols, triangle and circle symbols represent the location of the Cavaillon, Avignon, Port-de-Bouc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

3.4. Proposed procedure for the modelling of atmospheric concentrations of pesticides

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

1. Improve spatio-temporal pesticide application:

- Use a database of the spatialized usage of pesticides. In France, the BNVD-S database based on the sales of pesticides provides the most complete source of information to this date. This tool is indispensable when we are looking to spatialize the behaviour of pesticides in the environment, such as their emission into the atmosphere as in this study. It is essential that this tool can be deployed over several years in order to continue the modelling work for more recent years. However, another issue is that pesticide may be distributed over agricultural areas where pesticide is not applied in reality, in relation to hypothesis that have to be made to identify potential treated crops leading thus to uncertainties and requiring a re-evaluation of the surface onto which pesticides are applied to conserve realistic doses and locations. This re-evaluation may not be straightforward because of the range of potential application doses (e.g., estimated to be

from 1 to 2.5 kg ha^{-1} for S-metolachlor and from 0.225 to 1.5 kg ha^{-1} for folpet).

- Estimate application periods as precisely as possible. In our case, for the purpose of the Modelling exercise, application periods specific of the PACA region were used and were refined according to wind velocities and precipitation. However, it appears that more refined application periods may be necessary and that the application periods may vary significantly from one region to another. Enquiries with farmers could provide precise information but may be difficult to obtain at the scale of a region or a country. One possible option could be to use parameterizations on plant growth or fungi/insect 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 [Calonnet et al. \(2008\)](#); [González-Fernández et al. \(2019\)](#) or [Lagomarsino Oneto et al. \(2020\)](#) could be used.

2. Improve pesticide emission calculation

- 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

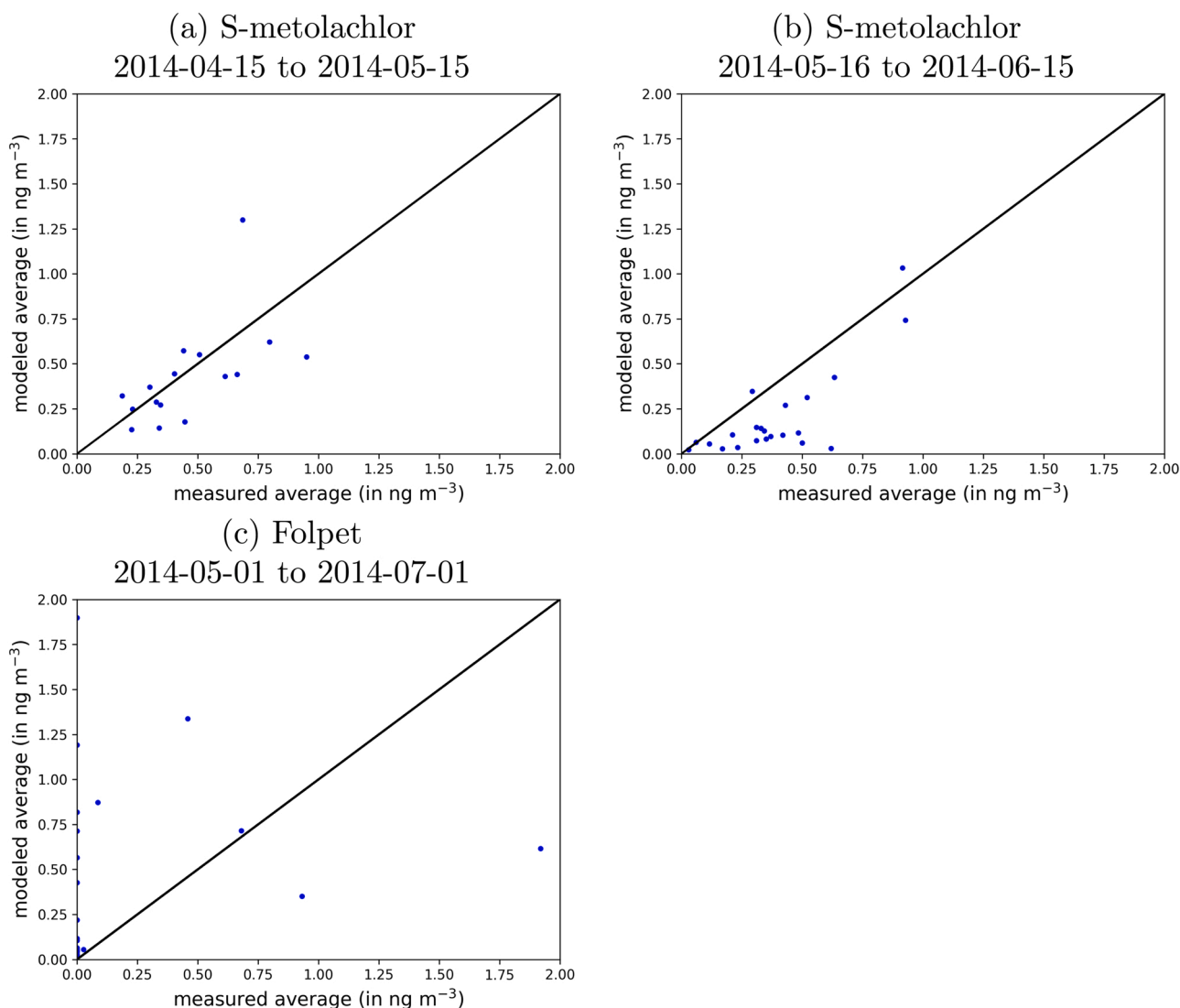


Fig. 7. Comparison of averaged measured and modelled concentrations for S-metolachlor during the application period (a) during one month after the application period (b) and folpet during the application period (c).

S-metolachlor, the temperature of the soil surface can follow a very marked diurnal cycle, with maximums higher than 45 °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 cell 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 formulation influences the penetration of the compound within the leaf.

(b) For each pesticide, compare the modelled emission fluxes to multiple flux measurements carried out into different conditions. Doing this could be useful 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 the 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 variability of the volatilization fluxes under various pedoclimatic conditions as discussed by Prueger et al. (2017), the determination of volatilization fluxes are also

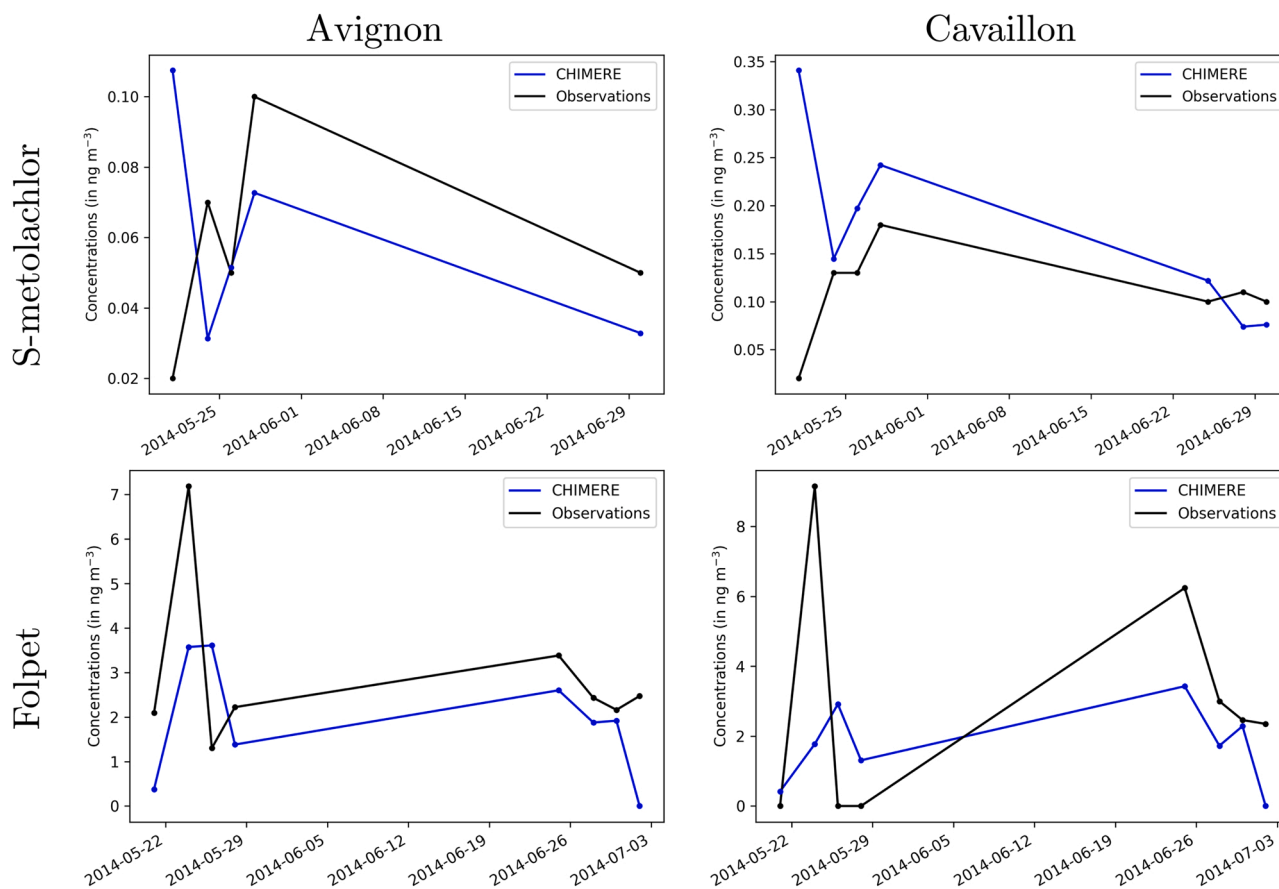


Fig. 8. Temporal evolution (in ng m^{-3}) of simulated and measured concentrations of S-metolachlor and folpet at the Avignon and Cavaillon stations.

uncertain (Loubet et al., 2010; Yates et al., 2016; Alfieri et al., 2017). Under these conditions, calibration of the models may be challenging.

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

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

4. Conclusions

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

Concentrations of two pesticides were simulated on France with a focus on the PACA region: S-metolachlor (a herbicide used mainly on crops at a early stage of the plant growth) and (folpet a fungicide used mainly to treat mildew in vineyards). The two compounds were selected because they are among the pesticides frequently detected in the PACA region, because they are mostly used on one type of crops and because they are representative of two types of emissions: volatilization from the bare soil in the case of S-metolachlor and volatilization from the layer of pesticides covering plants. Emissions simulated by CHIMERE were compared to the emissions simulated by the Volt'Air model. The simulated concentrations are compared to measurements.

The comparison of emissions show that the calculation of pesticide emissions may be uncertain (particularly for the evolution of long-term emissions). Volatilization from the soil is driven by processes happening in the first centimeters of the soil. The soil moisture and temperature were taken from the results of the IFS meteorological model. However,

as the first soil layer covers a depth down to 15 cm and as the model may not be representative of agricultural fields, the choice of using the IFS simulation results could lead to an underestimation of pesticide volatilization. Additionally, regarding emission calculations with the Volt'Air model, the results could be improved using a model designed especially for vineyard application as the crop structure (with rows of vine) may impact the energy budget and in consequences the surface conditions and the volatilization rate. The physicochemical soil properties may be also a source of uncertainty. The SoilGrids database was used to provide data on the soil organic carbon content (a key parameter for the volatilization from the soil). In this database, constructed by machine learning, the first layer covers a depth of 5 cm while the other databases cover a depth of 15 cm but it may still be too coarse to represent the processes at the Soil/Atmosphere interface. However, the representativeness of such a database for agricultural fields could be questioned. The volatilization of pesticides is also computed using the physicochemical properties of the compounds alone (for example volatilization from plants are computed as a function of the saturation vapour pressure). This may not be appropriate if the co-formulants present in the products act on the pesticide volatilization. As it is difficult to deal with all these issues, we recommend that comparison to measurements of pesticide volatilization fluxes are performed in order to constrain some parameters of the model and therefore integrating by this way the error due to all these uncertainties.

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

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

The simulation of folpet proved to be challenging with a lack of correlation at the France level and an underestimation of folpet concentrations over the PACA domain. These features could be due to difficulties to temporalize applications appropriately and to do comparison to measurements (which were done on limited periods and not on the whole simulation period).

CRedit authorship contribution statement

Florian Couvidat: Conceptualization, Methodology, Software, Writing – original draft. **Carole Bedos:** Conceptualization, Methodology, Writing – original draft. **Nathalie Gagnaire:** Software, Data curation. **Mathilde Carra:** Investigation. **Bernadette Ruelle:** Investigation. **Philippe Martin:** Data curation, Writing – review & editing. **Thomas Poméon:** Data curation. **Lionel Alletto:** Writing – review & editing. **Alexandre Armengaud:** Investigation. **Etienne Quivet:** Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.127497.

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