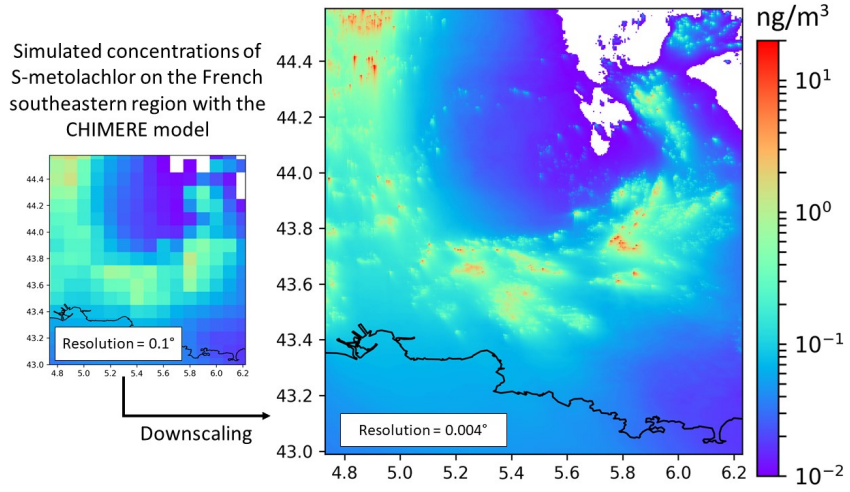
Graphical Abstract

An online downscaling method to simulate high resolution atmospheric concentrations of pesticides with the 3D chemistry-transport model CHIMERE: application and evaluation

Florian Couvidat,, Carole Bedos, Philippe Martin, Thomas Poméon, Etienne Quivet



An online downscaling method to simulate high resolution atmospheric concentrations of pesticides with the 3D chemistry-transport model CHIMERE: application and evaluation

Florian Couvidat,[a,*], Carole Bedos[b], Philippe Martin[c], Thomas Poméon[d], Etienne Quivet[e]

[a] *INERIS, Institut National de l'Environnement Industriel et des Risques, Parc Technologique ALATA, Verneuil-en-Halatte, 60550, France*
[b] *Paris-Saclay Univ. INRAE AgroParisTech UMR ECOSYS 78850 Thiverval-Grignon France*
[c] *UMR SADAPT AgroParisTech INRAE Paris-Saclay Univ. 78850 Thiverval-Grignon France*
[d] *US ODR INRAE 31326 Castanet-Tolosan France*
[e] *Aix Marseille Univ CNRS LCE Marseille France*

Abstract

High resolution databases on atmospheric concentrations of pesticides are necessary in order to perform epidemiological studies but there is currently no modeling method to provide high resolution mapping of pesticides concentrations over a whole region. In this study, we propose an online downscaling method for CHIMERE to perform simulations at a sub-kilometer resolution. The main idea of this downscaling approach is to redistribute or interpolate some information simulated on the coarse grid to simulate the transport over a finer subgrid. The performance of the downscaling is analyzed by comparing the CHIMERE nested simulation results at 0.02° and CHIMERE simulation results downscaled from 0.1° to 0.02°.

By applying this method to S-metolachlor, we diagnosed an error generated by the downscaling of a few percents on both background and hotspot concentrations. The method was used to simulate concentrations over France at a resolution of 0.004° with a limited increase of the computational time. Based on these simulations, we estimated that around 3 000 inhabitants were exposed to concentrations of S-metolachlor above 10 ng/m^3 from April 15th to May 15th 2014.

Keywords: Pesticide, Air quality, Modelling, Downscaling

1. Introduction

Pesticides are chemical products widely used in agriculture for pest management and therefore to prevent yield losses. Because pesticides can be emitted into the atmosphere by the drift of spray droplet and by the volatilization from

*Corresponding author, email: florian.couvidat@ineris.fr

treated surfaces, pesticides can be present in the atmosphere. Numerous studies have confirmed the presence of pesticides in the atmosphere (e.g., studies of Moussaoui et al. (2012); Coscollà et al. (2017) or Désert et al. (2018)) and their possible health effects on residents (Cognez et al., 2019; Teysseire et al., 2020). However, their ubiquity in the atmosphere raises numerous concerns on the exposition of the population as a whole and not only residents living in proximity of crops where pesticide are applied.

Reliable estimates of pesticide exposure for the whole population are needed in order to perform national-scale or regional-scale epidemiological studies. 3D Chemical Transport Models (CTM) could be used to provide large scale maps of pesticide concentrations. This type of models 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).

Recently, Couvidat et al. (2022) implemented in the CHIMERE CTM (Mailler et al., 2017) a method to simulate the concentrations of pesticides and has shown that CTMs could be applied to the mapping of atmospheric concentrations of pesticides as long as the spatiotemporal distribution of pesticide applications can be adequately estimated. In this method, the model estimates the emissions by volatilization of pesticides from treated surfaces with a distinction between the volatilization from the soil and vegetation compartments. The authors applied the method to simulate the S-metolachlor and folpet atmospheric concentrations over France and its southeastern region. However, CTM simulations are generally performed at a low resolution (from a few kilometers to hundreds of kilometers) due to the high computational cost. While these models could be applied to estimate the background atmospheric concentrations, the hotspots of concentrations may be missed due to the low resolution. One challenge of applying CTM results for regional-scale epidemiological studies is therefore to reach a sufficient resolution.

Several methods are used to map atmospheric pollutants at high resolution based on CTM results. A general distinction can be made between the nesting approach and the downscaling approach. The former approach (by nesting) is used to run the model over a smaller geographical domain with higher resolutions (using the larger domain as boundary conditions). Although this method is suitable for simulating small regions, its use can be quickly limited by the CPU time required for simulations. Users would need to launch numerous time-consuming simulations over different nested domains to obtain high-resolution mapping of concentrations over large areas.

The latter approach (downscaling) can be calculated by interpolation (bilinear, kriging) from CTM outputs. However, in order to increase spatial accuracy while maintaining correct performance scores, accurate emission proxies (e.g. Bessagnet et al. (2023)) or a Gaussian dispersion model (Denby et al., 2020; Hooyberghs et al., 2022) need to be used with such methods. Finally, thanks to advances in machine learning and the increased availability of satellite data, statistical regression approaches based on land use characteristics (Land Use Regressions models) can offer promising spatial resolutions. However, temporal resolution is often limited to daily time steps at best (e.g. Hough et al. (2021); Shen et al. (2022)). LURs seem to have difficulty competing with CTMs in terms of process dynamics.

The objective of the present study is to develop an online method (applied directly inside the CHIMERE CTM and not on simulation results) in order to downscale simulated concentrations from a coarse resolution to a sub-kilometer resolution and to evaluate the performance of the downscaling. Instead of processing simulation results, this method consists in redistributing or interpolating fluxes calculated over the coarse grid onto a finer subgrid in order to compute the atmospheric chemical transport of compounds over this subgrid. This method aims therefore at reproducing the results that would be obtained by nesting without solving again all the physicochemical processes in order to save CPU time. To provide an illustration, the downscaling approach is applied to the simulation of S-metolachlor concentrations (the compound from the two pesticides simulated by Couvidat et al. (2022) with the best comparison to measurements performance).

The methodology for the downscaling is presented in the Method section. Finally, the performance of the downscaling is evaluated by comparing the results of the France simulation downscaled to 0.02° with the simulation results (without the downscaling) over four separate subdomains directly with a 0.02° resolution. The gain on the computation time due to the downscaling is also studied.

2. Method

Concentrations of S-metolachlor are simulated over France from mid April to mid May 2014 (application period of S-metolachlor) with a resolution of 0.1° and are downscaled either to 0.02° or to 0.004°. As simulations at the 0.004° resolution is too time consuming even over small spatial domains, the evaluation of the downscaling approach is performed only for the 0.02° resolution on several sub-domains.

Following Couvidat et al. (2022), the contribution of emission by spray-drift during application to atmospheric concentration was assumed negligible because of the resolution of the model. Indeed, due to the high diameter of spray-drift droplets and their low lifetime in the atmosphere, a resolution of a few meters would be needed to represent adequately their atmospheric transport. Therefore, the current downscaling method only aims at representing pesticide concentrations due to emissions by volatilization. Nonetheless, the model considers that spray-drift droplets are instantaneously deposited into the cell where they are emitted and can contribute to subsequent emissions by volatilization.

2.1. Presentation of the pesticide version of CHIMERE

In order to estimate the atmospheric concentrations of pesticides, the CHIMERE model computes the transport of compounds over a grid covering the studied domain by accounting for advection and vertical diffusion. The vertical grid is discretized into several vertical layers (9 layers in Couvidat et al. (2022) ranging from 30 m to more than 5 000 m). The model uses a soil/vegetation/atmosphere exchange module to compute the emissions by volatilization from treated surfaces. It is based on the approaches of Couvidat and Bessagnet (2021) and Lichiheb et al. (2016) for the volatilization from the soil and leaves, respectively.

This exchange module uses a resistance scheme and parameterizations to consider the multiphase partitioning and diffusion in the soil compartment as

well as lifetime of the compounds in the different compartments. The model also accounts for:

- The atmospheric degradation of pesticides by the OH radical (the model can also account for direct photolysis and degradation by O_3 and NO_3 radicals if experimental data on reaction constants are available).
- The gas-particle partitioning of semivolatile pesticides between the gas and the particle phases estimated with the Secondary Organic Aerosol Processor model (Couvidat and Sartelet, 2015).
- The wet deposition (both by in-cloud and below-cloud scavenging) of gases (based on Henry's law constants) and the wet and dry deposition of particles.

In order to use the model, the spatiotemporal distribution of pesticide applications have to be estimated to compute the emissions by volatilization. In Couvidat et al. (2022), the spatial distribution was given by the French BNVD-S ("Banque Nationale des Ventes de produits phytopharmaceutiques par les Distributeurs agréés - Spatialisée") database (Martin et al., 2023) that uses mandatory register on pesticide sales to estimate the spatialized usage of pesticides over parcels. The temporal distribution was estimated based on enquiries on agricultural practices over the southeastern region of France.

2.2. The online downscaling method

The online downscaling method consists in dividing the CHIMERE grid into a subgrid with a finer resolution and in determining the necessary variables for the computation of concentrations over the subgrid. Emissions rates over the subgrid are determined by redistribution (the amount of emitted pesticides onto a cell is redistributed on the different subcells). Other variable values (meteorological parameters, deposition kinetics, chemical destruction kinetics) are determined by an horizontal bilinear interpolation (interpolation between the four closest cell center of the CHIMERE coarse grid). With this method, concentrations can be efficiently computed without representing explicitly some time consuming processes (such as the transport of all the model, gas-phase chemistry, pesticide volatilization, gas-particle partitioning) over the subgrid . The fraction of the different landuse categories inside each sub-cells is calculated in order to determine the appropriate vertical mixing and deposition over the subgrid.

In CHIMERE, concentrations at each cell of the grid are computed with a semi-implicit numerical method in order to solve the following equation:

$$\frac{\partial C_{t,X,Y,Z}}{\partial t} = Prod_{t,X,Y,Z} - Loss_{t,X,Y,Z} \times C_{t,X,Y,Z} \quad (1)$$

With t,X,Y and Z the cell indexes for time, longitude, latitude, and altitude. $Prod_{t,X,Y,Z}$ is the production rate of C in cell X,Y,Z (due to emissions or transport of the compound into the cell) and $Loss_{t,X,Y,Z}$ is the loss kinetics of C in cell X,Y,Z (due to chemical degradation, transport, and deposition).

In CHIMERE, a sectional approach is used where particles are separated into N_{bins} (number prescribed by the user) bins according to their diameter. As pesticides are semi-volatile compounds existing in both the gaseous and particle

phases, each pesticide is represented by N_{bins}+1 CHIMERE species (for the N_{bin} size diameter bins and the gas phase fraction).

In the downscaling method, developed in this study, each cell of the CHIMERE simulation grid is divided into $N_{red} \times N_{red}$ sub-cells (N_{red} representing an integer number by which the resolution is reduced). The method consists in estimating the production rate $Prod_{t,X,Y,Z}$ and kinetics of loss $\text{Loss}_{t,X,Y,Z}$ over the sub-grid by redistributing or interpolating the rates over a finer grid in order to calculate the concentrations at a finer resolution. Eq. 1 is adapted to simulate the evolution of the concentrations on the finer grid such as:

$$\frac{\partial C^{sub,x,y}_{t,X,Y,Z}}{\partial t} = Prod^{sub,x,y}_{t,X,Y,Z} - Loss^{sub,x,y}_{t,X,Y,Z} \times C^{sub,x,y}_{t,X,Y,Z} \quad (2)$$

where x,y represent the longitudinal and latitudinal indexes of the sub-cell inside the cell X,Y,Z. $Prod^{sub,x,y}_{t,X,Y,Z}$ and $Loss^{sub,x,y}_{t,X,Y,Z}$ represent the production rate and loss kinetics of the sub-cell x,y inside cell X,Y,Z, respectively.

Moreover, in the downscaling approach, only one new model species (instead of the N_{bins}+1 CHIMERE species) representing both the gas and particle phases is transported on the CHIMERE subgrid. The total loss kinetics is determined by ponderating the loss kinetics for the gas-phase and each of the particle bins accounting for chemical degradation and deposition. More details are provided in sections 2.2.1 to 2.2.3.

By simulating a limited number of CHIMERE species (instead of a hundred of CHIMERE species) on the subgrid and by avoiding the computation of some Central Processing Unit (CPU) consuming processes (computation of pesticide volatilization and of the gas-particle partitioning), concentrations of pesticides on a subgrid can be computed with limited CPU time.

$Prod^{sub,x,y}_{t,X,Y,Z}$ and $Loss^{sub,x,y}_{t,X,Y,Z}$ are decomposed as follow:

$$Prod^{sub,x,y}_{t,X,Y,Z} = Emissions^{sub,x,y}_{t,X,Y,Z} + ProdHTrans^{sub,x,y}_{t,X,Y,Z} + ProdVTrans^{sub,x,y}_{t,X,Y,Z} \quad (3)$$

$$Loss^{sub,x,y}_{t,X,Y,Z} = WetDep^{sub,x,y}_{t,X,Y,Z} + DryDep^{sub,x,y}_{t,X,Y,Z} + ChemLoss^{sub,x,y}_{t,X,Y,Z} + LossHTrans^{sub,x,y}_{t,X,Y,Z} + LossVTrans^{sub,x,y}_{t,X,Y,Z} \quad (4)$$

with $Emissions^{sub,x,y}_{t,X,Y,Z}$ the emission rate on the subgrid, $ProdHTrans^{sub,x,y}_{t,X,Y,Z}$ the production rate due to horizontal transport on the subgrid, $ProdVTrans^{sub,x,y}_{t,X,Y,Z}$ the production rate due to vertical transport on the subhgrid, $DryDep^{sub,x,y}_{t,X,Y,Z}$ the dry deposition kinetics on the subgrid, $WetDep^{sub,x,y}_{t,X,Y,Z}$ the dry deposition kinetics on the subgrid, $ChemLoss^{sub,x,y}_{t,X,Y,Z}$ the chemical degradation kinetics on the subgrid, $LossHTrans^{sub,x,y}_{t,X,Y,Z}$ the loss kinetics due to horizontal transport on the subgrid and $LossVTrans^{sub,x,y}_{t,X,Y,Z}$ the loss kinetics due to vertical transport on the subgrid. $DryDep^{sub,x,y}_{t,X,Y,Z}$ and $Emissions^{sub,x,y}_{t,X,Y,Z}$ are equal to zero for altitudes above the ground level (no dry deposition and no emission of pesticides).

Currently, concentrations of pesticides entering the French domain are assumed to be null due to the lack of information on pesticide usages at the European scale (that would be necessary to perform a simulation at the European scale and obtain appropriate boundary conditions).

2.2.1. Dry deposition

In CHIMERE, the deposition kinetics is calculated as the function of the deposition velocities (with different parameterizations for gases and particles) and the landuse.

In each cell of the coarse domain, deposition velocities are computed for each landuse categories (even if this category is absent from the cell) by computing a vertical wind profile with the roughness length of the considered landuse. For each landuse category, the deposition velocities on the subgrid are interpolated and are combined to the fraction of the landuse category in the cell of the subgrid.

The apparent deposition kinetics $DryDep_{t,x,y,landuse}$ for a particular landuse of the grid is calculated as a function of the loss kinetics of gaseous and particle compounds such as:

$$DryDep_{t,x,y,landuse} = \sum_i f_i DryDep_{t,x,y,landuse,i} \tag{5}$$

with i the index for the considered pesticide of the gas-phase CHIMERE species (i=1) and for the particle species for each of the bins (i=2 to i=N_{bins}+1), f_i the fraction of CHIMERE species to the total concentration of the pesticide (gas + particle) and $DryDep_{t,x,y,landuse,i}$ the loss kinetics of i due to dry deposition for a specific land use.

The loss kinetics due to dry deposition on the sub-cell is constructed by combining the land use on the sub-cell and the interpolated apparent deposition kinetics for specific land use.

$$DryDep^{sub,x,y}_{t,X,Y,Z=0} = \sum_{landuse} L^{sub,x,y}_{x,y,landuse} Bilinear(DryDep) \tag{6}$$

with Bilinear the bi-linear interpolation function and $L^{sub,x,y}_{x,y,landuse}$ the surface ratio of the considered land use in the sub-cell.

2.2.2. Wet deposition

The loss kinetics due to wet deposition is obtained by interpolating the apparent loss kinetics due to wet deposition of total (gas + particles) pesticides such as:

$$WetDep^{sub,x,y}_{t,X,Y,Z} = Bilinear(\sum_i f_i WetDep) \tag{7}$$

With $WetDep_{t,X,Y,Z,i}$ the loss kinetics due to wet deposition of i (i being the index for the pesticides either in the gas-phase or one of the particle phase)

2.2.3. Chemical degradation

Similarly to Eq.7, $ChemLoss^{sub,x,y}_{t,X,Y,Z}$ is calculated by interpolating the apparent loss kinetics due to chemical degradation of total (gas + particles) pesticides such as:

$$ChemLoss^{sub,x,y}_{t,X,Y,Z} = Bilinear(\sum_i f_i ChemLoss) \tag{8}$$

With $ChemLoss_{t,X,Y,Z,i}$ the loss kinetics over the coarse grid due to chemical degradation of i (i being the index for the pesticides either in the gas-phase or

in one of the particle bins). As in this study, no heterogeneous degradation of pesticides is taken into account, $ChemLoss_{t,X,Y,Z,i} = 0$ for particles.

This interpolation is based on the assumption that the chemical degradation of pesticides is linear and that the concentrations of oxidants (only the OH radical in the case of S-metolachlor) can be interpolated. The impact of these assumptions is probably low except in areas with very strong local emissions of nitrogen oxides.

2.2.4. Emissions

The atmospheric emissions fluxes are computed with the exchange air/soil/plant cover exchange module with emissions being calculated by volatilization from the soil or the plant cover.

Two types of emissions are distinguished:

- Emissions from treated crops. In this case, the calculated mass of pesticide emitted over a cell is redistributed over the different sub-cells according to the applicated amounts given by the BNVD-S on the sub-cells

- Re-emissions (emissions by re-volatilization of pesticides deposited on non-treated surfaces). In this case, the re-distribution of emissions fluxes is calculated as a function of the accumulated amount of pesticides at the surface $Accum^{sub,x,y}_{t,X,Y}$ (due to dry deposition on the first atmospheric vertical level and the cumulated wet deposition on all vertical layer) calculated with the following equation:

$$Accum^{sub,x,y}_{t,X,Y} = \sum_{Z}(WetDep^{sub,x,y}_{t,X,Y,Z} C^{sub,x,y}_{t,X,Y,Z} \times \Delta H_Z) + DryDep^{sub,x,y}_{t,X,Y,Z=0} C^{sub,x,y}_{t,X,Y,Z=0} * \Delta H_{Z=0} - Accum^{sub,x,y}_{t,X,Y} k_{deg} \quad (9)$$

  with k_{deg} the degradation kinetics computed with the lifetime of compounds within the soil and ΔH_Z the thickness of the vertical layer.

2.2.5. Transport

The horizontal transport on the subgrid is solved with the same algorithm than the transport on the coarse grid. The necessary parameter (e.g., wind velocities) are downscaled by bilinear-interpolation.

In CHIMERE, the vertical transport is represented with the K-theory based on the K_z parameter calculated for each landuse categories. The vertical transport production rate and loss kinetics on the subgrid are computed for a level Z as a function of the K_z parameter on the interpolated on the subgrid and the concentrations on the level above (Z+1) and underneath (Z-1). It should be noted that following the treatment of deposition velocity the K_z explained in section 2.2.1, the K_z is calculated and interpolated for each landuse categories. The resulting K_z on the subgrid therefore accounts for the landuse.

In order to limit the number of cells, we added the possibility to simulate the vertical transport on $N_{lev,sub}$ vertical levels (inferior or equal to N_{lev} the number of vertical level of the coarse level). In that case, the model used interpolated concentrations from the coarse above $N_{lev,sub}$ to compute the vertical transport rate. The effect of $N_{lev,sub}$ on the results are discussed in section 3.3.

2.3. Evaluation of the downscaling method

The performance of the downscaling method to simulate high-resolution concentrations of S-metolachlor is evaluated by comparing to CHIMERE simulation results obtained by mesting at the same resolution (0.02°). In that order, the results of a 0.1° × 0.1° simulation downscaled to 0.02° × 0.02° are compared to CHIMERE simulations directly at 0.02° over four nested domains. Indeed, it would not have been possible to perform simulations for a domain covering the whole France with a 0.02° × 0.02° resolution (due to an important computation time). Simulations were performed over the four nested sub-domains illustrated in Fig. 1: NW (part of Northwestern France), NE (part of Northeastern France), SW (part of Southwestern France), and SE (part of Southeastern France). The SE subdomain corresponds to the French "Provence-Alpes-Côte d'Azur" subdomain studied by Couvidat et al. (2022). These four sub-domains were selected to cover the different situations encountered at the national scales (areas with high and low emissions, different climate conditions).

The results of a simulation over France at 0.1° × 0.1° are used to determine the boundary conditions over the four subdomains for all pollutants except for S-metolachlor. In order to remove the influence of boundary conditions on the analysis, the results from the downscaled simulation at 0.02° × 0.02° (with $N_{lev,sub}$=N_{lev}) were used as boundary conditions on the four subdomains (air masses entering the four subdomains have therefore the same concentrations than the downscaled simulation at 0.02°).

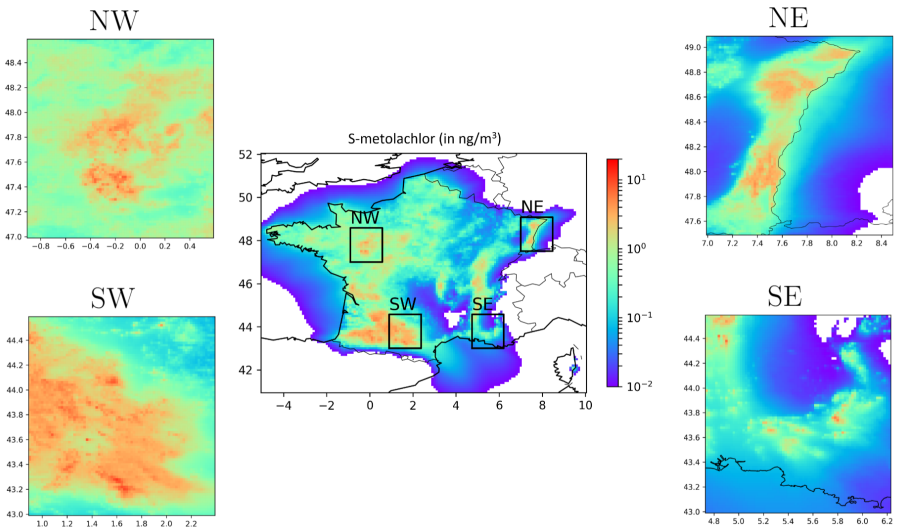


Figure 1: Simulated coarse concentrations of S-metolachlor (in ng/m^3) over France by CHIMERE at the 0.1° resolution (center) and on four nested sub-domains (in the four corners) at a resolution of 0.02° .

Several metrics are computed in order to evaluate the performance of the downscaling.

- The correlation coefficient R^2
- The Mean Normalized Bias (MNB): average of the bias (in %) between the downscaled simulation and the reference simulation at 0.02°.

- The Mean Normalized Error (MNE): average of the error (in %) between the downscaled simulation and the reference simulation at 0.02°.
- The Mean Normalized Bias computed for the 1% highest values (1%MNB)
- The Mean Normalized Error for the 1% highest values (1%MNE)

The last two metrics provide information on the ability to reproduce the simulated hotspots of pesticide concentrations in the 0.02° simulations.

2.4. Simulation configuration

The simulation configuration of Couvidat et al. (2022) was reproduced: anthropogenic emissions of gases and particles were taken from the European Monitoring and Evaluation Programme (EMEP) inventory (Vestreng, 2003) for the year 2014 and meteorology was taken from the operational analysis of the Integrated Forecasting System (IFS) model of the European Centre for Medium-Range Weather Forecasts (ECMWF). Nine vertical levels up to 500 hPa were used. The thickness of the first layer is around 30 m.

Concentrations of S-metolachlor are simulated from 2014-04-15 (beginning of the application period for S-metolachlor determined by Couvidat et al. (2022)) to 2014-05-15 (end of the application period).

3. Results

3.1. Downscaling results

Concentrations downscaled at 0.004° are shown in Fig. 2 and can be compared to the simulation results at 0.1° in Fig. 1. Similar pattern is found at the national scale with the same areas with high concentrations (southwestern France, the Rhône valley, several areas in western France, frontier between France and Germany) indicating that the model is able to simulate the background concentrations even at a low resolution.

The interest in downscaling the concentrations can be seen by zooming on the results on the different sub-domains. Fig. 3 shows the maps of coarse concentrations at 0.1° and of downscaled concentrations at 0.02°. Maps at downscaled concentrations at 0.004° can also be found in Supplementary Materials in figures S1 to S4. With a 0.1° resolution, the maps of concentrations are pixelated and hostpots of concentrations cannot be reproduced. The evolution of concentrations in the vicinity of areas with high emissions may not be well reproduced. When downscaled at a higher resolution, the hotspots of concentrations appear more and more clearly while the overall background pattern is unchanged. While the simulated average concentrations over France is around 0.2 ng/m^3 for all the coarse and downscaled simulations, the simulated maximum concentrations changed significantly: 5.3 ng/m^3 for the coarse simulation at 0.1°, 14.5 ng/m^3 for the downscaled simulation at 0.02° and 116 ng/m^3 for the downscaled simulation at 0.004°. By combining these simulation results to the French population database (Letinois, 2015), we estimated that a small part of the population (around 3 000 inhabitants, 0.005% of the French population) was exposed to concentrations of S-metolachlor above 10 ng/m^3 from April 15th to May 15th 2014.

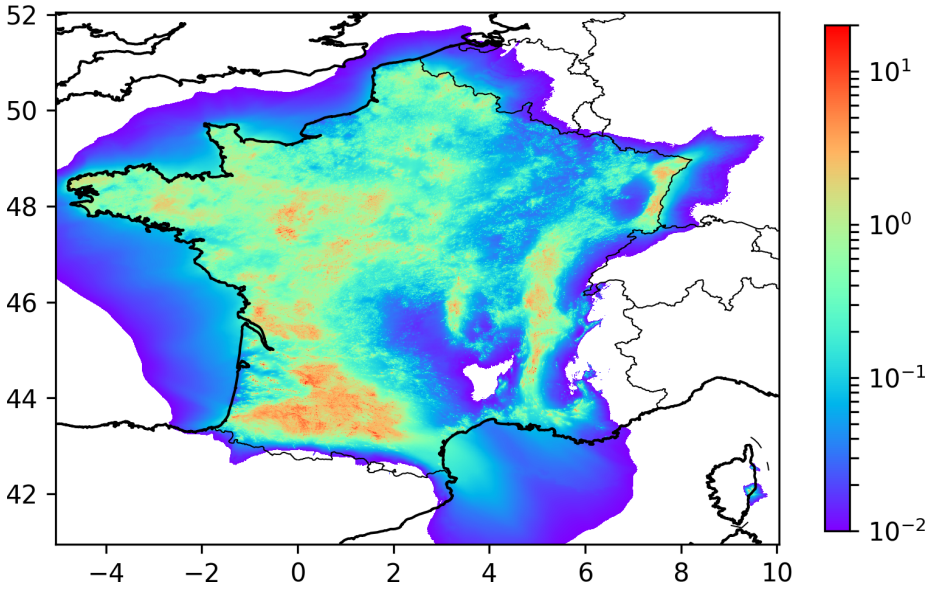


Figure 2: Simulations concentrations by CHIMERE (in ng/m^3) of S-metolachlor downscaled to a resolution of 0.004°. $N_{lev,sub}$ is chosen equal to N_{lev}.

3.2. Performance of the downscaling method

The performance of the downscaling method (illustrated by Fig. 4) is analyzed by computing R^2, MNB, MNE, 1%MNB, 1%MNE between the CHIMERE results at 0.02° (not downscaled) and the CHIMERE results at 0.1° downscaled to 0.02°over the four sub-domains. These metrics are shown in Table B1 in Supplementary Materials for the different subdomains and for different value of $N_{lev,sub}$. The metrics are also shown between the coarse simulation at 0.1° and the simulation at 0.02°.

The coarse simulation is characterized by a large MNE of 25% over all domains (and varying from 18.1% to 35.2% over each sub-domains) and on average concentrations tend to be overestimated (MNB=11%). However, the highest concentrations are strongly underestimated by the coarse simulation (MNB=-43.1%).

The downscaling method managed to reproduce concentrations with a low bias compared to the coarse simulation as 90% of the simulated values have a bias between -14% and 11% for the downscaled simulation at 0.02°against a bias between -32% and 82% in the coarse simulation. When applying the downscaling, the correlation coefficient is increased significantly and reaches near unity (R^2=0.99, R^2=0.9 for the coarse simulation) especially for the SW domain where the R^2 is increased from 0.62 for the coarse simulation to 0.99 for the downscaled simulation (with $N_{lev,sub}$=9). MNE is also significantly reduced from 43.1% to 6.2% (with $N_{lev,sub}$=9). While the concentrations tend to be overestimated by the coarse simulations, the concentrations seems to be underestimated by the downscaling method but at a low extent (MFB=-2.6% over the four subdomains and reaching -4.6% for the SW subdomain). The downscaling approach managed to capture the highest values as the 1%MNB is decreased from -43.1% to -2.0% with a 1%MNE (6.1%) close to the average MNE.

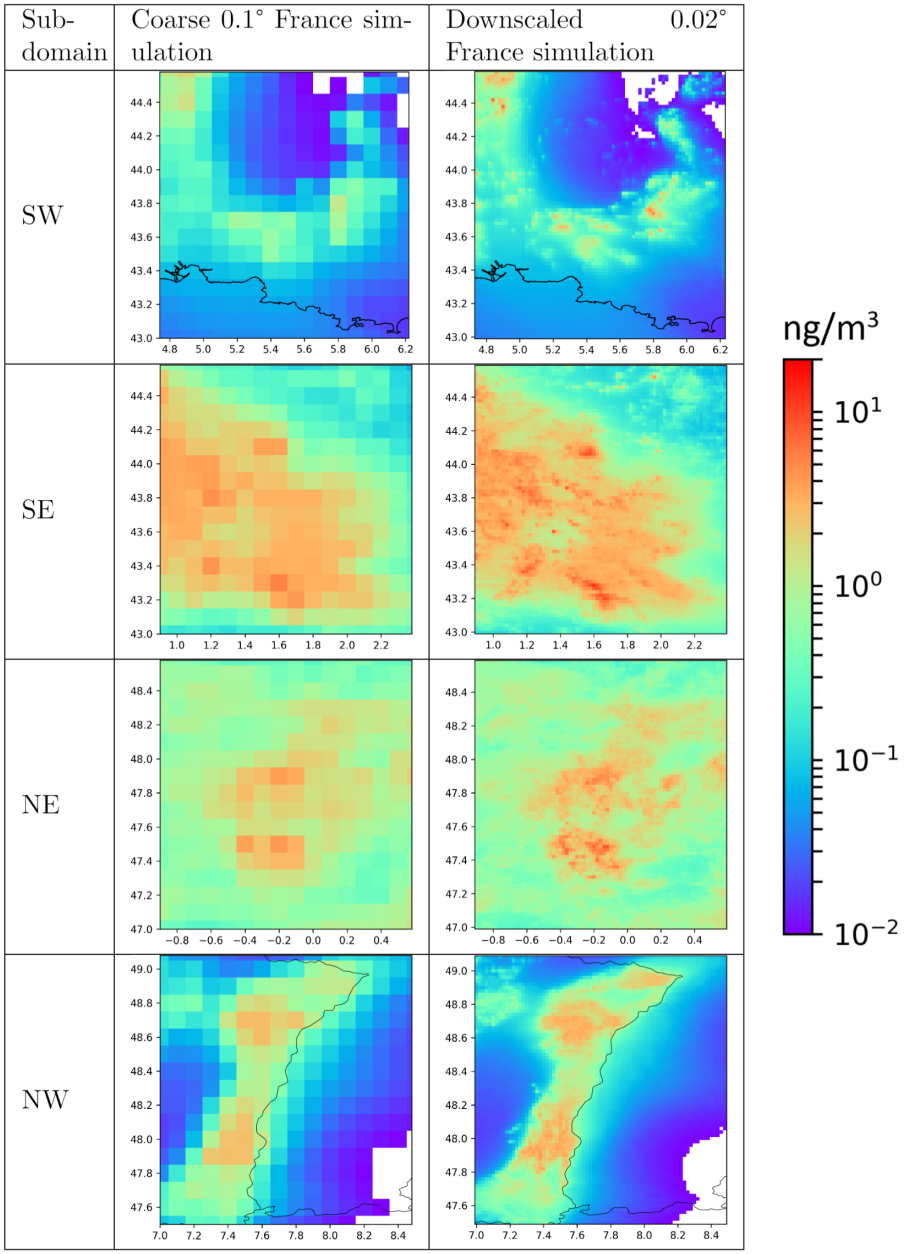


Figure 3: Maps of coarse simulated concentrations of S-metolachor at the 0.1° resolution and of the downscaled concentrations at 0.02° (in ng/m^3). $N_{lev,sub}$ is chosen equal to N_{lev}.

3.3. Computational time

The potential increase in computational time due to the downscaling approach has to be assessed. As CPU time can be an important limitation for the use of CTM, it is important to diagnose the impact of the downscaling method on CPU time. Table 1 shows the CPU time increase under different configurations (different downscaled resolution and different value of $N_{lev,sub}$).

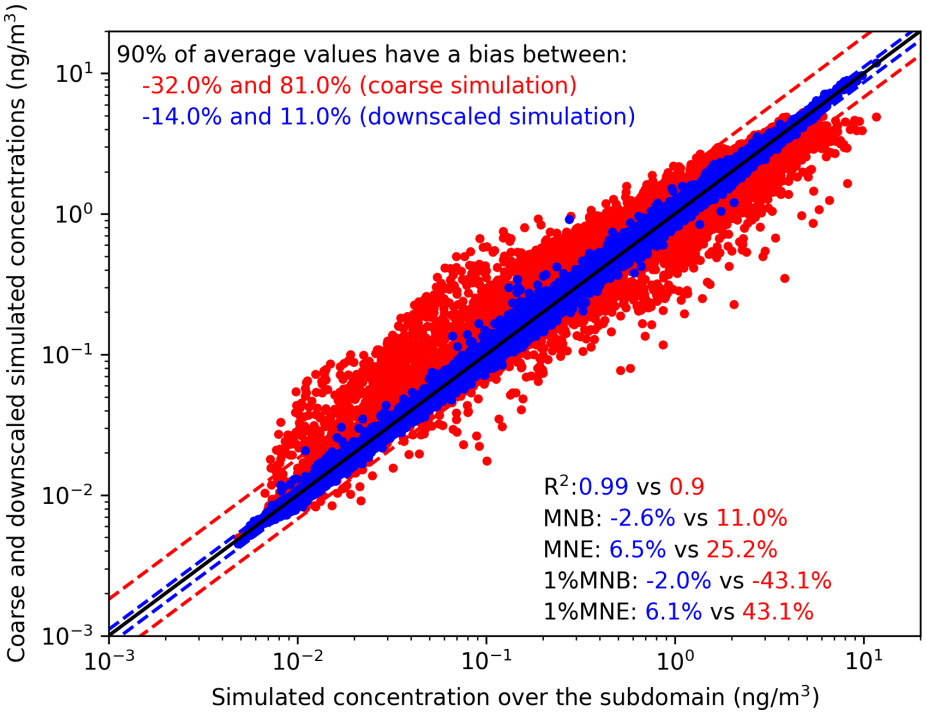


Figure 4: Distributions of the concentrations (in ng/m^3) on the coarse domain (0.1° in red) and of the downscaled concentrations (0.02° in blue) as a function of the concentrations simulated on the 4 subdomains. The dashed lines provide the 90% interval including 90% of the simulations values with the lowest bias.

Downscaling the 0.1° results to a 0.02° resolution leads to an increase of CPU time of only 7% while launching CHIMERE directly at the a resolution of 0.02° would result in a CPU time increase close to a factor 125 (a factor 5x5 to decrease the resolution of the horizontal grid combined to a factor 5 on temporal resolution in order to respect the Courant-Friedrich-Levy condition). The CPU time needed to run the downscaling approach is also much lower than the CPU time needed to perform simulations over the four nested sub-domains (increase of CPU time by a factor 3.79).

While the CPU time increase is modest for a downscaling to a 0.02° resolution, it may lead to an important increase of CPU time to downscale to a 0.004° resolution (increase by a factor 9.16 with $N_{lev,sub}$=9). It should be noted that downscaling several pesticide at the same time may result in even greater CPU time. One possible way to limit the CPU time is to limit the number of vertical layer on the subgrid $N_{lev,sub}$. According to Table B1, using $N_{lev,sub}$=3 (3 layers covering an altitude around 250 m) may consist in a good compromise as the performance (MNE=7.9%, 1%MNE=6.6%) is similar to the performance with $N_{lev,sub}$=9 (MNE=6.5%, 1%MNE=6.1%).

Configuration	Relative computation time
France simulation at 0.1°	1
France simulation at 0.02°	125
France simulation at 0.1° + simulation on the four nested sub-domains	3.79
France simulation at 0.1° downscaled to 0.02° ($N_{lev,sub}$=1)	1.03
France simulation at 0.1° downscaled to 0.02° ($N_{lev,sub}$=9)	1.07
France simulation at 0.1° downscaled to 0.004° ($N_{lev,sub}$=1)	1.63
France simulation at 0.1° downscaled to 0.004° ($N_{lev,sub}$=9)	9.16

Table 1: Relative computational time compared to the France simulation at a resolution of 0.1°. The number corresponds to a downscaling method applied only on a single pesticide (S-metolachlor).

3.4. Comparison with measurements

Atmospheric measurement data of pesticides are scarce. However, since 2011, the French Regional Networks for Air Quality compiled the atmospheric concentrations of pesticides in the PhytAtmo database. It aggregates about 7,000 samples at 176 sites throughout mainland France and overseas for 321 active substances sought (AtmoFrance, 2019). S-metolachlor was measured at 24 stations in 2014, and at 91 stations between 2015 and 2020. However, the temporal coverage of these measurements are often partial and occur generally during a few days over the month.

According to this database, while the stations are not necessarily located near hotspots, concentrations of S-metolachlor can exceed 10 ng/m^3 in coherence with our simulation results showing hotspots above 10 ng/m^3. Since 2014,

concentrations above 10 ng/m^3 and up to 51 ng/m^3 where detected 12 times at 3 different stations (for around 32 000 samples above the detection limit).

High S-metolachlor concentrations (around 14 ng/m^3) were measured at the Ohnenheim station. The simulated concentrations at this station is strongly underestimated with both the downscaled simulation at 0.004° (concentration around 0.35 ng/m^3) and the coarse simulation (concentration around 0.26 ng/m^3). Difficulties to reproduce exactly the spatiotemporal distribution of application may explain the differences between the model and measurements.

With the exclusion of this station, a better spatial correlation was obtained with the coarse simulation (0.75) than with the downscaled simulation (0.65). However, these differences in the correlation is probably not statiscally significant. On the 16 stations with measurements during the period of simulation, results were improved for 5 stations (relative error decreased by 16% to 67%) and degraded for 7 stations (relative error increased by 11% to 38%). Due to low number of stations and the poor temporal coverage, it is therefore difficult to evaluate the gain of performance due to the downscaling approach. Moreover, errors due to the spatiotemporal distribution of applications in the vicinity of the station probably increases with the resolution. Valari and Menut (2008) has indeed shown that model results do not improve monotonously with resolution and that after a certain point discrepancies with measurements become larger due to insufficient precision in input data.

4. Conclusions

A downscaling method have been developed and applied on the simulation of high resolution concentrations of S-metolachlor. The developed downscaling method performs reasonably well (MNE around 7.9%) and can be used to simulate the hotspots of pesticide concentrations. The method developed in this study is an important step toward high-resolution CTM simulations and the use of CTM simulation for epidemiological studies on pesticides.

The current methodology does not account for spray-drift droplets as the lifetime of these droplets can be considered too low compared to the resolution of the model. One possible solution could be to implement plume-in-grid approaches (Karamchandani et al., 2006), in which a subgrid-scale representation of plumes is embedded into CTMs. Other models aiming at representing the local transport of spray-drift in the vicinity of the crops could also be used (Raupach et al., 2001; Tsai et al., 2005; Zhang et al., 2018).

Acknowledgements

This work has been carried out thanks to the support of the COPP'R project funded by the PRIMEQUAL – AGRIQA "Agriculture et qualité de l'air" and the ECOPHYTO programs. We would like to thank all the participants of the project for the useful discussions: Sophie Vannier (Vaucluse Chamber of Agriculture). We thank the other member of BNVD-S Team for providing the database and for the necessary discussions: Rémy Ballot, Corentin Barbu, Eric Cahuzac (INRAE), Christophe Lescot, Laure Malherbe (INERIS). We especially thank Eric Cahuzac who lead the BNVD-S project at the start of our work on the modeling of pesticides. Simulations were performed using the TGCC-CCRT supercomputers under the GENCI time allocation gen7485.

References

AtmoFrance, 2019. Base de donnée de surveillance de pesticides dans l'air par les aasqa à partir de 2002. https://atmo-france.org/wp-content/uploads/2021/02/PhytAtmo-donnees-pesticides_2002_2019.xlsx. Accessed: 2021-03-24.

Bessagnet, B., Pisoni, E., de Meij, A., Létinois, L., Thunis, P., 2023. A simple and fast method to downscale chemistry transport model output fields from the regional to the urban/district scale. Environ. Model Softw. 164, 105692. doi:10.1016/j.envsoft.2023.105692.

Cognez, N., Warembourg, C., Zaros, C., Metten, M., Bouvier, G., Garlantézec, R., Charles, M., Béranger, R., Chevrier, C., 2019. Residential sources of pesticide exposure during pregnancy and the risks of hypospadias and cryptorchidism: the french elfe birth cohort. Occup. Environ. Med. 76, 672–679. doi:10.1136/oemed-2019-105801.

Coscollà, C., López, A., Yahyaoui, A., Colin, P., Robin, C., Poinsignon, Q., Yusà, V., 2017. Human exposure and risk assessment to airborne pesticides in a rural french community. Sci. Total Environ. 584-585, 856 – 868. doi:10.1016/j.scitotenv.2017.01.132.

Couvidat, F., Bedos, C., Gagnaire, N., Carra, M., Ruelle, B., Martin, P., Poméon, T., Alletto, L., Armengaud, A., Quivet, E., 2022. 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. Journal of Hazardous Materials 424, 127497. doi:10.1016/j.jhazmat.2021.127497.

Couvidat, F., Bessagnet, B., 2021. Role of ecosystem-atmosphere exchanges of semi-volatile organic compounds in organic aerosol formation. Atmos. Environ. , 118541doi:10.1016/j.atmosenv.2021.118541.

Couvidat, F., Sartelet, K., 2015. The secondary organic aerosol processor (SOAP v1.0) model: a unified model with different ranges of complexity based on the molecular surrogate approach. Geosci. Model Dev. 8, 1111–1138. doi:10.5194/gmd-8-1111-2015.

Denby, B.R., Gauss, M., Wind, P., Mu, Q., Grøtting Wærsted, E., Fagerli, H., Valdebenito, A., Klein, H., 2020. Description of the uemep_v5 downscaling approach for the emep msc-w chemistry transport model. Geosci. Model Dev. 13, 6303–6323. doi:10.5194/gmd-13-6303-2020.

Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., Pochet, G., Savelli, J.L., Wortham, H., Quivet, E., 2018. Spatial and temporal distribution of current-use pesticides in ambient air of provence-alpes-côte-d'azur region and corsica, france. Atmos. Environ. 192, 241 – 256. doi:10.1016/j.atmosenv.2018.08.054.

Hooyberghs, H., De Craemer, S., Lefebvre, W., Vranckx, S., Maiheu, B., Trimpeneers, E., Vanpoucke, C., Janssen, S., Meysman, F., Fierens, F., 2022. Validation and optimization of the atmo-street air quality model chain by

means of a large-scale citizen-science dataset. Atmos. Environ. 272, 118946. doi:10.1016/j.atmosenv.2022.118946.

Hough, I., Sarafian, R., Shtein, A., Zhou, B., Lepeule, J., Kloog, I., 2021. Gaussian markov random fields improve ensemble predictions of daily 1 km pm2.5 and pm10 across france. Atmos. Environ. 264, 118693. doi:https://doi.org/10.1016/j.atmosenv.2021.118693.

Karamchandani, P., Vijayaraghavan, K., Chen, S.Y., Seigneur, C., Edgerton, E.S., 2006. Plume-in-grid modeling for particulate matter. Atmos. Environ. 40, 7280–7297. doi:10.1016/j.atmosenv.2006.06.033.

Letinois, L., 2015. Méthodologie de répartition spatiale de la population. Technical Report. LCSQA, Laboratoire central de surveillance de la qualité de l'air, France.

Lichiheb, N., Personne, E., Bedos, C., Van den Berg, F., Barriuso, E., 2016. Implementation of the effects of physicochemical properties on the foliar penetration of pesticides and its potential for estimating pesticide volatilization from plants. Sci. Total Environ. 550, 1022–1031. doi:10.1016/j.scitotenv.2016.01.058.

Mailler, S., Menut, L., Khvorostyanov, D., Valari, M., Couvidat, F., Siour, G., Turquety, S., Briant, R., Tuccella, P., Bessagnet, B., Colette, A., Létinois, L., Markakis, K., Meleux, F., 2017. CHIMERE-2017: from urban to hemispheric chemistry-transport modeling. Geosci. Model Dev. 10, 2397–2423. doi:10.5194/gmd-10-2397-2017.

Martin, P., Ramalanjaona, L., Truche, C., Ballot, R., Carozzi, M., Pomeon, T., 2023. Modelling the spatialisation of pesticide sales to monitor environmental policies in france. Journal of Cleaner Production 403, 136880. doi:10.1016/j.jclepro.2023.136880.

Moussaoui, Y., Tuduri, L., Kerchich, Y., Meklati, B., Eppe, G., 2012. Atmospheric concentrations of pcdd/fs, dl-pcbs and some pesticides in northern algeria using passive air sampling. Chemosphere 88, 270 – 277. doi:10.1016/j.chemosphere.2012.02.025.

Raupach, M., Briggs, P., Ahmad, N., Edge, V., 2001. Endosulfan transport: Ii. modeling airborne dispersal and deposition by spray and vapor. J. Environ. Qual. 30, 729–740. doi:10.2134/jeq2001.303729x.

Shen, Y., de Hoogh, K., Schmitz, O., Clinton, N., Tuxen-Bettman, K., Brandt, J., Christensen, J.H., Frohn, L.M., Geels, C., Karssenberg, D., Vermeulen, R., Hoek, G., 2022. Europe-wide air pollution modeling from 2000 to 2019 using geographically weighted regression. Environment International 168, 107485. doi:10.1016/j.envint.2022.107485.

Teysseire, R., Manangama, G., Baldi, I., Carles, C., Brochard, P., Bedos, C., Delva, F., 2020. Assessment of residential exposures to agricultural pesticides: A scoping review. PLOS ONE 15, 1–19. doi:10.1371/journal.pone.0232258.

Tsai, M.Y., Elgethun, K., Ramaprasad, J., Yost, M.G., Felsot, A.S., Hebert, V.R., Fenske, R.A., 2005. The washington aerial spray drift study: Modeling pesticide spray drift deposition from an aerial application. Atmos. Environ. 39, 6194 – 6203. doi:10.1016/j.atmosenv.2005.07.011.

Valari, M., Menut, L., 2008. Does an increase in air quality models' resolution bring surface ozone concentrations closer to reality? J. Atmos. Ocean. Technol. 25, 1955 – 1968. doi:10.1175/2008JTECHA1123.1.

Vestreng, V., 2003. Review and revision. Emission data reported to CLRTAP Tech. Rep., EMEP MSW-W. Technical Report. Norwegian Meteorological Institute, Oslo, Norway. URL: https://emep.int/publ/reports/2003/mscw_note_1_2003.pdf.

Zhang, X., Luo, Y., Goh, K.S., 2018. Modeling spray drift and runoff-related inputs of pesticides to receiving water. Environ. Pollut. 234, 48 – 58. doi:10.1016/j.envpol.2017.11.032.