Adaptation of a resistive model to pesticide volatilization from plants at the field scale: Comparison with a dataset

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HIGHLIGHTS

- We adapt a resistive model to predict pesticide volatilization from plants.
- We integrate in the model competing processes occurring at the leaf surface.
- The model satisfactorily simulates the energy budget and leaf temperature.
- The volatilization flux of chlorothalonil is well predicted by the model.
- High sensitivity of the model was shown to temperature and competing processes.

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ABSTRACT

Volatilization from plants is known to greatly contribute to pesticide emission into the atmosphere. Modeling would allow estimating this contribution, but few models are actually available because of our poor understanding of processes occurring at the leaf surface, competing with volatilization, and also because available datasets for validating models are lacking. The SURFATM-Pesticides model was developed to predict pesticide volatilization from plants. It is based on the concept of resistances and takes into account two processes competing with volatilization (leaf penetration and photodegradation). Model is here presented and simulated results are compared with the experimental dataset obtained at the field scale for two fungicides applied on wheat, fenpropidin and chlorothalonil. These fungicides were chosen because they are largely used, as well as because of their differentiated vapor pressures. The model simulates the energy balance and surface temperature which are in good agreement with the experimental data, using the climatic variables as inputs. The model also satisfactorily simulates the volatilization fluxes of chlorothalonil. In fact, by integrating estimated rate coefficients of leaf penetration and photodegradation for chlorothalonil giving in the literature, the volatilization fluxes were estimated to be 24.8 ng m^{-2} s^{-1} compared to 23.6 ng m^{-2} s^{-1} measured by the aerodynamic profile method during the first hours after application. At six days, the cumulated volatilization fluxes were estimated by the model to be 19 g ha^{-1} compared to 17.5 g ha^{-1} measured by the inverse modeling approach. However, due to the lack of data to estimate processes competing with volatilization for fenpropidin, the volatilization of this compound is still not well modeled yet. Thus the model confirms that processes competing with volatilization represent an important factor affecting pesticide volatilization from plants.

1. Introduction

The occurrence of pesticides in the atmosphere is increasingly under investigation due to their potential impact on human health (Viel and Richardson, 1993) and ecosystems (Führ et al., 1998; Bakker et al., 1999). Experimental studies have shown that

volatilization may represent a major emission pathway for pesticides applied to soil or plants, accounting for up to several 10% of the application dose (Bedos et al., 2002). Moreover, this transfer pathway may take a few days to several weeks (Scholtz and Bidleman, 2007). The main factors affecting emission of pesticides after application are their physicochemical properties and environmental conditions (Stork et al., 1994; Van den Berg et al., 1999).

The volatilization from plants is higher and faster than volatilization from the soil (Bedos et al., 2002). For example, Rüdel (1997) has demonstrated that the volatilization of parathion-methyl, endosulfan, and fenpropimorph from plants is higher by a factor

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of 5–13 than volatilization from the soil. However the estimation of this transfer pathway remains problematic, first of all because of our poor understanding of processes occurring at the leaf surface (Leistra and Van den Berg, 2007) and secondly due to the lack of experimental data on the individual processes and also on the overall pesticide volatilization from the plants.

The complex interactions between agronomic and environmental conditions make necessary the use of modeling to study the volatilization of pesticides from plants into the atmosphere, requiring the understanding of complex processes involving those that occur in the atmosphere as well as those that occur on the leaf surface. A mechanistic description of pesticide volatilization from plants must involve: (i) a description of pollutant transfer in turbulent and laminar flow inside the canopy using e.g. the transfer resistances concept (Wolters et al., 2003), (ii) the integration of an energy budget model that makes possible to confirm the reliability of the resistive scheme and simulate surface temperature for which volatilization is very sensitive (Scholtz et al., 2002a), and (iii) the description of competing processes at the leaf surface required to estimate the fraction of pesticide residues on leaves available for volatilization (Leistra and Wolters, 2004).

With previous modeling efforts the combining of these key points was not possible, except for the PEM model (Scholtz et al., 2002a,b). This model simulates water and heat fluxes in the air, as well as pesticide volatilization from the canopy using the resistive scheme. It takes into account competing processes occurring at the leaf surface such as penetration into the waxy cuticle, degradation due to chemical and photo-chemical reactions, and wash-off. Moreover, it has the option to distinguish the partitioning of pesticide within a wet or dry canopy. Hence, it accounts for four compartments around the leaf surface: (i) an air compartment, (ii) a water film, (iii) an active ingredient layer, and (iv) the leaf cuticle. However, such a detailed model required many input data not always available. Moreover, it could not be validated with a data set comprising volatilization rates measured from plants due to the lack of datasets at that time.

Concerning the other existing models which describe pesticide volatilization from plants, we can mention the PLANTX model (Trapp et al., 1994) and the Cemos-Plant model (Trapp and Matthies, 1995). These models study the uptake of chemical compounds into plants and describe their volatilization from leaves using a transfer resistance concept and integrating a partition coefficient between leaves and air. They take into account the metabolism processes at the leaf surface using elimination rates which are difficult to measure. However, they do not integrate an energy budget model. Another model is PEARL (Leistra and Wolters, 2004) which is based on the concept of diffusion through a laminar air-boundary layer to calculate pesticide volatilization from plants. This model has the option to distinguish between two pesticide deposit fractions in the canopy: a fraction of the spray liquid which is well-exposed to volatilization, leaf penetration and photo-degradation and a poorly-exposed one. Moreover, processes competing with volatilization, such as penetration into plants, photodegradation and wash-off, are estimated by the model. However, PEARL does not simulate water vapor fluxes and surface temperature. A new version of PEARL is under development which includes the concept based on transfer resistances (Wolters et al., 2003). Indeed few models exist but no simplified model which comprises a resistive approach adapted for pesticides, an energy budget at the leaf and soil level and a description of processes competing with the volatilization is available.

SURFATM is a biophysical model described by Personne et al. (2009) based on the concept of resistances. It consists of two coupled models: (i) an energy budget model (Choudhury and Monteith, 1988) and (ii) a pollutant exchange model (Nemitz
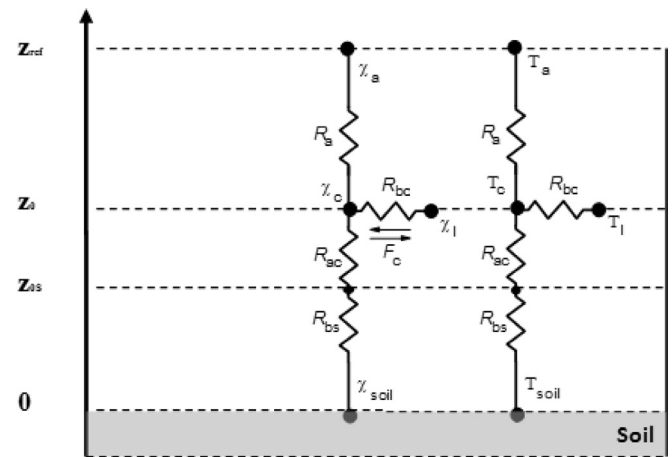
Fig. 1. Resistive scheme for Pesticides and heat exchange models. Where z is the height above ground; R_a, R_{ac}, R_{bc}, and R_{bs} are respectively aerodynamic resistance above the canopy, aerodynamic resistance inside the canopy, canopy boundary layer resistance, and soil boundary layer resistance; F_c is the pesticide volatilization flux from the canopy surface; χ_a, χ_c, χ_l, and χ_{soil} refer to pesticide concentration in the air, pesticide concentration in the canopy, pesticide concentration just above the leaves, and pesticide concentration in the soil; T_a, T_c, T_l, and T_{soil} refer to air temperature, canopy temperature, leaf temperature, and soil temperature; z_{ref}, z_0 and z_{os} refer to reference height, canopy roughness height and soil roughness height respectively.

et al., 2000), which distinguishes the soil and plant exchange processes. The pollutant exchange is directly coupled to the energy balance via the soil and leaf surface temperatures. This model has achieved satisfactory results for the ammonia exchanges (Personne et al., 2009) and ozone exchanges (Stella et al., 2011).

The aim of this work is to adapt the SURFATM model to pesticides in order to develop a simplified model for the volatilization of pesticides from plants, which comprises the three key points presented above. We focus in this study on describing pesticide volatilization from plants, the contribution of soil will be implemented in a further step. SURFATM-Pesticides describes the process of volatilization in a mechanistic way but processes occurring at the leaf surface and competing with volatilization are described empirically. As a first step, we do not take into account the rainfall wash-off process. In this study, SURFATM-Pesticides is evaluated with a data set comprising: (i) the energy budget components as well as leaf temperature, and (ii) the volatilization rates measured at the field scale of two fungicides applied on wheat which are fenpropidin and chlorothalonil (Bedos et al., 2010). This test involved a comparison of modeled fluxes with measured ones. Then, a sensitivity analysis on selected parameters was carried out. In addition, volatilization, leaf penetration, photodegradation and pesticide residues on leaves predicted by the model were expressed as a percentage of the residue measured on the leaves just after the application to study the evolution of each fraction as a function of time and to evaluate the relative contribution of competing processes for the two pesticides studied.

2. Material and methods

2.1. SURFATM-Pesticides description

The SURFATM-Pesticides model is a mechanistic model elaborated upon the model described in Personne et al. (2009). It includes one vegetation layer and one soil compartment. The model is based on the transfer resistances concept (aerodynamic, boundary layer and soil resistances) to simulate heat, water vapor and chemical compound fluxes between the biogenic surfaces and