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Development of methods to assess the release of pheromones in the air from dispenser products for improvement of biocontrol solutions

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Abstract: Facing the multiple consequences of the use of pesticides, the international objective is to reduce their use in agriculture until their suppression in the future to fight insect pests. M2i develops different types of products (sprays and breads) based on sex pheromones synthesized in laboratory and which are then introduced in crops to create a mating disruption and reduce the insect population. This is an alternative and cost-effective solution in integrated biological control for crop protection. Some drawbacks remain like the diffusion of active molecules in the air towards the target is not evaluated in the field due to the lack of sampling and analysis methods suitable for low levels of concentrations to be measured (a few ng/m³) (Gavara et al., 2020). To the aim, a model product developed by M2i called “Gamme Press” containing a model pheromone, the lauryl acetate, was tested in a closed emission chamber under various conditions to assess the parameters describing the release rate of pheromone from the formulation and transpose it to the field. Key parameters are the diffusion coefficient in the product (D_m), the initial emittable concentration in the product (C_0), the product/air partition constant (K) and the mass transfer coefficient (h_m) were determined by using two model variable volume loading (VVL) method and the C-history model (Xiong et al., 2011 a and 2011 b). The low value of C_0/C_{total} (total concentration of lauryl acetate in the formulation) indicates that the parameters are determined under experimental boundary conditions, which leads to switching to open chamber tests, more representative of field conditions (greenhouse). Therefore, the adjustment of a dynamic model to greenhouse tests is considered to determine the specific emission rate of the formulation.

Key words: biocontrol, pheromones, air analysis, release kinetics, emission modelling

Introduction

Among the various control strategies used in biocontrol, trapping or mating disruption are tools that continue to prove their worth. Indeed, insects can communicate with each other through chemical signals detected by their sensory system. Pheromones are volatile organic compounds (VOCs) or semi-volatile organic compounds (SVOCs) with long carbon chains and one or more chemical functions (e.g., alcohol, carbonyl, ester). To diffuse these active compounds in the air, different systems (devices) have been developed, notably based on solid or liquid matrices (Desauziers et al., 2022). At present, the evaluation of the effectiveness of pheromone-based products on the target insect pest population is mainly studied by monitoring the damage caused

to the crops (monitoring). To ensure the best efficiency of the various treatments, it is important to determine the dose of active substance to be introduced in the fields. However, various drawbacks remain regarding current dispensers such as, the difficulty in maintaining a sufficient release rate over a prolonged period (several days) and generating concentrations around the dispenser that are detectable by the insect. Due to the lack of suitable sampling and analytical methods due to the very low levels of concentrations to be measured in air (a few ng/m^3), the diffusion of active molecules in the air to the target is not characterized (Gavara et al., 2020). Thus, there is a lack of information about the area of action and the persistence over time of pheromones at a concentration sufficient to maintain effectiveness. Modelling the release phenomena and dispersion of pheromones in field is therefore essential. For this, the experimental devices that reproduce the kinetics of pheromone diffusion in the laboratory should be developed. The release process of the pheromones from formulation is characterized by several parameters: the diffusion coefficient in the product (D_m), the initial emittable concentration in the product (C_0), the formulation/air partition constant (K) and the mass transfer coefficient (h_m). The determination of all parameters allows to describe the emission processes of a semi-volatile compound from a solid to the air in order to optimize a formulation and to parameterize a model. To determine them, the monitoring of the release process can be studied and performed in closed emission chamber. Compared to other determination methods described in the literature, the approach in an environmentally controlled emission test chamber appears to be the most accurate and appropriate method for estimating the release rate of dispensers (Zhu et al., 2015). This method allows to obtain all parameters simultaneously through experimental data, these parameters are then included in predictive models, which allows to easily study the emission of SCOV and the associated characteristic parameters, these techniques are applicable to various types of formulation. Indeed, the main obstacle to the development of predictive models to realistically simulate the emission of compounds in ambient air is the availability of experimental data to obtain the parameters involved in the equations. The emission chamber study offers the possibility of obtaining accurate experimental data in a controlled environment that leads to the reliability of the parameters determined using the predictive models (Wang et al., 2022). Indeed, the parameters can be determined by using the combination of two different approaches, the VVL method and the extended C-history method. This approach was therefore developed in the laboratory, firstly under closed conditions (Figure 1) and then under dynamic conditions (air exchange rate/h) in order to transpose the model in the field conditions and estimate a specific release rate for the studied formulation.

Materials and methods

The pheromone studied (lauryl acetate) is a model pheromone microencapsulated in a solid emulsion. The release process from the formulation to the air was performed in a closed emission chamber (3.36 l) with controlled humidity and temperature conditions. The gaseous concentration of pheromone was monitored in the chamber using a solid phase microextraction (SPME) sampling method and analysis by GC/MS-FID (Ghislain et al., 2017). To determine the emission parameters, variable volume loading (VVL) method was used and allow to determine C_0 and K applying a steady-state mass balance for three sets of experiments with different loading volumes arranged in pillboxes. Loading rate should be chosen to be within a range of linearity to maintain the performance of the method (Wang et al., 2022). Then, these parameters are included in the extended C-history model to determine h_m and formulation D_m (Xiong et al., 2011 a and 2011 b).

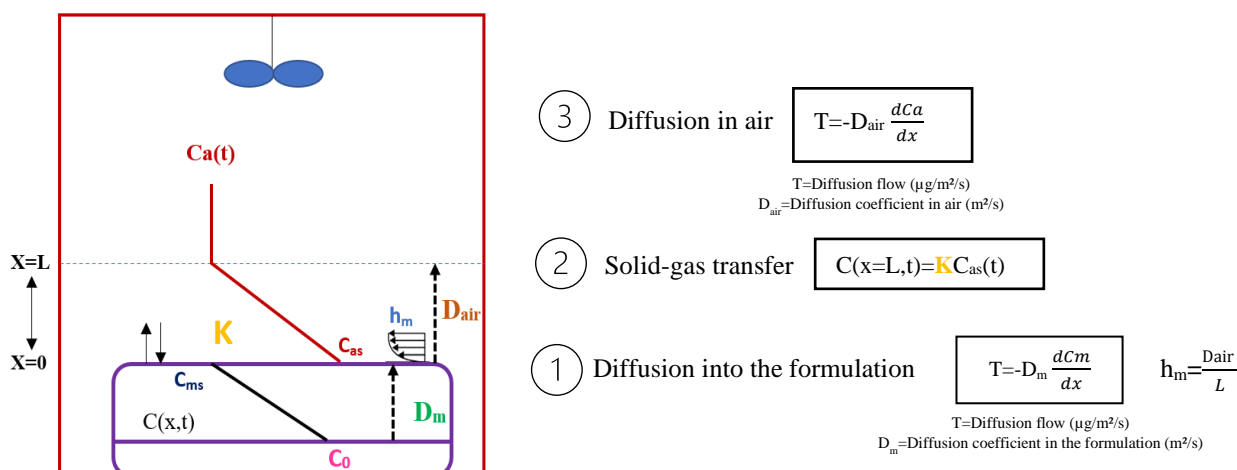


Figure 1. Diffusion processes in a closed emission chamber.

Results and discussion

The kinetics modelled with the parameters determined by the VVL method and the extended C-history model (green line) fits perfectly with the experimental data (blue points) obtained with the closed system chamber. The value of D_m in the formulation is $1.10 \times 10^{-9} \text{ m}^2/\text{s}$ and the value of K obtained is 1.3×10^4 (dimensionless). This parameter is described as the ratio of the concentration of lauryl acetate in the formulation to that in air under equilibrium conditions ($C_{\text{formulation}}/C_{\text{air}}$). K reflects the transfer capacity of the compound from the formulation to air. The higher K is, the greater is the affinity of the compound for the formulation. The content lauryl acetate in the formulation is 9.13 % by mass, which is equivalent to a total concentration in the formulation, noted C_{total} , of $84909 \text{ g}/\text{m}^3$. Compared to C_{total} , the concentration in air of the compound is very low and gives a high K value. The value of K indicates that the amount of compound transferred to the gas phase is less than 1 % of the total amount of compound in the formulation when the steady state is reached. Thus, the concentration of lauryl acetate in the formulation can be considered constant throughout the test, which is one of the limits of application of the VVL method in our case. Thus, in the conditions of closed emission chamber, the released fraction in air appears as mainly dependent on the partition coefficient K , which allows to guide towards a type of emission model suitable for the field.

Other parameters are available following the use of the extended C-history model such as Bim/K which is described as the ratio between the Biot number and the partition coefficient. This ratio is dimensionless and compares the internal mass transfer resistance and the external mass transfer resistance. One of them shows that the release of the pheromone is explained by the external transfer (into the air) under static conditions (closed emission chamber). This allowed the development of a simplified model without considering the diffusion in the formulation that matches the experimental data (orange line in Figure 2). It should be noted that all parameters are dependent under the test conditions. It is therefore possible to consider a system without internal diffusion which may explain that the extended C-history model with and without any account being taken of the diffusion in the formulation provides results close to experimental data (Figure 2). This result indicates- that the release could be governed by the partition

coefficient K in dynamic conditions. A dynamic model considering only the partition coefficient K is developed to reproduce the field data.

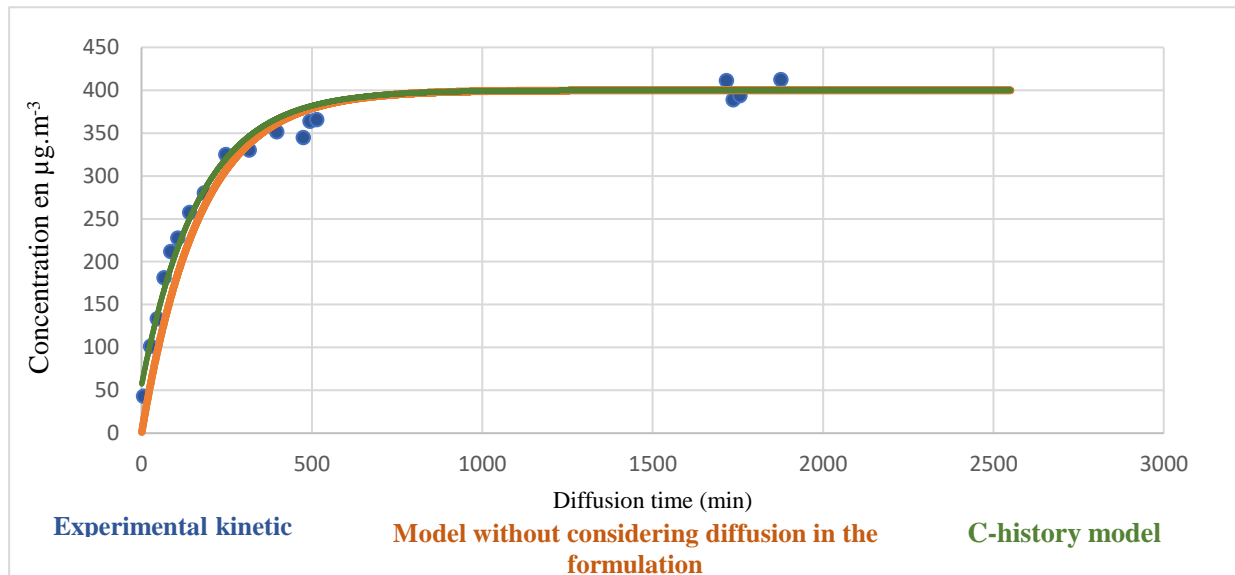


Figure 2. Comparison of C-history model, experimental values, and model without considering the diffusion in the formulation (2×0.25 g).

The release of a pheromone from formulation evaluated in the laboratory allows for a better understanding of the transfer processes involved and better guidance for pausing the diffusers in the field by determining the concentrations that prevail in the air after pausing a diffuser.

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