Development of mathematical models for the uptake of agrichemicals through plant leaves; influence of adjuvants on plant and product interactions

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Note. Many academics and research students were involved in this project; a full list of contributors will appear in the full technical paper.

Plant Protection Chemistry New Zealand (PPCnz) is a small company that undertakes research on improving the efficacy of agrichemical formulations. The four key components of that research involve: deposition of spray droplets on leaf surfaces; adhesion and retention of the spray droplets on leaf surfaces; uptake of active ingredient at the leaf surface; and translocation of the active ingredient throughout the plant. The company asked MISG to consider the third of these components (uptake of active ingredient) from a mathematical modelling point of view. The aim of the project was to develop mathematical models for the diffusion of agrichemicals through the surface of a plant leaf, with particular reference to the complex roles of the leaf surface, the surfactant in the formulation, the spreading and/or evaporation of the droplet. In the usual way, the request was for the mathematical models to be physically realistic, but not burdened by a large number of parameters that are difficult to measure in practice.

Research into the uptake of an active ingredient in a leaf is vitally important as diffusion through the leaf surface is a critical component of a complex system, but also because many of the mechanisms involved are still not well understood. Further, it is vital to consider the uptake processes in the broader context of spray formulation efficacy, as the key chemical and fluid properties of agrichemical formulations from a deposition and retention perspective affect the dominant chemistry and physics of the diffusion of the active ingredient at the leaf surface. In addition, the desirable mode of translocation affects the optimal outcome from an uptake perspective. These related issues act to highlight the possible dominant factors at play, such as the manner in which surfactant in the agrichemical formulation can interact with the active ingredient as it is transported through the leaf surface, or whether the time-scale at which droplet spreading or evaporation occurs is significant.

The above considerations led the team of researchers to divide up into smaller groups, each focusing on a different aspect of the broader problem. The goal of one group was to revisit a compartment-type mathematical model that was originally proposed by Dr Norbert Satchivi (of Dow AgroSciences) and coworkers, and published in a series of papers between 2000 and 2007. This model is complex. It is presented as a dynamic, nonlinear simulation model integrating xenobiotic physicochemical parameters with plant anatomical, physiological and biochemical characteristics. The model describes the transport of a xenobiotic (such as the active ingredient) within a whole plant and includes foliar uptake from a treated leaf, accounting for transport through the cuticular membrane, the leaf apoplast and symplast and wax layer retention in the treated leaf. Metabolic degradation of a xenobiotic within the treated leaf, leaves above and below the treated leaf and within the roots is also accounted for. In addition, xylem and phloem transport within the plant leaves and stems (in the treated leaf and above and below the treated leaf) and within the roots is included. Water translocation is also taken into account. Further comments on this approach are included below.

After a number of discussions between the industry representative and the mathematicians, it was agreed that an important component that required further attention was the transport of active ingredient into and possibly out of the leaf cuticle. The cuticle is the thin outer protective layer of the leaf surface, characterised by its waxy nature. It covers the epidermis, which has a high water content. Below the epidermis is the dermis, which contains the vascular tissue. For certain active ingredients, the ideal outcome is for much of the chemical to enter and then remain in the cuticle, so that it can be consumed by insects, for example. On the other hand, if the objective is for the active ingredient to be translocated to the body of the plant (either eradicating weeds or to act as a fertiliser, say), the goal is for the chemical to enter and then pass through the cuticle. Given the lipophilicity of the waxy cuticle, it was recognised that mathematical models needed to be developed for diffusion of an active ingredient through the cuticle, with extensions that take into account the manner in which surfactants in the formulation act to transport the active ingredient in question. Comments on these diffusion-type models are below.

Compartment modelling of xenobiotic transport in plants. Here we summarise the analysis and implementation of a compartment model introduced by Dr Norbert Satchivi and co-workers in a series of publications in the 2000s. The complexity of the model, in terms of the number of physiological and chemical processes accounted for, suggests that it could form the basis of a useful simulation tool for the industry partner of this project.

Reviewing the Satchivi papers revealed a convoluted formulation of the model equations with an often-confusing description of the functions involved (made less clear by the presence of numerous typographical errors and inconsistencies in the function definitions). Moreover, the papers do not present a clear and complete description of the parameter values used to obtain the simulation results presented.

With reference to a compartment overview diagram provided in the first Satchivi paper, we were able to rederive the Satchivi model equations as a consistent system of ordinary differential equations (with time as the independent variable) for the concentration of a xenobiotic in each of the 19 spatially homogeneous and coupled compartments of the plant considered by Satchivi and co-workers. The functional forms of the source and sink terms of these coupled equations were also rederived by applying physicality constraints to clarify inconsistencies in these functions as presented in the literature. In addition, all of the parameters of the model have been identified and values for these have been sourced from the Satchivi papers where possible and from the broader literature otherwise.

A MATLAB code has been produced that implements the model equations and plots the concentration time series of xeniobiotic in each compartment. A key realisation in writing this code was that the solution must be constrained from being negative in any compartment at any time as there is no mechanism in the naive model formulation that prevents this from occurring.

The code can now be used to investigate xenobiotic transport within given plant species. It is intended that further work on this simulation model will include a sensitivity analysis of each of the parameters and validation of the model outputs with data provided in the Satchivi papers and/or by the industry partner. Some parameters may need to be determined for a given species, and it is hopeful that this experimentation could be carried out in the laboratories of PPCNZ.

Simple diffusion models through cuticle and epidermis. By stripping back all the complexity involved in foliar intake, and as a first step towards taking account the spatial geometry of the cuticle, one group of researchers concentrated on developing a simple model that assumes the active ingredient is transported through both the cuticle and epidermis via simple diffusion.

The key assumptions of the model is as follows:

- The domain of interest is made up of two adjacent regions, the cuticle and the epidermis.
- The diffusion coefficient, which is different in both regions, depends on whether the active ingredient is lipophilic or hydrophilic.
- At the lower boundary of the epidermis, it is assumed that the active ingredient passes into the vascular system at a rate that depends on the concentration itself.
- At the cuticle surface, a variety of boundary conditions were considered, taking into account the complex nature of a spreading and evaporating droplet.

The model was coded in MATLAB, and simulations have been obtained for a variety of parameter values. It was observed that the key features of the model were delicately dependent on what was assumed to happen at the leaf surface surface.

A novel diffusion model through the cuticle. The simple diffusion model described above does not include the role of the surfactant directly. One group had numerous discussions about how this could be achieved in the most fundamental way, agreeing on the following principles and mechanisms:

- Surfactants are made up of compounds that have hydrophilic heads and lipophilic tails. In a water droplet, the lipophilic tail may extend radially out of the surface, reducing the surface tension and promoting spreading.
- Above a certain concentration, surfactant compounds in water may form micelles, which are spherical aggregates with the lipophilic tails all pointing towards the centre and the hydrophilic heads facing outwards.
- Similarly, surfactant compounds in the waxy (lipophilic) cuticle may form inverted micelles, which are spherical aggregates with the hydrophilic heads all pointing towards the centre and the lipophilic tails facing outwards.
- Micelles and inverted micelles may completely encapsulate the active ingredients, and transport them in unfavourable environments.

  For example, for a lipophilic active ingredient, both the agrichemical formulation and the epidermis are unfavourable. Thus micelles may encapsulate a molecule of a lipophilic active ingredient in the agrichemical formulation and then release it at the cuticle surface. The lipophilic active ingredient is then free to diffuse through the waxy cuticle, which is favourable. In the meantime, the surfactant compounds can orient themselves into inverted micelles and themselves can be transported through the cuticle. At the cuticle-epidermis interface, once again micelles must form and encapsulate the active ingredients, at which point they may be transported into the vascular system.

A mathematical model for the above process was formulated, with both the concentration of active ingredient and surfactant acting as dependent variables. The encapsulating and releasing of the active ingredients were represented in the model by simple chemical reactions. The model was coded in MATLAB, with preliminary results suggesting that this modelling approach has great potential to provide insight into the role of surfactant at the cuticle level. An observation was that further experiments are required that focus on measuring the surfactant concentration, not just the concentration of active ingredient, which is the standard approach.

Additional work. In the above diffusion-based models, boundary conditions were required on the surface of the cuticle, which is assumed to be covered by droplets of agrichemical formulation. Much attention at the Study Group was given to these issues, with a variety of proposed avenues for future work. A summary of these details is deferred to the full technical paper.