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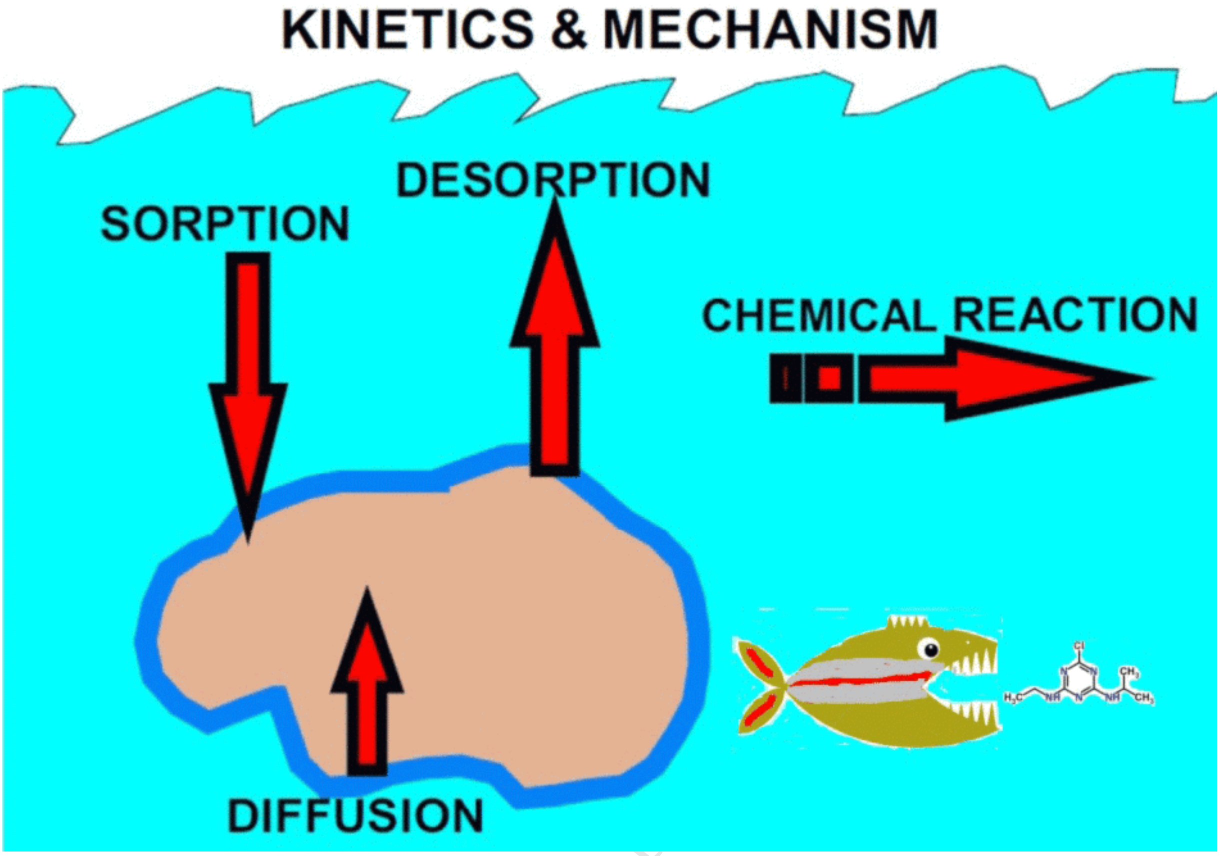
KINETICS & MECHANISM
DESORPTION
SORPTION
CHEMICAL REACTION
DIFFUSION

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Review

THE CHEMISTRY COMPONENT OF AGRICULTURAL PESTICIDE REGULATORY TECHNOLOGY

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Abstract: Government regulators of agricultural pesticides use multidisciplinary computer models with which they make product licencing decisions. Hydrology engineering and chemistry components are integrated into the multidisciplinary models. Although the scientific quality of the hydrology components is reasonably good, the scientific quality of the chemistry component does not match this good quality. These models often use chemically meaningless parameters and assumptions that are not supported by experiments. During the past 25 years chemical kinetics and mechanisms based on experiments and stoichiometry have been published for most agricultural pesticides in soil and water. Thus, the chemistry components should now be replaced with those that use the kinetics and mechanisms currently available. They should next be continuously upgraded as the chemical mechanisms research evolves.

Keywords: soil physical chemistry soils; pesticide soil stoichiometry; pesticide soil kinetics; pesticide regulatory flaws

1. Introduction

Regulatory agencies in North America, the United Kingdom, and the European Union use multidisciplinary computer models for the regulation of agricultural pesticides. The PRZM GW (pesticide root zone model, groundwater) model is an example. More than three dozen of these models have been reported, used for predicting the risk of pesticides to groundwater. They are based mainly on hydrology engineering but attempt to account for the chemical effects of soils on the pesticides. The multinational corporations that market agricultural pesticides submit applications with test data, for product registration. Licences for the sale and use of the pesticides depend on the submitted test data and computer predictions used by the regulatory agencies. However, the legally binding decisions are only as good as the model predictions. The safety of both people and their environment ultimately depends on the quality of the science from which the regulatory technology is derived. The hydrology and chemistry components of the computer models are discussed here.

2. Pesticide regulatory practice

The pesticide regulatory technology used by government regulators in collaboration with industry is multidisciplinary. Its central components are hydrology engineering and chemistry.

They are integrated into computer models. These components are briefly described below:

a) Hydrology component: some progress

The hydrology components of the models solve differential equations that account for rainfall, temperature, and soil porosity on the gravitational leaching of the water that can transport pesticides. Hydrology engineers have used both laboratory packed columns and field trials for their development [1]. Reasonably good mathematical descriptions of the hydrology processes have been produced [2].

b) Chemistry component: Experiments published but not used

Experiments show what actually happens when pesticides escape int soil and water [3]. Fig. and 2 show examples of total pesticide experimentally resolved into labile sorbed, chemically reacted, and intraparticle diffusion fractions. This is required for kinetics and mechanisms calculations.

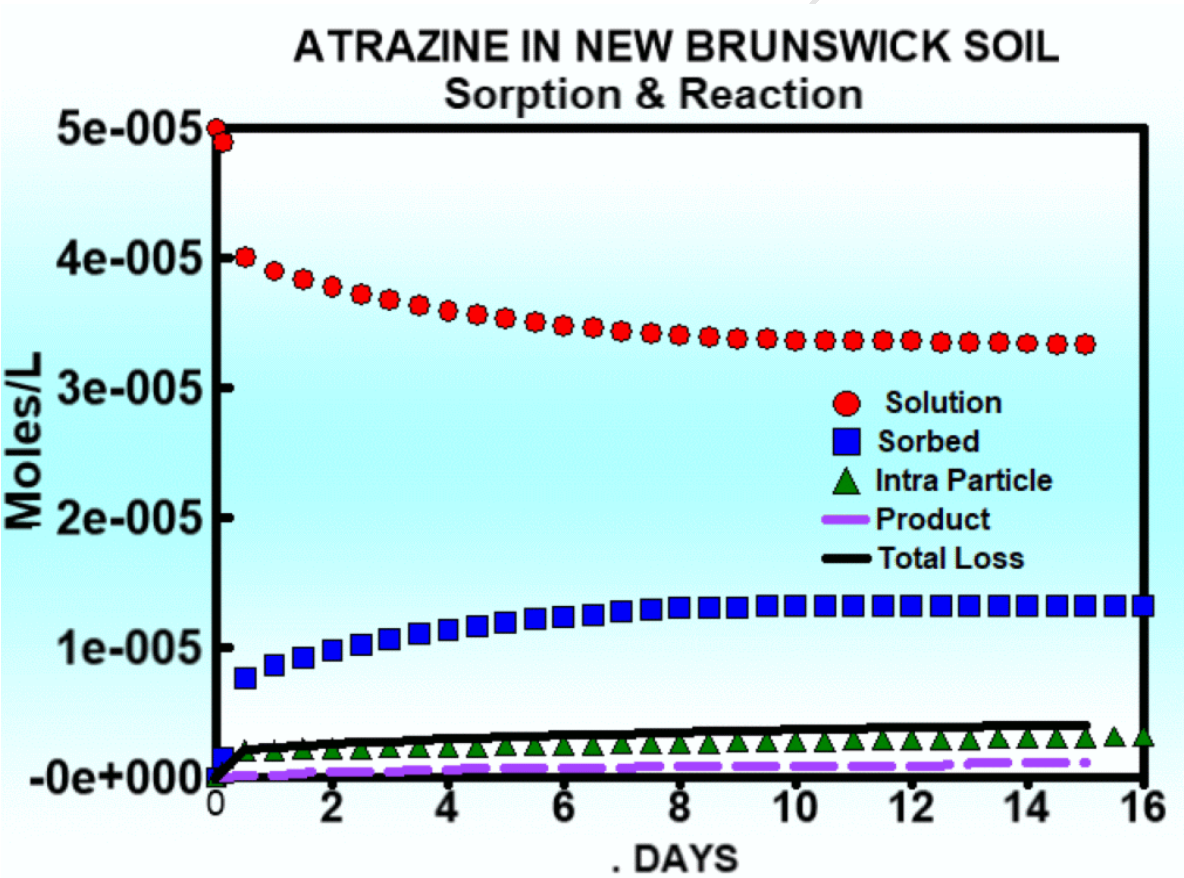

Fig. 1. The herbicide atrazine in a soil from New Brunswick, Canada. Experimental conditions: Initial Concentration, 5.0 X10^{-5} M; Soil Mass 0.5 g; volume 25 mL; 25.0℃.

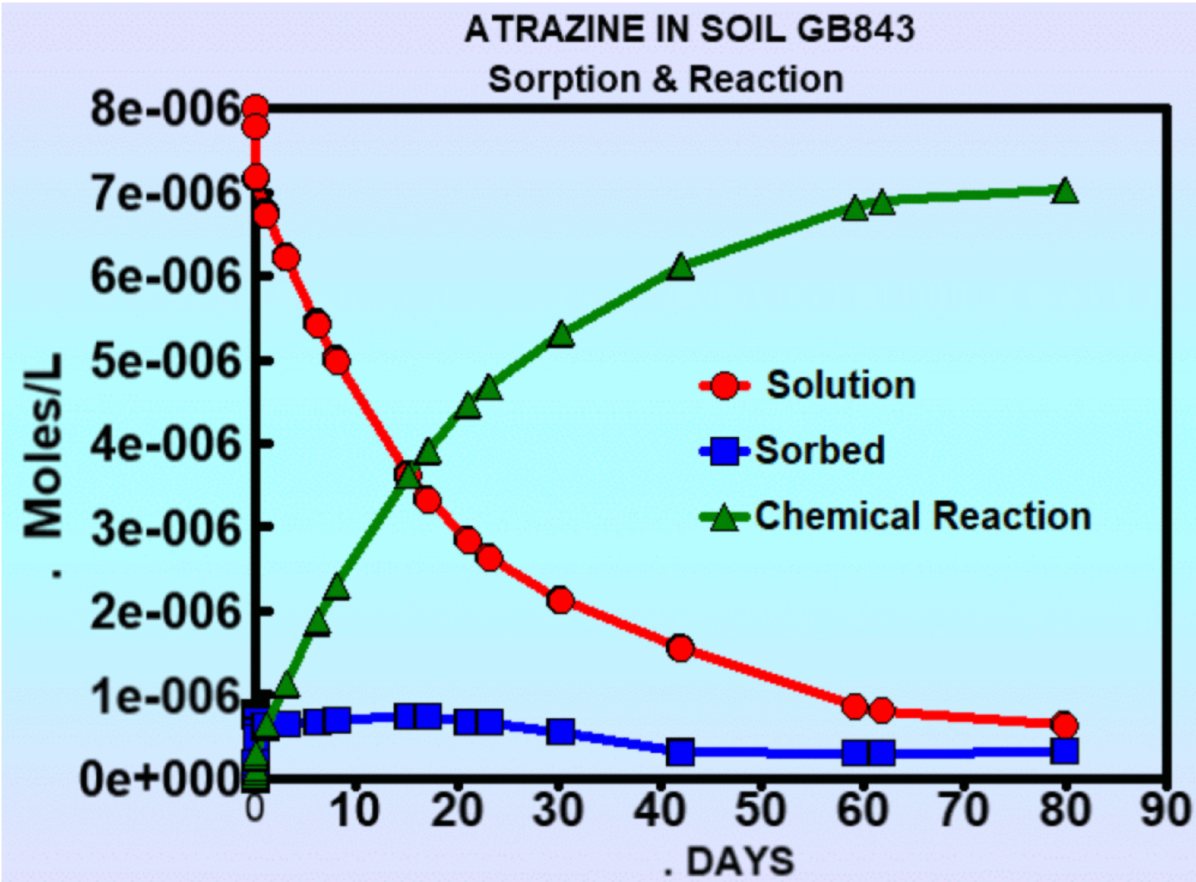

Figure 2. The herbicide atrazine in a soil from the Agriculture & Agri-Food Canada farm, Ottawa, Canada. Experimental conditions: Initial Concentration, 8.0 X10^{-6} M; Soil Mass 0.5 g; volume 25 mL; 10.0℃.

Chemical kinetics are usually described with kinetic rate constants. A comprehensive review has reported, however, that the reactions of chemicals with soil components give Langford kinetic rate coefficients [3]. Like the examples in Fig. 3, they decrease with reaction time. Experimental limits for labile sorption sites were also found [3]. Those limits help to define the chemical stoichiometries that are needed for the chemical kinetics equations [4].

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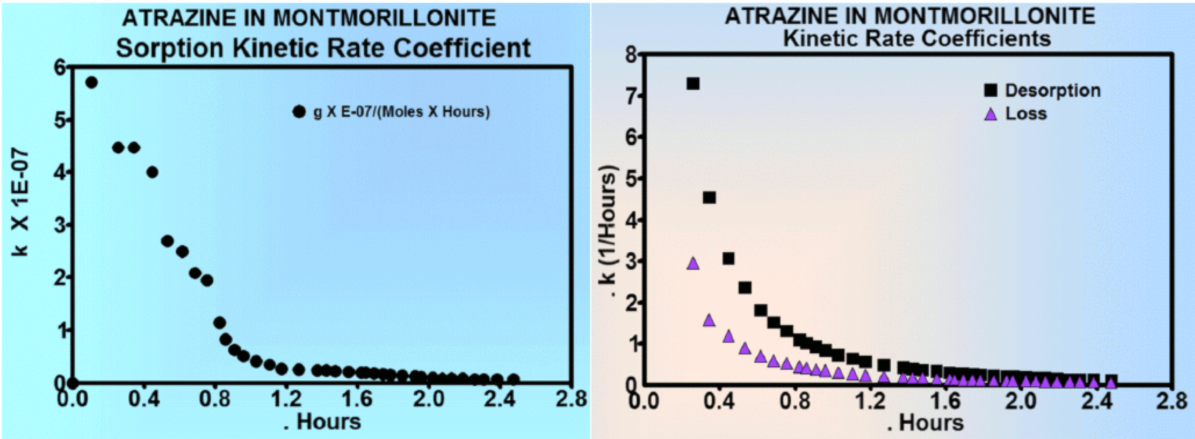

Figure 3. the herbicide atrazine in montmorillonite clay. Experimental conditions: Initial Concentration, $1.0 \text{ X}10^{-6}$ M; Soil Mass 0.51 g; volume 25 mL; 25.0°C. The loss was caused by a chemical reaction.

c) Chemistry component: misinformation published and used

The experimentally revealed facts referred to above should have been used for the chemistry component. That is not what has happened. For 50 years pesticide soil investigators measured the wrong variables, used the wrong units, calculated the wrong parameters, and ignored chemical stoichiometry [5]. Independently of each other, two reviews reported what was wrong with that [6,7]. Authors, reviewers, editors, and regulatory agencies all avoided citing those two reviews. They also ignored the issues that they raised. Instead, the incorrect assumptions and parameters were put into the chemistry component[8]. The wrong assumptions are listed here.

#1 Dynamic processes like those in Fig. 1 and 2 could be represented by equilibrium parameters.
#2 Chemical stoichiometry could be ignored in the use of parameters and kinetics equations for physical chemical processes.
#3 Physical chemical mechanisms could be described without the use of chemical units.
#4 All of the processes could be lumped together for one overall kinetics description.
#5 Second order kinetics could be ignored for sorption which has two reactants.
#6 Kinetic rate coefficients are constants and can be represented by half lives.
#7 The effects of humic materials could be accounted for without the types and amounts of oxygen bearing functional groups being specified.

These are the wrong parameters.
#1 Distribution coefficients k_D; wrongly assumes equilibrium and not consistent with the law of mass action; no chemical units, which prevented the use of chemical stoichiometry.
#2 Distribution constant k_{OC}; the problems of k_D plus the chemistry of humic materials was ignored.
#3 Kinetic half lives $t_{½}$; wrongly assumed that the kinetic rate coefficients were constant;

used only for all of the reactions and processes lumped together.

The incorrect chemistry component of multidisciplinary models has consequences. Government regulatory agencies make legally binding pesticide decisions based on computer predictions that can be wrong by 1 to 3 orders of magnitude [5].

3. Chemistry component reform

The progress reported to date for the chemistry component has only scratched the surface. Some physical chemistry topics have emerged that need the attention of chemists. Here is a list.

#1 Labile sorption capacities $\boldsymbol{\theta}_{\mathbf{C}}$ and kinetic rate coefficients are key experimental parameters that should be used to characterize the types of materials found in soils. They include clays, metal oxides, and humic materials. There are homologous series of clays. Metal oxides can be crystalline or amorphous. Humic materials have ionized and unionized carboxyl groups, quinone structures, and other oxygen bearing groups.
#2 The parameters $\boldsymbol{\theta}_{\mathbf{C}}$ and kinetic rate coefficients should be related to the sizes, shapes, and electron density maps of pesticide molecules.
#3 The effects of soil catalysts on $\boldsymbol{\theta}_{\mathbf{C}}$ and kinetic rate coefficients are unknown. The catalysts might include H^+, carboxyl groups, metal oxides, and enzymes.
#4 The temperature dependence of $\boldsymbol{\theta}_{\mathbf{C}}$ has been reported for only one case [3]. A systematic temperature study is needed for $\boldsymbol{\theta}_{\mathbf{C}}$ and kinetic rate coefficients.
#5 The saturation of labile sorption sites affects the kinetics and mechanism. This needs a systematic investigation.
#6 Initial sorption is too fast for the experimental methods, which produce incomplete data for the first 10 to 30 minutes of kinetic runs. Better methods need to be developed or adapted for the first 30 minutes.
#7 The analytical chemical methods reported for the kinetics experiments need to be improved, with the use robotic sample handling and mass spectrometry detection.

A dozen predictive spreadsheet models have been created using experiments referred to above. The experiments support conventional chemical kinetics. One of the models has been published [4]. More realistic chemistry components could be integrated with the hydrology to make multidisciplinary models. Government regulators could then base legally binding decisions on better computer predictions.

4. Conclusions

Government regulators of agricultural pesticides base legally binding decisions on computer predictions. The multidisciplinary computer models used for this have two integrated components. One is hydrology engineering and the other is chemistry. The good scientific quality of the hydrology engineering component is not matched by the quality of the chemistry component. They often use chemically meaningless parameters and assumptions not based on experiments. Kinetics and mechanisms models that are based on conventional chemical kinetics, stoichiometry, and experiments have been published for pesticides in soil and water. The chemical components should now be prepared with these concepts and methods, and integrated with the hydrology engineering in new types of multidisciplinary models.

Acknowledgments

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HIGHLIGHTS

$ Soils are physically and chemically irregular unstable mixtures.

$ Conventional chemical kinetics are applied to pesticide reaction mechanisms in soils.

$ Chemically incorrect technology for the regulation of agricultural pesticides is used.

$ Research results should be improved for correct regulation of agricultural pesticides.

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