O. Richter, B. Diekkrüger, P. Nörtersheuser

Environmental Fate Modelling of Pesticides
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From the Laboratory to the Field Scale
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Preface

The fate of a substance in the environment is determined by physical, chemical and biological processes. These processes take place simultaneously and are closely interlocked. Environmental systems do not conform with manmade distinctions between different branches of sciences.

Therefore environmental fate modelling demands an interdisciplinary approach. This concerns not only interdisciplinarity between different disciplines such as soil physics, mathematics, soil chemistry and biology, but also interdisciplinarity within a discipline. Mathematics may serve as an example. Kinetic processes, if they are mediated by biological processes, are nonlinear. They are modelled by sets of nonlinear ordinary differential equations, which, in general, are not amenable to analytical solutions. The understanding of the dynamics of such equations is based on knowledge of dynamical systems theory and on numerical methods for obtaining approximate solutions. Coupling kinetics with transport leads to systems of partial differential equations. Furthermore, these processes are imbedded into a random environment. Soils are by no means homogeneous media. As a consequence variability itself has to be modeled by stochastic approaches based on modern geostatistical theory. All the methods mentioned above stem from different fields within the realm of mathematics.

Models cannot be derived from first principles alone. Models summarize experimental knowledge at the abstract level of mathematics. Therefore, many experimental data are necessary at various stages of model development. In the beginning experimental knowledge guides us in the conception of models and in later stages, thoroughly designed experiments serve to identify model parameters and to validate models. Parameter estimation techniques both in ordinary and in partial differential equations are therefore necessary tools to provide the link between models and experiments. These techniques combine aspects of numerical mathematics and statistics.

Model parameters such as sorption constants, degradation rates and diffusion coefficients are all closely related to soil properties. The translation of models across scales, from the laboratory scale to field and catchment scales, therefore demands first the mapping of geo-referenced soil information to model parameters. This is mediated by so-called pedotransfer functions. The link between spatial information and pesticide environmental fate models can best be achieved in the frame of a geographical information system.

If processes are only vaguely known, fuzzy-theory provides a promising new concept to deal with uncertainty. At the end of the book, a simple fuzzy-expert system is presented apt to predict decay modes and half-lives of a herbicide.

It is the objective of this book, to bring together many different aspects of environmental fate modelling of pesticides comprising such diverse subjects as

- linear compartment theory
- nonlinear biological degradation models
- biological temperature and humidity response of degradation
- herbicide dynamics, i.e. modelling toxicity
- parameter identification in ordinary and partial differential equations
- parameter estimation in sparse data situations
- coupled reaction and diffusion processes in form of coupled
  partial differential equations
- coupling of physical and biological processes
- transport processes in random environments
- pedotransfer functions
- coupling of random soil parameter fields and reactive transport models
- the translation of models across scales
- coupling of geographical information systems with models
- fuzzy approaches

This book has several origins. Part of the material is based on a course on environmental
modelling for environmental science students of the new course "Geoecology" at
Braunschweig University. More advanced parts and many experimental data are due to the
activities of the Collaborative Research Program 179 "Water and Matter Dynamics in Agro-
Ecosystems", which was established in 1986 at the Technical University of Braunschweig,
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was the development and validation of physically, chemically and biologically based transport
and reaction models for pesticides in soils. The subprojects "Integrated Site and Catchment
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O. Richter
B. Diekkrüger
P. Nörtersheuser
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1 Introduction

Environmental Fate of Pesticides

If one regards the environmental fate of a substance such as a pesticide one is intrigued by the number of interacting processes. Let us follow a pesticide in the plant soil system after spraying. Fig. 1.1 depicts the main processes. Before it reaches the soil, the substance may undergo decay by photodecomposition, it may be transported in the air and it may adsorb to plant leaves. Once it enters the soil, it is subject to various transformation processes. It may decay by a simple chemical process, e.g. by hydrolysis. Most important, it may be transformed by biochemical reactions mediated by microorganisms. These reactions are called metabolic if microorganisms are able to use the substance as C-source, otherwise they are called cometabolic. The latter notation expresses the fact that degradation is connected to microbial activity for instance by the release of hydrolytic enzymes. Degradation processes mostly take place in the liquid phase. In the soil the substance partitions between the liquid phase, the solid phase and the gaseous phase. Furthermore it is sorbed to binding sites with different strength of binding.

Fig. 1.1: Main processes in the plant soil system.
Solute transport through soil is mediated by water flow and is strongly influenced by solute sorption. To complicate matters, soil structures are heterogeneous. There are wormholes, cracks and complex soil structures caused by e.g. glacial processes (cf. Fig. 1.2) giving rise to preferential flow facilitating the transport of pollutants into the subsoil. All these processes are embedded in a spatio-temporal hierarchy (cf. Tabs. 1.1 and 1.2). If one considers all these processes in detail it does not seem feasible to devise mathematical models able to cope with this sort of complexity. However, the experience of systems at the laboratory scale - continuously stirred reactors, soil columns and lysimeters - show that in spite of this apparent complexity decay curves and breakthrough curves can well be described by mathematical models with different degree of sophistication.

Fig. 1.2: Preferential flow paths in a highly variable soil of a push moraine. The flow region is colored by Rhodamine applied during a tracer experiment.
Simple Mathematical Models

Notations

\[ y \quad : \text{concentration [M/L}^3\text{]} \]
\[ y_0 \quad : \text{initial concentration [M/L}^3\text{]} \]
\[ t \quad : \text{time [T]} \]
\[ T \quad : \text{temperature [°C, resp. K]} \]
\[ k \quad : \text{rate constant [1/T]} \]
\[ R \quad : \text{gas constant} = 8.314 \text{JK}^{-1} \text{mol}^{-1} \]
\[ \Delta E \quad : \text{activation energy [J/mol]} \]

The simplest kinetics encountered is the mono-exponential decay with an Arrhenius law for the dependence of the rate constant on temperature. Figure 1.3 shows decay curves for several temperature values obtained in the laboratory.

\[ \frac{dy}{dt} = -ky \quad \text{with} \quad y(t=0) = y_0 \]  \hspace{1cm} (1.1)

which is easily integrated to yield (cf. section 2.1)

\[ y(t) = y_0 e^{-kt} \]  \hspace{1cm} (1.2)

The Arrhenius law establishes the following dependence of the rate constant \( k \) on temperature \( T \)

\[ k(T) = k_0 e^{-\frac{\Delta E}{RT}} \]  \hspace{1cm} (1.3)