

O. Richter,
B. Dieckrüger,
P. Nörtersheuser

Environmental Fate Modelling of Pesticides

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, Germany, sponsored by the Deutsche Forschungsgemeinschaft. Part of the research program 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 Models", "The Dynamics of Herbicides", "Investigations on Pesticide Residues and corresponding Metabolites" deserve special mention. Furthermore, the research was sponsored by BASF, where several kinetic studies were carried out by PhD students.

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August 1996
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O. Richter
B. Dieckkrüger
P. Nörtersheuser

Contents

1	Introduction	1
2	Mathematical Preliminaries	9
2.1	Ordinary Differential Equations	9
2.2	Partial Differential Equations	15
2.3	Geostatistics	22
3	Kinetics	31
3.1	Linear Models	31
3.1.1	The Compartment Concept	31
3.1.2	Simple Linear Systems	34
3.1.3	Solution by Matrix Methods	37
3.1.4	Solution by Laplace Transformation	50
3.2	Nonlinear Models	60
3.2.1	The Limits of Linear Models	60
3.2.2	Nonlinear Kinetics due to Adsorption	62
3.2.2.1	Equilibrium Approach	62
3.2.2.2	Kinetic Approach	64
3.2.3	Nonlinearities due to Spatial Heterogeneity	66
3.2.4	Nonlinearities Encountered in Biological Degradation	71
3.2.4.1	Capacity Limited Degradation	71
3.2.4.2	Substrate Inhibition	73
3.2.4.3	Population Dynamic Effects	74
3.2.4.4	Long Term Persistence of Activity	77
3.2.4.5	Stochastic Approach for Activity Life Times	80
3.2.4.6	Shift of Population Composition	83
3.2.4.7	Interactions	87
3.3	Kinetics of Dose-Response	89
3.3.1	Linking Concentration and Effect	89
3.3.2	Mathematical Form of Dose-Response-Curves	90
3.3.3	Time Courses of the Response	94
3.3.4	Optimal Application Schedules	97
3.4	Environmental Covariates	101
3.4.1	Temperature and Humidity	102
3.4.1.1	Chemical and Biological Temperature Response-Functions	102
3.4.1.2	Influence of the Time Resolution of Temperature Pattern on the Kinetics	105

3.4.1.3	Influence of the Response-Function on Degradation	107
3.4.1.4	Humidity	109
3.4.1.5	Combined Effect of Temperature and Humidity	109
3.4.2	Soil Parameters	112
3.4.2.1	Organic Matter Content	112
3.4.2.2	pH-Value	113
3.4.2.3	Combined Effect of Organic Matter Content and pH-Value	114
4	Parameter Estimation in Kinetic Models	117
4.1	Problem Statement	117
4.1.1	The Estimation Problem	117
4.1.2	Performance Criteria of the Estimates and Experimental Design	118
4.1.3	Multi-Experiment Problems	120
4.2	Models in Explicit Form	120
4.2.1	A Multicompartment System	121
4.2.2	Strong Sorption and Degradation	124
4.3	Models in Form of Ordinary Differential Equations	130
4.3.1	Initial Value Method	132
4.3.2	Boundary Value Method	137
4.4	Sparse Data Analysis	141
5	Transport and Reactions in the Soil	149
5.1	Water Movement	149
5.1.1	The Classical Approach: Richards' Equation	149
5.1.2	Two-Region Models	154
5.2	Applications of the Convection Dispersion Equation	159
5.2.1	Derivation of the Convection Dispersion Equation	159
5.2.2	Analytical Solutions in the One-Dimensional Case	161
5.2.3	Linear Sorption and First Order Degradation	165
5.2.4	Volatilization	169
5.2.5	Kinetic Adsorption	173
5.2.6	Two-Region Transport Model	176
5.2.7	Three-Dimensional Form of the Convection Dispersion Equation	178
5.3	Coupling of Nonlinear Kinetics and Transport	179
5.3.1	Nonlinear Sorption	179
5.3.2	Coupling Transport and Microbial Population Dynamics	181
5.3.3	Soil Aggregate Model	188
5.3.4	Metabolites	197
5.4	Soil Temperature Fields	199
5.4.1	The Heat Conduction Equation	199
5.4.2	Influence of the Temperature Field on Degradation and Transport	203

6	Parameters for Water Transport Models	205
6.1	Pedotransfer Functions for Water Retention Curves and Saturated Hydraulic Conductivities	205
6.2	Inverse Problems in Partial Differential Equations	208
6.3	Worked Examples	211
7	Regionalization	217
7.1	Transport Processes in Random Environments	217
7.2	The Concept of Random Soil Columns	218
7.2.1	Introduction of Variability into Deterministic Models	218
7.2.2	The Latin Hypercube Method	224
7.3	Microscale Variation of Spatial Structure	227
7.3.1	Random Spatial Processes	227
7.3.2	Transport Processes over Realizations of Random Fields	230
7.4	Effective Parameters	237
7.4.1	Performance Criteria	237
7.4.2	Guidelines for the Use of Effective Parameters	239
7.5	Macroscale Variation	241
7.5.1	The Implementation of Simulation Models into Geographical Information Systems	241
7.5.2	Case Study	243
7.6	Fuzzy-Approaches	252
Appendix	261
A.1	Table of Laplace Transforms	261
A.2	Basic Distributions	262
References	267
Subject Index	277

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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.

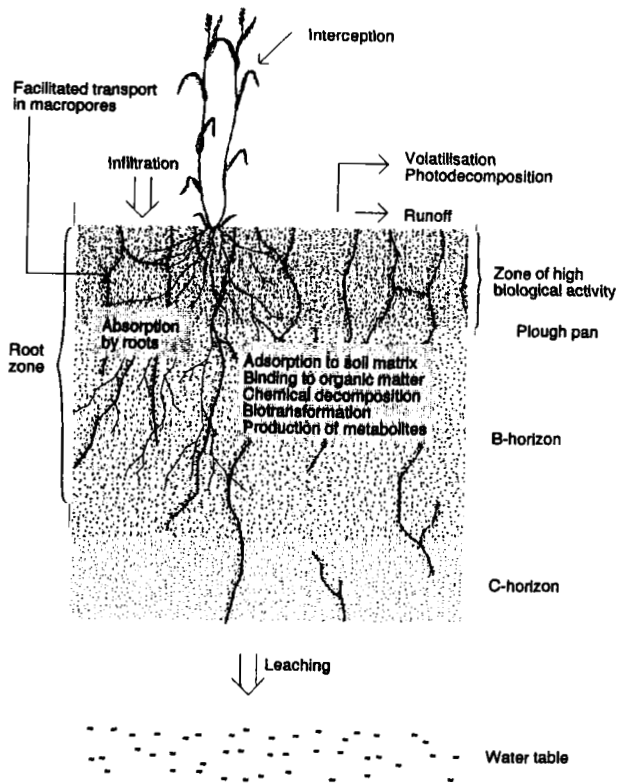


Fig. 1.1: Main processes in the plant soil system.

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	: concentration [M/L ³]
y_0	: initial concentration [M/L ³]
t	: time [T]
T	: temperature [°C, resp. K]
k	: rate constant [1/T]
R	: gas constant = 8.314 JK ⁻¹ mol ⁻¹
ΔE	: 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.

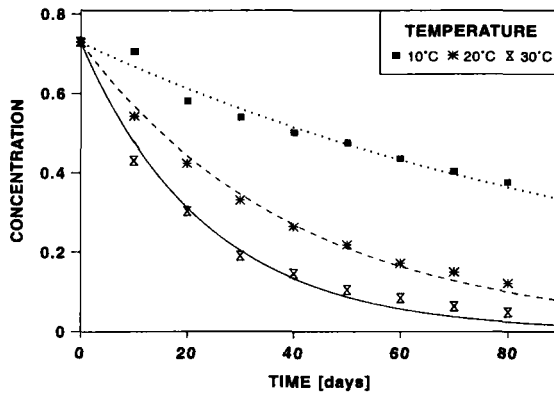


Fig 1.3: Decay curves for several temperature values obtained in the laboratory.

Assuming that the rate of decay is proportional to the amount of pesticide present the adequate model in differential form is

$$\frac{dy}{dt} = -ky \quad \text{with} \quad y(t=0) = y_0 \quad (1.1)$$

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

$$y(t) = y_0 e^{-kt} \quad (1.2)$$

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

$$k(T) = k_0 e^{-\frac{\Delta E}{RT}} \quad (1.3)$$

This is one of the simplest models. There are no nonlinear effects such as lag times or other forms of non-mono-exponential kinetics. If one wants to apply this model to time varying temperatures $T(t)$, one has to start from the underlying differential equation Eq. (1.1) introducing a time dependent rate constant:

$$\frac{dy}{dt} = -k(T(t))y \quad \text{with} \quad y(t=0) = y_0 \quad (1.4)$$

Integration of this differential equation yields (cf. section 2.1)

$$y(t) = y_0 e^{\int_0^t -k(T(\tau))d\tau} \quad (1.5)$$

This example demonstrates, that it is possible to apply a model, which has been derived from simple experimental conditions, to a more complex situation. However, care has to be taken, if one is leaving the range of those experimental conditions which served to establish the temperature law. If degradation is mediated by microorganisms, the validity of the Arrhenius law is confined to only a small temperature range (cf. section 3.4.1).

However, simple mono-exponential models do not always apply. Frequently, one is faced with significant deviations from this simple kinetic behavior due to nonlinear effects at the microbial level. Figure 1.4 shows decay curves of 2,4-D (2,4-dichlorophenoxyacetic acid), which obviously cannot be described by a mono-exponential model, because it is not capable of simulating lag-phases. Effects like this pose a challenge to model builders and render environmental fate models interesting from the mathematical point of view.

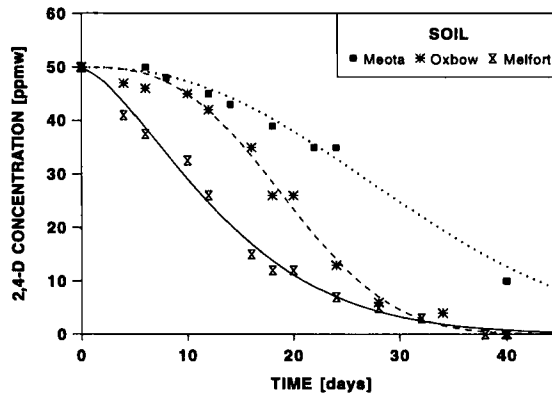


Fig. 1.4: Decay curves of 2,4-D. This example will be discussed in section 4.4.

Spatial and Temporal Scales

Once released pesticides become part of agricultural ecosystems. Therefore it is important to study the scales involved in agricultural ecosystems first and then to see how pesticides fit into this scheme. Table 1.1 summarizes some basic processes in an agricultural ecosystem and their characteristic times.

Tab. 1.1: Processes in (agricultural) ecosystems and their characteristic times.

Process	State variables	Characteristic time
enzymatic reactions, e.g. the hexo-kinase reaction	glucose (substrate) and glucose-6-phosphate (product)	minutes
growth of a microbial population	biomass in C units, N-content, activity	30 minutes
nitrification and denitrification	NH_4^+ , NO_3^- , N_2O , N_2 , microbial activity	1 day - several weeks
short-term population dynamics of pests and diseases	density of eggs, larvae and adults	1 week (eggs) 2 - 7 weeks (adults)
long-term population dynamics of pests and diseases	density of eggs, larvae and adults	period of crop rotations, several years
crop growth	biomass of shoot and root, N-content, leaf area index, yield	several weeks
long-term population-dynamics of weeds	seedbank, density	vegetation period to years
water transport in the soil	water content, water potential	1 h to several days
matter transport and degradation in the unsaturated zone	concentration in liquid, solid and gaseous phase	weeks to several years
evolutionary processes induced by agriculture: enhanced biodegradation of pesticides, emergence of resistance	biodegradation rates, response to pesticides	~1 to 10 years
change in biodiversity, dying back of species, immigration of species (e.g. weeds)	number and abundance of species	~1 to several 100 years

In dealing with pesticides one has to consider in addition various levels of experimentation. Following Blackburn (1989) one can distinguish the continuously stirred tank reactor level,

the column reactor level, the field-scale and last the catchment or aquifer-scale. It is important to note that there are long-term processes associated with periodic applications of pesticides at the evolutionary level of microbial populations and the target populations. Enhanced biodegradation has been frequently observed, although the molecular and genetic mechanisms for this effect are still being investigated. Figure 1.5 shows enhanced degradation of EPTC as measured by Ogrigawitch et al. (1983).

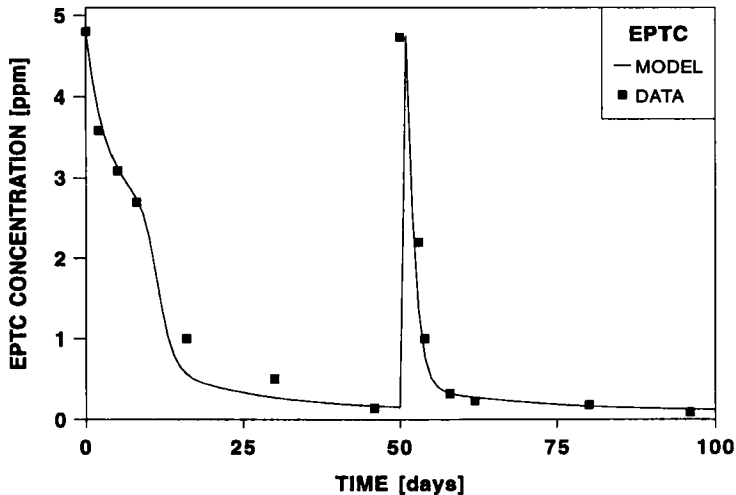


Fig. 1.5: Degradation of EPTC as measured by Ogrigawitch et al. (1983). This example will be discussed in section 3.3.3.

Target populations may eventually become resistant against the pesticide. These biological long-term effects pose a major problem for the conception of deterministic fate models. In chapter 3 some possible modeling approaches are presented.

Dealing with Spatial Heterogeneity

If one proceeds from the laboratory level to higher spatial scales one has to include the dependence of rate constants on soil properties. The spatial distribution of soil properties has both, a deterministic (soil type) and a random component. The random component has to be modeled explicitly. This implies that in addition to deterministic process models for laboratory conditions one has to devise stochastic models for the spatial distribution of parameters. In the simplest case these are probability density functions. If three-dimensional transport in a soil is considered, the models are spatial stochastic processes yielding realizations of parameter fields (cf. section 7.3). By combination of stochastic models for soil parameters and deterministic models for the kinetics one is able to tackle the problem of spatial heterogeneity. A key concept is the notion of ecotope. An ecotope is defined as the intersection of a pedological unit and the landuse pattern. At the catchment scale the landscape is composed of a large number of ecotopes each with characteristic soil properties (cf. section 7.5). Table 1.2 summarizes spatial scales and possible model approaches taking into account spatial heterogeneity.

Tab. 1.2: Model approaches on different scales.

Scale	Soil Heterogeneity	Model
continuously stirred tank reactor	homogeneous	kinetic models in form of ordinary differential equations
column reactor	almost homogeneous microscale variation	kinetic models coupled with one-dimensional transport models in form of partial differential equations
field scale (intersection of pedological unit and landuse)	random soil properties	stochastic models for soil properties plus deterministic model
catchment scale	large deterministic structures (several pedological units) with random soil properties	pedotransfer functions plus stochastic model plus deterministic model

Tab. 1.3: Information hierarchy associated with spatial scales.

Scale	Information Density	Information Quality
continuously stirred tank reactor	high temporal resolution	interval scale level
column reactor level	high temporal resolution	interval scale level
experimental plot	high temporal and spatial resolution	detailed measurements at interval scale level, low spatial variability
experimental field	reduced temporal and spatial resolution	detailed measurements at interval and ordinal scale level, spatial variability
experimental farm	reduced temporal and spatial resolution	detailed measurements at interval scale and ordinal scale level, increasing spatial variability
ordinary farm, catchments and landscapes	only few measurements	qualitative information (linguistic level, fuzzy information)

Information Hierarchy

The various approaches mentioned above to cope with spatial heterogeneity all demand large data bases. In order to identify the parameters of a spatial random process one has to collect data with a high spatial resolution by nesting grids of different mesh sizes. This method is referred to as "nested sampling design". Such extensive experimental efforts are only possible in the frame of a large collaborative research program. One can state that an information hierarchy is associated with the hierarchy of spatial scales. Table 1.3 illustrates the relation between spatial scales and information density and information quality. This is one of the major issues in environmental fate modelling: the translation of models across spatial and temporal scales in view of this information hierarchy. We will address this problem in chapter 7, but we admit that here many questions still remain open.

2 Mathematical Preliminaries

2.1 Ordinary Differential Equations

In this book, ordinary differential equations are applied to the dynamics of chemical reaction systems. They are modeled by systems of simultaneous first-order differential equations of the general form

$$\begin{aligned}\frac{dy_1}{dt} &= f_1(y_1, \dots, y_n) \\ \frac{dy_2}{dt} &= f_2(y_1, \dots, y_n) \\ &\vdots \\ \frac{dy_n}{dt} &= f_n(y_1, \dots, y_n)\end{aligned}\tag{2.1}$$

The y_i are the state variables, which are unknown functions of time t . In our applications the y_i will denote concentrations of chemicals in various phases, e.g. liquid phase and solid phase pesticide concentrations. The system is of first order, because only the first derivative of the y_i with respect to time t appears in the equations. The system behavior is specified by the initial conditions of the state variables:

$$y_1(t=0) = y_{10}, \quad y_2(t=0) = y_{20}, \dots, \quad y_n(t=0) = y_{n0}\tag{2.2}$$

The mathematical problem to solve the equation system (Eq. (2.1)) together with the initial conditions (Eq. (2.2)) is referred to as an **initial value problem**. In physical applications, one is frequently lead to second order differential equations, because the basic physical laws involve second derivatives with respect to time. E.g., the differential equation for the motion of a damped mass-spring system is

$$m \frac{d^2x}{dt^2} + r \frac{dx}{dt} + kx = 0\tag{2.3}$$

Here, x means the displacement of the mass, m the mass, r the coefficient of friction and k the spring constant. However, it is always possible to write a higher order equation as a system of coupled first-order equations. Consider the above example. By the introduction of the auxiliary variable $v = dx/dt$, which has the meaning of a velocity, the first order equation is replaced by the system

$$\frac{dv}{dt} = -\frac{r}{m}v - \frac{k}{m}x\tag{2.4}$$

A system is defined to be **linear** if the functions on the right hand side (r.h.s.) of Eq. (2.1) are all linear functions of the state variables y_i . The number of equations is referred to as the **dimension of the system**. The constants appearing in the equations, e.g. m , r and k in Eq. (2.3) are referred to as **parameters**. They reflect the material properties of the system to be modeled. We consider now simple first order systems, which are amenable to analytical solutions, i.e. solutions in closed form, by elementary methods. The simplest model of a chemical reaction is based on the assumption, that the reaction rate is proportional to the actual mass or concentration.

$$\frac{dy}{dt} = -ky \quad \text{with } y(t=0) = y_0 \quad (2.5)$$

The negative sign of the r.h.s. means that a loss occurs because the rate of change is negative. This equation is linear. A famous example of a nonlinear equation is the differential equation of logistic growth.

$$\frac{dy}{dt} = ry \left(1 - \frac{y}{K} \right) \quad \text{with } y(t=0) = y_0 \quad (2.6)$$

Population growth is limited by the parameter K , which is - in the context of population dynamics - referred to as environmental capacity. Both equations are of the general form

$$\frac{dy}{dt} = ag(y) \quad (2.7)$$

where the parameter a is a constant.

Method of Separation of Variables

Equations of this type are solved by the method of separation of variables. This procedure implies the following steps.

1. Step: separation of variables

$$\frac{dy}{g(y)} = a dt \quad (2.8)$$

2. Step: integration

$$\int_{y_0}^y \frac{dy}{g(y)} = a \int_{t_0}^t d\tau \quad (2.9)$$

$$G(y) - G(y_0) = a(t - t_0)$$

3. Step: deriving the explicit form of the solution

$$y(t) = G^{-1}[G(y_0) + a(t - t_0)] \quad (2.10)$$

where G^{-1} is the inverse function of G . In the following examples, t_0 is set equal to zero. For the initial value problem Eq. (2.5) these steps are:

1. step: separation of variables

$$\frac{dy}{y} = -k dt \quad (2.11)$$

2. Step: integration

$$\int_{y_0}^y \frac{dy}{y} = -k \int_0^t d\tau \quad (2.12)$$

3. Step: deriving the explicit form of the solution

$$\begin{aligned} \ln(y) - \ln(y_0) &= -kt \\ y(t) &= e^{(\ln(y_0) - kt)} = y_0 e^{-kt} \end{aligned} \quad (2.13)$$

In the same way the solution of the initial value problem Eq. (2.6) is obtained as

$$y(t) = \frac{Ky_0}{y_0 - (y_0 - K)e^{-rt}} \quad (2.14)$$

Even if an analytic expression of the integral of $1/g(y)$ is known, it is not always possible to get an explicit solution as the following example shows. Consider the enzymatic degradation of a substance according to the Michaelis-Menten kinetic law (cf. section 3.2).

$$\frac{dy}{dt} = -\frac{Vy}{y + K} \quad \text{with } y(t=0) = y_0 \quad (2.15)$$

After separation of variables and integration one obtains

$$y - y_0 + \frac{K}{V}(\ln y - \ln y_0) = -t \quad (2.16)$$

This equation cannot be explicitly solved for y .

Non-Autonomous Equations

In the foregoing examples the r.h.s. does not explicitly depend on time t . Equations of this type are referred to as autonomous. If one considers for example the degradation of a

pesticide in the field, changing temperature conditions render the degradation "constant" time dependent.

$$\frac{dy}{dt} = -k(t)y \quad \text{with } y(t=0) = y_0 \quad (2.17)$$

This equation is a special case of the general form

$$\frac{dy}{dt} = f(t)g(y) \quad \text{with } y(t=0) = y_0 \quad (2.18)$$

Equations with explicit time dependency of the r.h.s. are called non-autonomous. Again, the solution of this initial value problem can be obtained by application of the method of separation of variables.

1. Step: separation of variables

$$\frac{dy}{g(y)} = f(t)dt \quad (2.19)$$

2. Step: integration

$$\int_{y_0}^y \frac{dy}{g(y)} = \int_{t_0}^t f(\tau)d\tau \quad (2.20)$$

$$G(y) - G(y_0) = F(t) - F(t_0)$$

3. Step: deriving the explicit form of the solution

$$y(t) = G^{-1}[G(y_0) + F(t) - F(t_0)] \quad (2.21)$$

where G^{-1} is the inverse function of G . In the following example, t_0 is set equal to zero.

Consider the initial value problem Eq. (2.17) with a periodical time dependence of the degradation rate according to

$$k = k_0 + a \sin(\omega t) \quad (2.22)$$

1. Step: separation of variables

$$\frac{dy}{y} = f(t)dt \quad (2.23)$$

2. Step: integration

$$\int_{y_0}^y \frac{dy}{y} = - \int_0^t (k_0 + a \sin(\omega\tau)) d\tau \quad (2.24)$$

$$\ln(y) - \ln(y_0) = -k_0 t - a \left(-\frac{1}{\omega} \cos(\omega t) + \frac{1}{\omega} \right)$$

3. Step: deriving the explicit form of the solution

$$y(t) = y_0 e^{\left[-k_0 t - \frac{a}{\omega} (1 - \cos(\omega t)) \right]} \quad (2.25)$$

Inhomogeneous equations and the trick of the integrating factor

We consider differential equations of the general form

$$\frac{dy}{dt} + a(t)y = f(t) \quad (2.26)$$

Equations of this type model for example the situation that a substance, which decays with time dependent rate constant $a(t)$, is entering the system with time dependent rate $f(t)$. An equation of this type is called inhomogeneous. The first step of the solution procedure is the solution of the homogeneous equation

$$\frac{dy}{dt} + a(t)y = 0 \quad (2.27)$$

Applying the method of separation of variables one obtains

$$y(t) = y_0 e^{A(t_0)} e^{-A(t)} \quad (2.28)$$

$$A(t) - A(t_0) = \int_{t_0}^t a(\tau) d\tau$$

This solution can also be obtained by the following trick: the differential equation is multiplied by the "integrating factor" $e^{A(t)}$. One easily verifies that the l.h.s. of the differential equation can be written as the derivative

$$\frac{d}{dt} \left[e^{A(t)} y(t) \right] = e^{A(t)} \frac{d}{dt} y(t) + e^{A(t)} a(t) y(t) \quad (2.29)$$

so that the homogeneous equation takes the form

$$\frac{d}{dt} [e^{A(t)} y(t)] = 0 \quad (2.30)$$

Integration yields the solution of the initial value problem Eq. (2.26). In the inhomogeneous case multiplication by the integrating factor leads to

$$\frac{d}{dt} [e^{A(t)} y(t)] = e^{A(t)} f(t) \quad (2.31)$$

Integration and multiplication both sides by $e^{-A(t)}$ yields

$$y(t) = e^{-A(t)} \left[y_0 e^{A(t_0)} + \int_{t_0}^t e^{A(\tau)} f(\tau) d\tau \right] \quad (2.32)$$

Consider the simple case that $a(t) = \text{const} = k$ and that $f(t) = \text{const} = v$. The integrating factor is then given by e^{kt} and application of the general formula Eq. (2.32) yields the solution (t_0 is set equal to zero)

$$y(t) = e^{-kt} \left[y_0 + \int_0^t e^{k\tau} v d\tau \right] = \frac{v}{k} (1 - e^{-kt}) + y_0 e^{-kt} \quad (2.33)$$

Further examples will be given in the next chapter.

Remarks on Existence and Uniqueness of the Solutions

The fundamental theorem of Picard-Lindelöf ensures that the solution of the initial value problem

$$\frac{dy}{dt} = f(t, y) \quad \text{with } y(t=0) = y_0 \quad (2.34)$$

exists and is unique, if the r.h.s. of the differential equation is **Lipschitz-continuous**.

Def.: $f(t, y)$ is called Lipschitz-continuous with respect to y , if there exists a positive constant L such that

$$|f(t, y) - f(t, y^*)| \leq L |y - y^*| \quad (2.35)$$

This condition is always fulfilled for the class of kinetic equations encountered in this book.

2.2 Partial Differential Equations

Modelling Processes by Partial Differential Equations

Ordinary differential equations (ODEs) have only one independent variable, which is in the context of our applications, the time. They are thus lacking any spatial component. The application of ODEs to dynamic systems makes only sense, if the compartments of the system under study are spatially homogeneous. This is for instance realized for reaction systems in a "well stirred" medium in a laboratory. However, if the fate of a substance in the environment is considered, transport processes in inhomogeneous soils prevail. Therefore models are needed, which contain explicitly spatial coordinates and which yield the evolution in time of the concentration field, i.e. the concentration as function of time and space. The resulting differential equation therefore contains also derivatives of the state variables with respect to the space coordinates. Such an equation is called a partial differential equation (PDE).

Derivation of the Continuity Equation

The basic equation for the derivation of transport models is the mass balance equation for a volume element. Although the shape of the elements is arbitrary, we consider, for ease of presentation, a rectangular box centered at $P(x,y,z)$ with dimensions Δx , Δy and Δz (cf. Fig. 2.1). Imagine that this box is placed into a flow field \vec{J} . This is also referred to as control volume or control box. Let c denote the mass of a substance (or any other extensive property) in a volume element ΔV . Then the rate of change of c in ΔV is the excess of inflow over outflow during a time interval Δt . Summing up the flows in x , y and z direction through the surfaces of the control box yields the conservation equation

$$\frac{\Delta c}{\Delta t} \Delta V = [J_{in} - J_{out}]_x \Delta y \Delta z + [J_{in} - J_{out}]_y \Delta x \Delta z + [J_{in} - J_{out}]_z \Delta x \Delta y \quad (2.36)$$

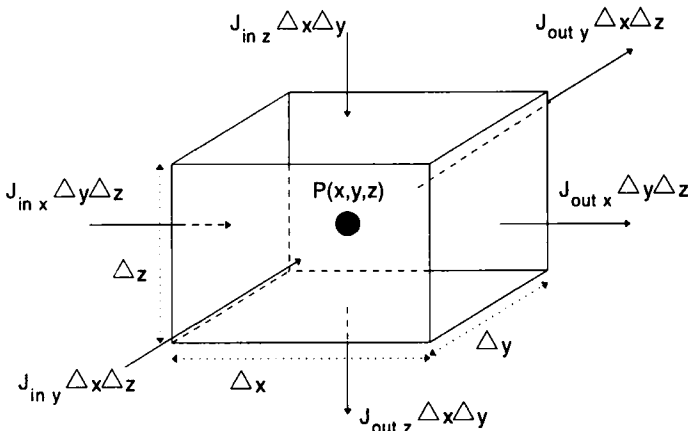


Fig. 2.1: Flux balance for a control volume.

Under the assumption that the flow field is continuous, the value of \vec{J} at the surfaces can be derived from the flow at the center by a Taylor expansion

$$J_x\left(x - \frac{\Delta x}{2}, y, z\right) = J_x(x, y, z) - \frac{\partial J_x}{\partial x}\bigg|_x \frac{\Delta x}{2} \quad (2.37)$$

$$J_x\left(x + \frac{\Delta x}{2}, y, z\right) = J_x(x, y, z) + \frac{\partial J_x}{\partial x}\bigg|_x \frac{\Delta x}{2} \quad (2.38)$$

so that the excess of inflow over outflow in x -direction is given by

$$\left[J_{in} - J_{out}\right]_x \Delta y \Delta z = -2 \frac{\partial J_x}{\partial x}\bigg|_x \frac{\Delta x}{2} \Delta y \Delta z \quad (2.39)$$

Summing up the excess in all three directions gives the expression

$$\frac{\Delta c}{\Delta t} \Delta x \Delta y \Delta z = - \left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} \right) \Delta x \Delta y \Delta z \quad (2.40)$$

In the limit $\Delta V \rightarrow 0$ and $\Delta t \rightarrow 0$ one finally obtains the fundamental conservation equation

$$\frac{\partial c}{\partial t} + \left(\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} \right) = 0 \quad (2.41)$$

By use of the gradient operator ¹

$$\nabla = \left(\frac{\partial}{\partial x} \frac{\partial}{\partial y} \frac{\partial}{\partial z} \right) \quad (2.42)$$

this equation is written in condensed form as

$$\frac{\partial c}{\partial t} + \nabla \cdot \vec{J} = 0 \quad (2.43)$$

The second term is the scalar product of the vectors ∇ and \vec{J} :

¹"A differential operator is something hungry to differentiate something" (The Feynman Lectures on Physics)

$$\nabla \cdot \vec{J} = \begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} \begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix}$$

If there are any sources or sinks in the control volume, i.e. any processes creating or consuming the substance, the mass balance is completed by a sink or source term Q :

$$\frac{\partial c}{\partial t} + \nabla \cdot \vec{J} = Q \quad (2.44)$$

This equation can also be derived from a famous theorem of vector analysis. Let V denote any volume and \vec{n} the unit vector normal to the surface. For this volume the mass balance equation is

$$\int_V \frac{\partial c}{\partial t} dV = - \int_S \vec{J} \cdot \vec{n} da \quad (2.45)$$

stating that the rate of change of c in V equals the integral over the flow over the surfaces of V (cf. Fig. 2.2). By application of Gauss' divergence theorem

$$\int_S \vec{J} \cdot \vec{n} da = \int_V \nabla \cdot \vec{J} dV \quad (2.46)$$

the mass balance equation is written as

$$\int_V \left(\frac{\partial c}{\partial t} + \nabla \cdot \vec{J} \right) dV = 0 \quad (2.47)$$

This is the fundamental mass balance equation in integral form, from which Eq. (2.44) is obtained by letting $V \rightarrow 0$.

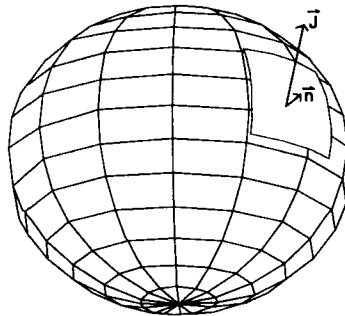


Fig. 2.2: The total rate of change of the quantity c within the volume V equals the integral over the fluxes across the surface. \vec{n} is the outward normal vector to the surface element da , and \vec{J} is the flux vector across da .