pesticide/soil interactions

some current research methods

Juan Cornejo,
Paul Jamet,
coord.

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Foreword

This workbook is an output of the COST Action 66 "Fate of pesticides in the soil and the environment" that was managed by the General Directorate "Research" in Brussels during 6 years, from January 1993 to October 1998. It has been written not only as a final report but mainly to assist scientists, professionals and Ph.D. students in better studying the environmental fate of pesticides.

This workbook provides research methods and mathematical models for those seeking to understand and to predict the environmental fate of pesticides. It is not an exhaustive catalogue of laboratory tests, outdoor experiments or mathematical models and it does not give definitive answers to evaluate the risks of soil and water pollution.

The purpose of this workbook is to gather technical and objective description of some current research methods and mathematical models developed and/or used in Europe. Each method is described following the same sections, especially on what enables its setting up, on its advantages and drawbacks. References are split up in two groups to separate those in which the proposed method was already used (Set 1) and those dealing with other similar methods (Set 2).

The different sections are opened by an introduction chapter to provide to the reader with comparison and guidance on the proposed methods. The introduction chapter provides an overview of the behaviour of pesticides in soil and the environment.

It is hoped that these research methods and mathematical models will be widely used to learn more about the fate of pesticides and to plan ahead for soil and water pollution as well as for preparing future European guidelines for pesticides registration.

Prof. Juan Cornejo, Scientific Editor
Dr. Paul Jamet, Chairman of COST 66

In memory of Mohamed MANSOUR

Dr. Mohamed Mansour, research chemist at the Centre for Environment and Health (G.S.F) Neuherberg-Munich, Germany, died unexpectedly on February 1st, 2000. He was born in 1942 in Casablanca, Morocco and came to Germany in 1964. He received a degree in Chemistry (1973) and Ph.D. in the field of Organic Chemistry and Pharmacology (1975), both from the university of Bonn. He spent a few months at the University of La Sapienza in Rome in the department of Chemistry as a guest Professor. He moved to the GSF Research Centre in Neuherberg where he studied abiotic degradation processes of chemicals, mainly pesticides and their metabolites. In 1977 he was asked to study environmental photochemistry in the GSF Freising-Attaching. Around ten years after he became senior scientist in a research unit again in the GSF Research Centre in Neuherberg.

Dr. Mohamed Mansour is the author or a co-author of more than 130 publications. He serves on the editorial Advisory Boards of Fresenius Environmental Bulletin. He has organised and chaired or directed a series of ecotoxicological symposia since 1986. He conducted International co-operation and he received the 1986 International award for research in the field of environmental protection from the Technical University of Lublin in Poland.

Dr. Mohamed Mansour suggested in 1987 to create a European network on the environmental fate of pesticide. On 30.05-01.06.90 he organised a workshop at the GSF Research Centre Munich/Neuherberg which contributed to set up a European network, namely COST Action 66 "Fate of pesticides in the soil and the environment". During more than 6 years (1992 – 1998) he contributed to the success of this COST Action. His research interests were the fate and transport of organic compounds in soil and water. Current areas include the development of techniques concerning the photo process formation of pesticides on soil surfaces. In France, Spain and Morocco as well as in Germany, Dr. Mohamed Mansour was deeply involved in student and PhD education. He welcome many young scientists in his laboratory in the GSF Research Centre, encouraged them and supported their work.

Above all, Dr. Mohamed Mansour was a wonderful and stimulating colleague, always available to listen and to help us. He will be greatly missed by his family, friends, and colleagues.

Our thoughts are with his wife and two sons.

The members of the Management Committee
The members of COST Action 66

Contents

3. Adsorption – desorption studies

3.1. Preparation of samples

3.2. Adsorption/desorption on soils

1. Semi-controlled conditions, including greenhouses

1.1. Microlysimeters

1.2. Lysimeters

1.3. Others (greenhouses, run-off, ...)

2. Non-controlled conditions

2.1. Run-off studies (run-off waters and sediments) and others

Introduction

J. Cornejo, P. Jamet and F. Lobnik

Agrochemicals are special case of widely used chemicals. In less than half a century the advent of pesticide use has coincided with the tremendous increase in agricultural productivity. They are used worldwide in plant protection to control or destroy weeds, insects, fungi and other pests. The recent trend toward conservation-tillage systems has also meant an increase reliance on chemical pesticide use, such as the integrated pest management approach combining nonchemical means with the chemical use for pest control. Whatever their patterns of use, most of them reach the soil during or after treatment. The soil, which is the main recipient of all pesticides, plays a leading role in the environmental fate of these chemicals and in the protection of surface and ground waters. The environmental fate of pesticides in soil is viewed with great concern today mostly due to the problems resulting from the use of persistent and mobile molecules affecting the surface and ground water quality. Along with the increasing concern about chemical contamination of various ecosystems, much emphasis has been put on designing suitable methods to characterize the different processes affecting the fate of pesticides in soil.

Field experiments under semi-controlled or non-controlled conditions and short-term laboratory mobility studies (leaching, volatilization and run-off test), together with soil adsorption-desorption and degradation studies under controlled conditions have been widely performed. But as the systems investigated become more and more complex, it's obvious that close collaboration and use of large and expensive equipments in research centres become a necessity. It is obvious that an harmonization on research methods is absolutely necessary.

An insight into the behaviour of pesticides in the soil

The soil appears as the principal recipient of all active ingredients used in plant protection. The soil behaves as an **active filter**, where the chemicals are degraded by biological and non biological processes and as a **selective filter** because it is able to retain some chemicals to prevent their leaching to ground water. Both the fate of the agrochemicals in the soil and their dispersion in the environment mainly depend on the characteristics and the overall functioning of this ecosystem (Fig. 1). In the soil, pesticides are affected by the simultaneous influence of transfer, adsorption-desorption, physicochemical degradation and biodegradation phenomena. All these processes are **dynamic** and **non-linear** processes.

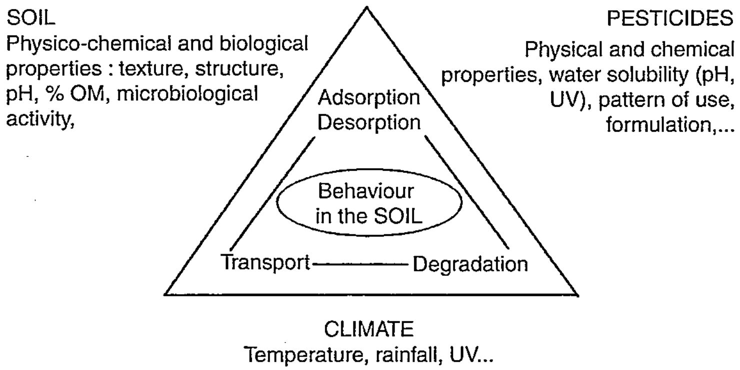

Figure 1. Factors and processes affecting the behaviour of pesticides in soil.

Transfer phenomena

Volatilization

Volatilization occurs mainly during application, especially spraying. After it concerns essentially the quantities of the products that remain at the surface of the soil or of the plants. The vapor pressure and the partition coefficients (air/water, air/solid phase) relevant to the compound are the main factors together with the temperature and the airing at the soil surface.

Leaching

Pesticide can move in the soil in two directions, laterally and vertically. Leaching can vary widely according to the compound, to soil and climate conditions and to the agricultural practices. It may control the efficiency of the application according to the distribution of the active ingredient in the soil. Laboratory and field experiments are carried out to determine the vertical distribution of agrochemicals in the soil profile and to assess the risk of leaching toward ground water. In the laboratory, the two basic methods, soil column and soil thin-layer chromatography, have a fundamental analogy with conventional chromatography in that with they allow a direct measurement of leaching. Field experiments with mini-lysimeters and lysimeters, and monitoring of water pollution levels (drainage waters, water catchment, ...) allow follow-up and prediction of the transfer.

Run-off

Run-off depends on the slope of the soil, the rainfall characteristics, the structural stability of the soil, the agricultural practices and the crop cover. Run-off, whether in solution or in suspension, also depends upon the water solubility of the compounds and their adsorption by the soil components and contributes to the pollution of surface waters and sediments.

Adsorption-desorption phenomena

The origin of the adsorption-desorption phenomena is the molecular attraction by the surfaces of the mineral and organic soil components (clays, organic matter, oxides). The water solubility and the ionization or the polarity of the molecule are the factors relevant to the active ingredient; the other factors depend upon the soil (composition of the soil, nature and properties of the mineral and organic soil components, soil pH, ...). The adsorption-desorption phenomena have an effect upon the behaviour of pesticides in soils. An adsorbed molecule is not generally bio-available, carried away by the movement of water in the soil and generally less rapidly degraded. When it desorbs, the molecule becomes bio-available again, and it may be degraded and carried away by leaching or run-off. Laboratory experiments are carried out to assess the amount of active ingredient adsorbed by the soil (OECD guideline N° 106), and to estimate adsorption and desorption velocities.

Degradation phenomena and persistence

The soil is an ecosystem that is endowed with high degradation potential. The degradation processes, chiefly biological processes, produce more or less toxic metabolites, and mineral compounds such as H_2O, CO_2, NH3, ...

Biodegradation, i.e., decomposition effected by the soil microbial population, is due to the activity and diversity of the very complex soil microflora (mainly bacteria and fungi). The chemical stability of the compound, its adsorption by soil components and its effects on the soil microflora control the degradation as well as the factors relevant to the environment: all the parameters such as temperature, water content, and soil composition that act on the growth and functioning of the soil microflora affect biodegradation.

Nonbiological or abiotic degradation may be quit significant because most pesticides are chemically reactive and results from decomposition by the sunlight or to catalytic breakdown at the surfaces of clays and organic matter.

Different laboratory incubation systems have been proposed to study the degradation kinetics (assessment of DT_{50} & DT_{90} in soil), and to determine the metabolic pathways (chemical structure of metabolites). Under field conditions the monitoring of the residue levels and the study of simultaneous leaching and degradation using lysimeters are increasingly performed.

Outdoor experiments and monitoring

Greater attention has been focused on the potential problems of water contamination. Pesticide presence in open water bodies (ponds, rivers, lakes, ...) may originate from surface run-off, industrial wastes, accidental spills, direct applications. So, the objective of field experiments would be to determine the degradation and transport of the parent and relevant metabolites through the vertical profile of the soil or at the soil surface. Either a small scale plot or lysimeters could be used; soil cores and drainage water samples are analyzed. Run-off studies need specific experimental plots and devices to collect run-off samples which permit partition between solid and liquid phases. Pesticides concentrations in the sediments may be much higher than concentrations in the water. Strategies for monitoring agrochemicals in surface and ground waters are developed in many countries.

Mathematical modelling

Only a small number of the different situations can be covered by laboratory and field experiments. So, computer modelling is generally used to estimating the likely variability in behaviour. During the passed years different models have been developed to evaluate just one dissipation phenomenon, whereas others take into account the roles and the interactions between several phenomena.

Simulation models are currently in development or under validation. They are used for calculating run-off and leaching potential. These models are now used in a truly predictive way. Nevertheless, much work is needed to calibrate and to validate them before they can be relied on as primary methods of assessment or as screening tools for establishing standardized registration criteria.

COST 66 contribution to the studies of soil-pesticide interactions

Much research aims to improve standardized procedures to obtain basic laboratory data on the behaviour of pesticides in soil and water bodies. Mathematical models begin to provide essential data for risk assessment and risk management. Nevertheless, for the coming years, outdoor experiments will continue to provide detailed data on the fate of plant protection products under different farming and environmental conditions. New strategies for monitoring will be developed, data will be used for validation of predictive models and monitoring will have a more explicit role in pesticide registration.

At last but not least, since soils play a leading role in the protection of surface and ground water, soils must be protected especially against degradation by erosion. Maintaining the quality of our soil resource constitutes the environmental challenge. Within the European Union, COST Action 66 underlines the real urgency for support of research in this broad area of environmental science.

The idea for this book was originated some years ago by prof. J. Cornejo during a COST 66 Management Committee Meeting, as a tool for future research on pesticide-soil interactions, compiling the efforts of many european laboratories. But, how the COST 66 Action was born ?

After four European workshops organized from 1988 to 1991, the COST Action 66 "Fate of Pesticides in the Soil and the Environment" was launched on 27 January 1993 during the first Management Committee (MC) Meeting held in Brussels. P. Jamet was elected Chairman and F. Lobnik was elected Vice-Chairman. The Action aims "*to enlist European laboratories that intended to cooperate in investigating the topic* ***Pesticides-Soil-Environment*** *by research on both the consequences of using pesticides in crops and the ecotoxicological problems resulting from the dispersion of pesticides in the environment*". From January 1993 to October 1998 COST 66 brought together **'100 members' laboratories from 18 countries,** *i.e.*, around 300 scientists.

Four working groups were constituted; their scientific programmes are managed by two up to four coordinators:

- Sorption & Mobility (J. Cornejo, A. Piccolo, I. Scheunert): research activities concern sorption parameters, sorption on organic matter and clay minerals, leaching and volatilization.
- Degradation & Transformation (F. Andreux, M. Mansour, D. Suett & L. Tortensson): research activities address the biotic and abiotic aspects of transformation within two main topics, abiotic transformations and biodegradation.
- Outdoor experiments & monitoring (A. Copin, S. Kurppa & G. Puchwein): Harmonization of the monitoring studies, standardization of field lysimeters and efficacy of

buffer strips in stopping the chemical outflow from agricultural areas are the main research topics.

• Mathematical modelling (J. Boesten & A. del Ré): the main activity is to test available mathematical models. Four data sets have been selected and will be applied to fourteen models.

These scientific programmes *"aim to develop and improve those laboratory and field methods required for predicting the environmental fate of pesticides, especially the hazards involved by qualitative and quantitative transfer of the active ingredients and their metabolites to aquatic environments".*

The research methods for pesticide/soil interaction studies described in this book have been grouped following the above mentioned Working Groups recommendations. Each section has been introduced by the corresponding coordinators. It has been quite difficult in some occasions to place properly the contribution in the corresponding section. Previously, as an introduction to the differentt methods a chapter dovoted to EUROSOILS has been considered to be adequated for the readers.

From a whole survey of the cycling of pesticides in the environment this book gives an insight into the behaviour of pesticides in the soil through the scientific programmes of COST Action 66.

The preparation of this book has been possible due to the cooperation between all the authors and the Management Committee Members. We thank them for their participation in this task.