AgEcon SEARCH
RESEARCH IN AGRICULTURAL & APPLIED ECONOMICS

The World's Largest Open Access Agricultural & Applied Economics Digital Library

This document is discoverable and free to researchers across the globe due to the work of AgEcon Search.

Help ensure our sustainability.

Give to AgEcon Search

AgEcon Search
http://ageconsearch.umn.edu
aesearch@umn.edu

*Papers downloaded from **AgEcon Search** may be used for non-commercial purposes and personal study only. No other use, including posting to another Internet site, is permitted without permission from the copyright owner (not AgEcon Search), or as allowed under the provisions of Fair Use, U.S. Copyright Act, Title 17 U.S.C.*

Australian Government

Australian Centre for International Agricultural Research

Safer selection and use of pesticides

Integrating risk assessment, monitoring and management of pesticides

Australian Government

Australian Centre for
International Agricultural Research

Safer selection and use of pesticides

Integrating risk assessment, monitoring and management of pesticides

Edited by Angus N. Crossan, Nguyen Thi Thu Trang,
Pham Ngoc Ha and Ivan R. Kennedy

Contributors – Angus N. Crossan, Pham Ngoc Ha, Nguyen Thi Thu Trang, Nguyen Thu Trang, Bui Quoc Anh, Tran Van An, Bui Van Thin, Vo Thanh Hau, Le Van To, Pham Hung Viet, Bui Cach Tuyen, Chu Pham Ngoc Son, Francisco Sanchez-Bayo, Sundaram Baskaran, Nazir Ahmad, Jeevan Khurana, Nguyen Minh Tue, Phung Vo Cam Hong, Nanju Alice Lee and Ivan R. Kennedy

ACIAR Monograph 117
Australian Centre for International Agricultural Research
2005

The Australian Centre for International Agricultural Research (ACIAR) was established in June 1982 by an Act of the Australian Parliament. Its primary mandate is to help identify agricultural problems in developing countries and to commission collaborative research between Australian and developing country researchers in fields where Australia has special competence.

Where trade names are used this does not constitute endorsement of nor discrimination against any product by the Centre.

ACIAR MONOGRAPH SERIES

This peer reviewed series contains the results of original research supported by ACIAR, or material deemed relevant to ACIAR's research and development objectives. The series is distributed internationally, with an emphasis on developing countries.

© Australian Centre for International Agricultural Research, GPO Box 1571, Canberra, ACT 2601, Australia

Crossan A.N., Nguyen Thi Thu Trang, Pham Ngoc Ha and Kennedy I.R., ed. 2005. Safer selection and use of pesticides. ACIAR Monograph 117.

ISBN 1 86320 491 1
1 86320 492 X

Technical editing:
Elizabeth Beckmann, Beckmann & Associates

Design and layout: Design ONE Solutions

Printing: Pirion Pty Ltd

Foreword

Pesticide contamination can have undesirable environmental impacts and can cause long-term health problems in people exposed to the contamination. Misuse can affect livestock and farm workers as well as consumers. There may also be effects on other species such as fish and native animals. Increasingly, public attitudes towards pesticides mean that food for sale must comply with internationally accepted maximum residue limits for pesticides. This requirement can have major economic ramifications.

Pesticides are complex organic molecules that require sophisticated and expensive instruments and chemical techniques for detection at very low concentrations. Another way of detection, which can also be accurate and sensitive as well as being more portable, involves the use of antibodies. This method, known as enzyme-linked immuno-assay (ELISA), can be incorporated in a kit and used in the field but is often too expensive for widespread use in developing countries. The ACIAR project which was a forerunner to the CARD project from which this book arises, developed local technical capacity and new ELISA kits for key pesticides of concern in Vietnam. It is anticipated that experience in the development and use of these kits will enable cheaper, in-country production to occur in future. The key output of the CARD project was the development of an integrated system to assess the risk of chemicals used in crop production (choice of pesticide, application mode, topography and meteorology, crop factors and land and water use). Results from these risk models will provide Vietnamese planning authorities with tools for guiding future land-use development, assessing potential environmental risks associated with farm chemicals and designing cost-effective monitoring programs.

ACIAR is pleased to publish this important book in both English and Vietnamese languages. The procedures and case studies presented here will help to train experts in quality assurance and methods for reducing the impacts of pesticides.

This publication is also available for free download from ACIAR's website www.aciar.gov.au.

Peter Core
Director
Australian Centre for
International Agricultural Research

Contents

Foreword iii

Preface vi

Glossary viii

Part A: A practical guide for risk assessment and management 1

1 Introduction 3

1.1 Scope of this book 3

1.2 Background 3

1.3 How this book is structured 5

1.4 The importance of feedback 5

2 Identifying the problem 6

2.1 What are pesticides? 6

2.2 Pesticide use and the concept of risk 7

3 Risk assessment 8

3.1 Introduction 8

3.1.1 Quality of information and assumptions 9

3.2 Field site characterisation 11

3.2.1 Description of the site 11

3.2.2 Field investigation 12

3.3 Identifying hazards and formulating problems 13

3.4 Risk characterisation 14

3.4.1 The need for exposure and effect data 14

3.4.2 Data collection and requirements 14

3.4.3 Exposure (e) characterisation 14

3.4.4 Analysis of environmental samples 18

3.4.5 Effect (E) characterisation 20

3.5 Risk assessment 23

3.5.1 The hazard quotient approach 24

3.5.2 Probabilistic risk assessment 27

3.5.3 Ecological Relative Risk (EcoRR) 31

4 Monitoring, validation and feedback 34

4.1 Quality assurance and quality control 34

4.2 Monitoring 35

4.2.1 Sampling and sample handling 35

4.3 Validation of risk assessment 39

4.4 Characteristics of ELISA (enzyme-linked immunosorbent assay) 40

4.5 How ELISA works 41

4.6 Validation of ELISA data using instrumental methods 42

5 Risk management 43

5.1 Integrated pest management 43

5.2 Remediation options 44

5.3 PIRAMS model parameters and data requirements 45

5.4 Risk management strategies 47

Part B: Case studies 51

6 Case study at Van Noi 52

6.1 Background 52

6.2 Field site characterisation 52

6.2.1 Field site description 52

6.2.2 Field site investigation 52

6.3 Hazard identification 54

6.4 Risk characterisation 54

6.4.1 Exposure characterisation 54

6.4.2 Ecotoxicity 54

6.5 Risk assessment 57

6.5.1 Hazard quotient approach 57

6.5.2 Probabilistic risk assessment approach 58

6.5.3 Ecological Relative Risk 58

6.6 Risk management 60

7 Case study at Ninh Thuan 62

7.1 Introduction to the Ninh Thuan region 62

7.2 Field site characterisation 62

7.2.1 Supplementary irrigation 62

7.2.2 Chemical use 63

7.3 Problem formulation and hazard identification 64

7.4 Risk characterisation 64

7.4.1 Exposure characterisation 64

7.4.2 Measured data 64

7.4.3 Validation of the fugacity model 67

7.4.4 Toxicity characterisation 68

7.5 Risk assessment 68

7.5.1 Hazard quotient approach 68

7.5.2 Probabilistic risk assessment approach 70

7.5.3 Ecological Relative Risk (EcoRR) 70

7.6 Risk management 71

8 Case study at Hoc Mon 73

8.1 Introduction to Hoc Mon 73

8.2 Field site characterisation 73

8.2.1 Supplementary irrigation 73

8.2.2 Chemical use 73

8.3 Problem formulation and hazard identification 74

8.4 Risk characterisation 75

8.4.1 Exposure characterisation 75

8.4.2 Toxicity characterisation 76

8.5 Risk assessment 78

8.5.1 Hazard quotient approach 78

8.5.2 Probabilistic risk assessment approach 78

8.5.3 Ecological Relative Risk (EcoRR) 79

8.6 Risk management 80

8.7 Conclusion 80

9 References 81

Appendix 84

Preface

With Vietnam's admittance to the World Trade Organization, the quality assurance of its produce with regard to pesticide residues will become even more important. The government's challenge for education, research and extension is to cope with the public demand for clean and safer agricultural practices by reducing the environmental impact resulting from the excessive use of pesticides, while maintaining profitability in agriculture.

The AusAID CARD project CON0016—*An Integrated Approach to Strengthening Institutional Infrastructure for Environmental Risk Assessment, Monitoring and Remedial Action for Pesticide Residues,* conducted in 2001-2003—was designed to help develop the technology and operational tools needed to ensure that Vietnam's agricultural produce would meet requirements for maximum residue limits (MRLs). This project aimed to meet these challenges by developing recognised risk assessment methodologies for use in Vietnam. This project specifically aimed to strengthen the scientific expertise of scientists, university teachers, policy makers and the Vietnamese rural community. Increasing the capacity for risk assessment and more informed decision-making usually reduces risk for all stakeholders. Capacity-building was achieved by providing simple tests based on enzyme-linked immunosorbent assay (ELISA) technology for pesticide monitoring, as well as by the application of risk assessment methods to quantify the impact of pesticides on farm produce and the environment.

Support was gained from ELISA tests developed by the Vietnamese partners in the major ACIAR project PHT/1996/004—*Monitoring mycotoxins and pesticides in grain and food production systems for risk management in Vietnam and Australia* (July 1999–June 2004). The stated objectives for that ACIAR project were:

- *To train and strengthen Vietnamese scientists' existing knowledge on the application of simple cost-effective analytical tests (ELISA) for monitoring pesticide residues, with proper validation by routine analysis using GLC and HPLC;*
- *In a workshop setting, to establish protocols for risk assessment using baseline monitoring data on the extent of environmental contamination by key pesticides at two contrasting sites in the northern and the southern areas of Vietnam; and*
- *To develop an integrated system to assess the risk of agrochemicals used in crop production (choice of pesticide, application mode, topography and meteorology, crop factors and land and water use). Results from risk models will provide Vietnamese planning*

authorities with tools for guiding future land-use development, assessing potential environmental risks associated with farm chemicals, and designing cost-effective monitoring programs.

The AusAID CARD project was designed:

- to extend the range of the impact of the ACIAR project by fostering expertise in pesticide monitoring tests within Vietnam, thus increasing its extent of application; and
- to develop expertise in the risk assessment and management of pesticides used in agricultural production in Vietnam. There is already significant Vietnamese expertise in pesticide analysis, using costly instruments, in a few laboratories. This expertise was accessed during this project in both Hanoi and Ho Chi Minh City. The application of ELISA technology is extending this expertise, by allowing more screening analyses of farm produce and environmental samples, more cheaply, and more sustainably.

This book describes the risk assessment process (Section 2; Fig 3.2) used in the project's three case studies, supported by explanatory notes to help managers and local scientists understand what information and decisions are needed to complete site-specific risk assessments. Preparation of this text was facilitated by a two-month visit by Pham Ngoc Ha and Nguyen Thi Thu Trang to the University of Sydney in late 2003: their significant contribution is gratefully acknowledged. This book also includes recommendations for future activities to ensure the CARD project has a sustainable outcome. Application of enzyme-linked immunosorbent assay (ELISA) technology for pesticide analysis is likely to play an important role in improving the quality of Vietnamese agricultural produce and supporting a cleaner environment.

The authors hope that the procedures and case studies described in this book will form a template for future work in Vietnam. In particular, there is a need to establish more effective residue surveys on a national basis, using the data as a base from which to monitor improved practices. There is also a need to carry the consequences of this work through to practical conclusions in smallholder agriculture in Vietnam, so that the probability of any contamination with pesticide residues is reduced to an acceptable level. That is a considerable challenge for Vietnamese science and technology.

Angus N. Crossan
Nguyen Thi Thu Trang
Pham Ngoc Ha
Ivan R. Kennedy
May 2005

Glossary

Application The action of applying a pesticide to a crop, such as by knapsack sprayers, an automated machine known as a ground-rig or as an aerial application sprayed from an aircraft

Bioconcentration The tendency of chemical substances to increase in concentration as a result of their consumption in a chain or organisms, each feeding on the other

BCF Biological concentration factor, indicating the tendency of a chemical substance to concentrate in organisms or particular tissues such as fat

Buffer zone A designated area around the point of application of a pesticide separating it from sensitive areas such as rivers or pastures where animals graze into which drift may occur

Chain of custody A recording system to indicate responsibility for environmental samples during stages in their transport and storage for the purposes of analysis as part of quality control (QC)

Concentration A measure of the amount of a substance dissolved in a physical phase (eg g/L, moles/L=M)

Distribution coefficient The ratio of concentrations of a chemical substance distributed between two phases (eg water and air, soil and water, oil and water)

Dose The total amount of a chemical substance delivered to an organism (eg by contact, ingestion or inhalation)

Drift The tendency of pesticide formulations to be transported downwind in air because of their limited rate of sedimentation — the smaller the droplet the greater the risk of drift

EcoRR Ecological relative risk — a quantitative measure of the risk of exceeding some critical value regarding toxic effects of chemicals

Ecotoxicity A measure of the degree of negative or lethal effect on organisms

ELISA Enzyme-linked immunosorbent assay — analysis using specific antibodies to bind analytes, quantified using the activity of an enzyme

Endpoint A quantitative value considered as of significant concern, such as **MRL** or **LD_{50}**

Exposure An amount or concentration of a toxicant potentially causing a significant effect

Fugacity The dynamic 'escaping tendency' of a chemical substance, related to its pressure, causing it to move from one phase where it has greater fugacity to another (eg water to air) where it has less.

GLC or GC Gas-liquid chromatography, an instrumental method of separating and analysing the chemical components of a mixture of volatile compounds as a result of differences in their distribution between gas and liquid phases

Half life ($t_{1/2}$) The time taken for the concentration of a chemical substance to decline to half its current value, by local degradation or dissipation to other environmental phases

Hazard Any factor causing a risk of harm

Henry's constant The vapour pressure divided by the concentration in water of a chemical substance; H = P/[Conc.]; substances with a high constant exert a high pressure for a relatively low dissolved concentration in water (eg endosulfan)

HPLC High performance liquid chromatography, an instrumental process of analysis similar to GLC but using redistribution of an analyte between a liquid and a solid to allow its analysis by a suitable detector

HQ Hazard quotient, indicating the ratio of an exposure divided by a hazardous effect

IPM Integrated pest management, a wide ranging process of managing pests using as much ecological (eg insect behaviour) and environmental information as possible, allowing natural processes of pest control (eg predation) to operate, thus reducing the need to apply toxic chemicals while optimising yields of crops

IFS Integrated farming system, optimising a range of inputs including pesticides, nutrients, crop rotations and agronomic practice whilst maximising profitability; the implementation of site-specific practices based on intensified knowledge of the local ecosystem

K_D The relative concentration at equilibrium and a stated temperature of a chemical distributed between two phases such as water and soil, or water and air

K_{ow} The relative concentration at equilibrium of a chemical distributed between oil and water

LC_{50} A 'lethal' concentration of a chemical in water that will kill half the test population

LD_{50} A 'lethal' dose of a chemical that will kill half the number of a test population

LOEL Lowest observed effect level, indicating the lowest dose or concentration causing a specified response

Modelling A description of some process, usually involving mathematical relationships developed from controlling factors allowing predictions to be made of outputs using known inputs

Monitor To observe over a period of time, usually by measuring

Maximum residue level (MRL) A defined level of concern, indicating a statutory maximum residue limit that is allowed in produce for a farmer following good agricultural practices

NOEL No observed effect level, indicating a dose or concentration with no observable toxic effect

Partitioning The process of redistributing across the boundaries of different phases in contact (eg between soil and water, or water and air)

PEC Predicted environmental concentration, determined spatially and temporarily by factors such as **fugacity** and **half life**

Pesticide Any chemical agent with lethal effects used to control pests

pH A measure of acidity, defined as $pH = -\log_{10}[H^+]$ where $[H^+]$ is the hydrogen ion concentration; pH 7 indicates neutrality where $[H^+] = [OH^-]$

PIRAMS Pesticide inventory risk assessment and management system, an integrated process allowing pesticide data to be used scientifically to manage and reduce risk

Probability The likelihood of an occurrence

QA Quality assurance — the application of a set of objective tests to establish defined standards or benchmarks

QC Quality control — the application of defined measures, such as freedom from pesticide residues, to ensure quality

Risk An estimate of the degree of hazard that some factor presents

Risk management An ordered process of minimising exposure to a hazard thus reducing risk

Sample Collect some material object (eg water, soil or air) using a standard method for the purpose of monitoring some characteristic value

Score An arbitrary value used to assign relative risk, but prone to error when used out of context because of the absence of a quantitative scale

SOP Standard operating procedure — a protocol or standard method indicating a procedure such as one for an **ELISA** analysis

Taxa The classified species of living organisms, organised into families and genera

Toxicity The likelihood of obtaining a negative effect on the health of an organism, typically measured as the $\mathbf{LD_{50}}$ or $\mathbf{LC_{50}}$

USEPA United States Environmental Protection Authority

Validation The process of confirming some method or predicted value

Vapour pressure The equilibrium pressure exerted by vaporisation of a pure substance

PART A

A practical guide for risk assessment and management

How to use this book

This book explains how to conduct risk assessments to select safer pesticides and to improve the management of pesticide use. The various stages presented here may be followed as a handbook for risk assessment. The format is intended to demonstrate the order of collecting and interpreting data to carry out meaningful risk assessments.

It is important that the data and information collected during a risk assessment are reported. This book explains the structure and detail necessary for such reports, and identifies the kinds of information that should be included in a report. The length and level of detail of a risk assessment report will vary, depending upon the complexity and size of the assessment. The three case studies presented here can be used as guides and sources of essential information, ensuring that your work is acknowledged and referenced appropriately. Remember that better pesticide management relies on the effective communication of your risk assessment .

Each section presents 'actions' , which describe the specific tasks required to fulfil the risk assessment process, and a brief rationale. Examples of completed 'actions' are shown in the case studies (Part B). Appropriate management requires good assessment: the authors believe this is achieved through informed action, hence the strong emphasis on practical application.

Introduction

1

1.1 Scope of this book

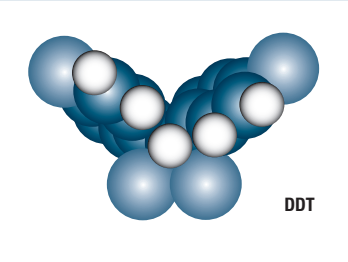
As custodians of their land, farmers and their advisers have a responsibility to continually improve their understanding of their land. Indeed, farmers usually understand their land and its needs better than anyone else. We believe that there are long-term benefits to be gained by improving people's basic understanding of pesticide risks and their management. This book is therefore designed to improve pesticide selection and management in Vietnam and Southeast Asia by providing detailed information about pesticide management skills.

The main challenge for pesticide management is the gathering of accurate information to ensure well-informed decision-making. Sometimes this information can be collected from standard texts, but at other times it is more feasible to use data from previous studies. There already exist books that describe methods of risk assessment, with the emphasis ranging from protecting human health to ecological risk. However, our project deliberately chose to develop methods that took a simple and logical approach to assessment, which could be adapted and applied without expert knowledge or the purchase of expensive licences. We believe that all users of pesticides should be able to make logical decisions about such use in specific farming systems. In this book, therefore, rather than simply providing tables or lists of solutions, we have chosen to describe a logical process for assessment and management, because we realise that the many site-specific factors within each management regime mean that such general rules do not exist. This book explains what information needs to be collected and how to use such information appropriately.

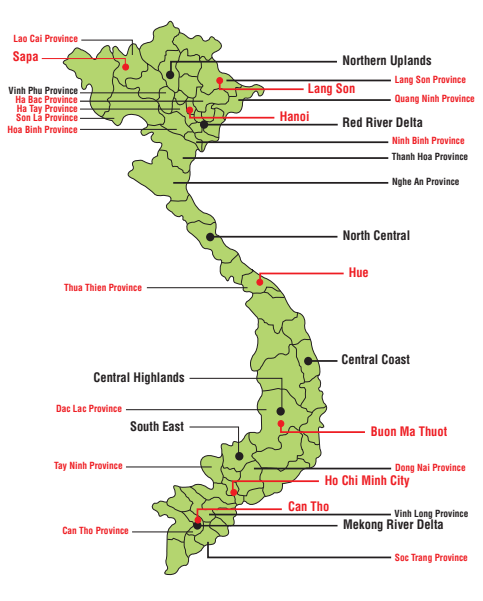
1.2 Background

This book's approach to risk assessment and information were developed as part of the AusAID CARD Project CON0016 *An Integrated*

1



Space-filling model of DDT



Vietnam

Approach to Strengthening Institutional Infrastructure for Environmental Risk Assessment, Monitoring and Remedial Action for Pesticide Residues. The project involved the co-ordination of workshops, field and laboratory activities, with interaction among all research facilities. The four original Vietnamese Institutes involved in the project were the Hanoi University of Science (HUS); University of Agriculture and Forestry, HCM City (UAF); Centre for Analytical Services and Experimentation (CASE); and the former Post Harvest Technology Institute, HCM City (PHTI, now Sub-Institute for Agricultural Engineering and Post Harvest Technology, SIAEP). As the project continued, it extended to include the Plant Protection Departments (PPD) from both Ho Chi Minh City and Hanoi, as well as the former Post Harvest Technology Institute (PHTI, now VIAEP) in Hanoi.

During the project, many challenges specific to the Vietnamese environment and local agricultural practices became apparent. To illustrate approaches to Vietnam's ongoing management of pesticide use, risk assessments were conducted. This book is based on the final project manual *Agricultural Pesticides in Vietnam: An Integrated Manual for Risk Assessment, Monitoring and Management*.

1.3 How this book is structured

Part A demonstrates the framework that should be used to conduct systematic risk assessments. This framework is presented as a step-by-step methodology (Section 3) that describes and explains the data requirements and the relatively simple calculations that are required at each stage. Flow diagrams (Figs 3.1 and 3.2) summarise this process, with all stages of the risk assessment and management process cross-referenced to the appropriate sections within this book. Section 4 explains monitoring, validation and feedback practices, while Section 5 describes risk management options.

Part B shows the methodology in practice by describing three Vietnamese field studies—from the regions of Van Noi (Section 6), Ninh Thuan (Section 7) and Hoc Mon (Section 8)—that were developed and performed as part of the project. These three examples illustrate the methods and actions described in Part A. The field studies also provide basic reference material for future risk assessments where required information is not readily available or easily obtained: although site-specific information and data are most desirable, the challenge of limited resources and skills in Vietnam often make this difficult.

1.4 The importance of feedback

Humans are naturally adaptive creatures and often learn by 'trial and error', producing a continuous series of improvements. Improvements in good pesticide management practice are gradual but deliver worthwhile rewards—improved crop quality, improving profits, improving farmer and community health and sustaining the environment, all of which contribute to long-term prosperity.

The key to good pesticide management, therefore, is to consider it as an ongoing process of improving practices. This involves using the collected data to provide feedback to test the assumptions or the precision of the original proposals. Effective feedback also monitors improvements in management practices. Logical and scientifically rigorous risk assessment has many benefits, can be validated by feedback and can be further assured by regulatory decisions. Good science thus ensures good policy and good regulation, leading to improved environmental protection and consumer protection. This book provides the framework through which a structured feedback process can be incorporated into pesticide management practices.

2 Identifying the problem

2.1 What are pesticides?

Pesticides are chemicals used to protect crops from insects (insecticides), other animal pests (eg rodenticides, miticides), weeds (herbicides) or diseases, in both dry land and irrigated agriculture. Pesticides are usually synthetic, toxic chemicals, with a wide range of differing properties designed either to kill pests or to inhibit their growth. **The very nature of pesticides—generally designed to kill target species and potentially able to harm non-target species, including humans—means that they can be dangerous**. Pesticides can be more hazardous when, through leaching or other processes, they move away from the farm where they were applied. For example, they can contaminate more susceptible areas, such as nearby water sources, or can become incorporated into agricultural crops or animals, becoming contaminants of food products (which can prevent the sale of produce on international markets). Pesticides can also pose health hazards to humans who ingest contaminated food or through skin/respiratory contact during pesticide use.

All these potential risks need to be managed. The first step is to accurately characterise the extent of the risk. However, it is difficult to assess the current safety of pesticide use in Vietnam because of a lack of information regarding their sale and use. Farming practices differ from region to region, but generally the instructions for pesticide application appear inadequate. The pattern of pesticide use varies from community to community because of different levels of knowledge and understanding. Also, different localities have different environmental qualities that should be considered when pesticides are being used.

Effective management of pesticides may therefore involve considering the specific qualities of the local area, with a deliberate

effort being required by every farm management group to ensure that all pesticides are used appropriately. However, with good education and a supportive attitude towards continually improving pesticide management, good practice can be achieved.

2.2 Pesticide use and the concept of risk

In agriculture, pesticide use has the potential to cause problems through contamination of farm produce or the local ecosystem. This 'potential' to cause problems is described as a '**risk**'—it exists because the wrong choice or misuse of pesticides may damage the environment, human health and international trade. It is the purpose of **risk assessment** to measure the risks, and hence to inform decision-making.

> *Risk assessment can be defined as the process of assigning magnitudes and probabilities to the adverse effects of human activities or natural catastrophes* (Suter, 1993).

There are two approaches to risk assessment; measuring **relative risk** or **actual risk**.

Relative risk is based mostly on comparisons of different pesticides, rather than determining real risk or actual exposure. A relative risk assessment thus uses comparisons based on a more theoretical approach: of two pesticides, it is the one with the longer half-life that will be labelled as the greater 'risk'. However, a pesticide with a longer half-life may not necessarily present more risk in the short term. Measuring actual risk thus incorporates the use of exposure data and modelling, including field validation.

3 Risk assessment

3.1 Introduction

The objective of risk assessment is to determine whether the probability of **exposure** of a contaminant is sufficient to cause an undesired **effect** (these terms—exposure and effect—are explained in more detail below).

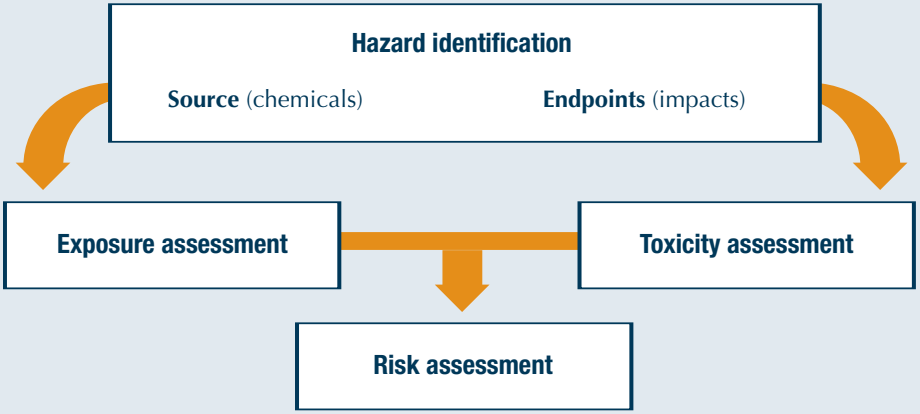
Risk assessment of agrochemicals, such as pesticides, measures and characterises the hazard of their use. Based on the common expression 'the dose makes the poison' (Paracelsus), a framework can be used to determine the dose with respect to a specific consequence (Figure 3.1). The identification of the hazard must include information on related exposure and toxicity to ensure meaningful assessment. Once a hazard is determined, then it must be measured. Usually such measurement involves field sampling to ensure environmental limits are not exceeded, or experiments may be conducted. Management or change can then be introduced to correct or improve an unfavourable practice. These changes can also be assessed to ensure improvement. The entire process is centred on the risk assessment framework, but draws on multidisciplinary skills.

The process of risk assessment must be transparent to enable discussion among all stakeholders and improvements to the process. To ensure risk assessment is worthwhile, therefore, it is essential that the assessment is reported. This book demonstrates how to collect and report data for risk assessment.

This section details the information required and the methods used to conduct a risk assessment (Fig 3.2—numbers in the diagram provide cross-referencing to the relevant section in this book, with the same system used throughout the case studies in Part B).

Risk assessment is the first step in improving pesticide selection and management. A good quality risk assessment will identify the likely effect of pesticide use. The process will first

Figure 3.1. Risk assessment framework



determine the likely concentration of pesticide resulting from a known use and exposure to non-target species. The risks associated with such use are then estimated. Different modes of use can then be compared and decisions made as to the most appropriate practices, considering all the relevant factors for a specific area.

3.1.1 Quality of information and assumptions

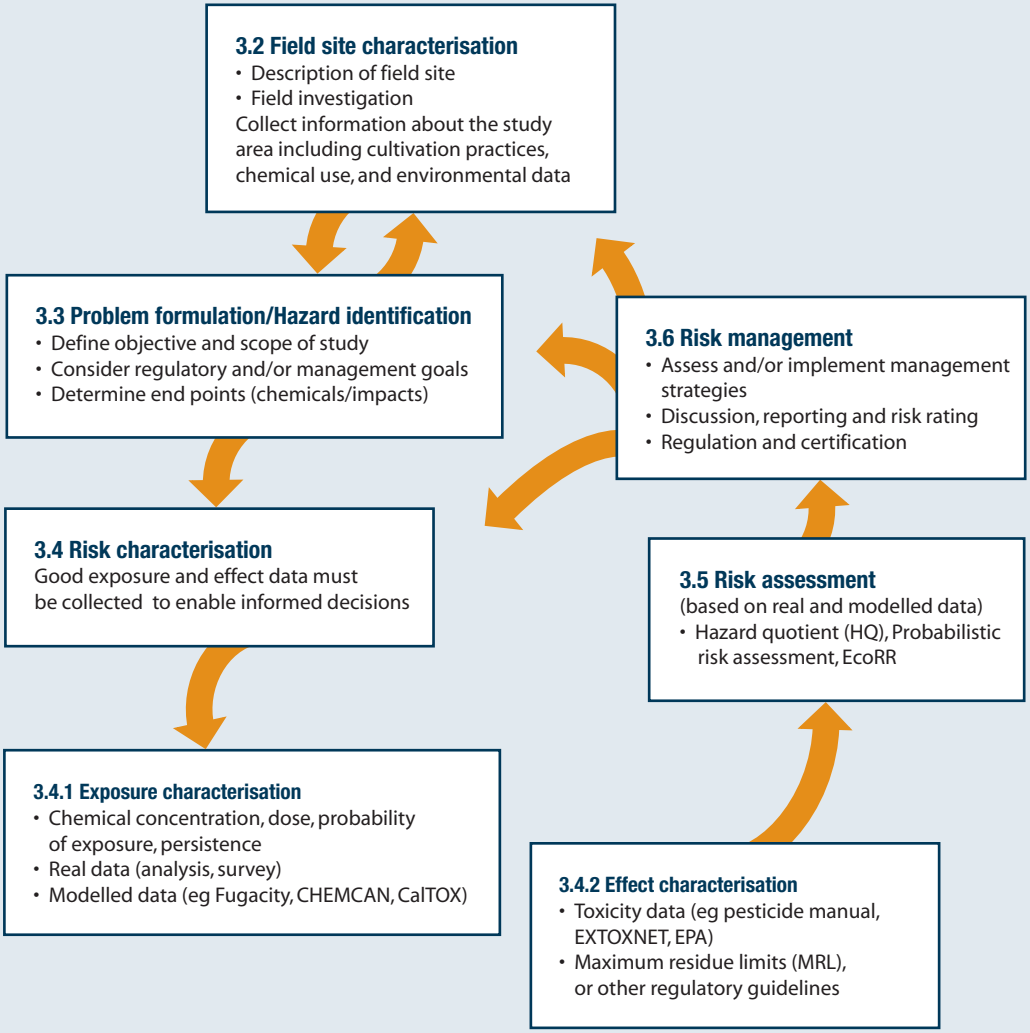
The quality of the collected information determines the quality of the risk assessment. When good quality data is used well, the risk assessment can be of high quality. However, the opposite is also true—when inadequate data is used, or good data is not used appropriately, then a poor assessment will result.

The person undertaking the risk assessment is responsible for selecting the most reliable/accurate data for an assessment. When data is lacking, it is their responsibility to make necessary assumptions and to include these assumptions in the report of the risk assessment.

It is essential to show what assumptions were made during the procedures to indicate how better assessments can be made. This could involve improving the quality of the data, or conducting some focused sampling and field studies to fill data gaps. This approach demonstrates a benefit of using risk assessment to select and manage pesticides.

The risk assessment method identifies where more knowledge (information or data) is needed

Figure 3.2. Flow chart of the risk assessment process



to feed back into the assessment process and to **improve** the overall assessment. On-going assessment takes place when **feedback** continues over time, establishing **best management practices**.

3.2 Field site characterisation

Identify an area to be the focus of the risk assessment

Often the field site is already the focus of attention because of some historical concern. As previously mentioned, the use of pesticides indicates potential risks.

Potential alarms or causes for concern may also include observed damage to the ecosystem (eg animal kills or vegetation dieback); the introduction of a new pesticide; or rejection of produce at market because of pesticide contamination, particularly where there is traceback evidence identifying the site. Any of these occurrences could suggest that a better pesticide could be used or that management practices need to be improved.

Once chosen, the field site should be investigated and adequately described.

3.2.1 Description of the site

Record the location of the field site—either an exact address or map reference. Record (or assign) the site's name and reference number. Include the details of a contact person associated with the site to enable effective follow-up if required.

Within the report, where possible include pictorial and descriptive aids (Table 1). A short description should accompany any maps or pictures that describe the scale and intensity of farming practices.

Table 1. Visual aids to help describe a site location

Aid*	Description and purpose
Maps	To show site's location and features
Aerial photographs	To show site's features, including vegetation and waterways
Geographical Information System (GIS)	Digital template containing selected features of field site

*These aids may be obtained from various agencies, including the Ministry of Agriculture and Rural Development (MARD), other research institutions or universities.

3.2.2 Field investigation

Develop a survey record pro-forma to complete when investigating field sites and collecting data.

A standard survey form (pro-forma) is useful for organising data collection, especially if there is an on-going risk assessment program or several sites to be compared. By consistently collecting the same relevant information (Table 2 and case-studies in Part B), better comparisons can be made.

The required details of pesticide use, water use and other information about cultivation practices (Table 2) can be obtained from local farmers or their advisers, who tend to be most knowledgeable about particular field sites. As it is farmers and local communities who will

Table 2. Required information about the field site

Type of information	Data to record
Pesticide use	**Name and type of chemicals used***
	Frequency of use*
	Rate of application*
	Timing of application (eg summer or winter)
	Any notes or observations
Water use	**Volume of water used for each irrigation***
	Number of irrigations*
	Description of the water system (possibly using the site map)
	Any notes or observations
Soil characterisation	**Organic matter (%)***
	pH, clay and sand content
	Soil texture and colour
	Any notes or observations
Meteorology of field site and region	**Rainfall characteristics***
	Temperature variations
	Wind speed
	Prevailing wind
	Number of storms
	Any notes or observations

* This information is considered the most important to collect and determine where possible, or to estimate if necessary.

benefit most from a greater understanding of the risks associated with pesticide use, and from improvements in the selection and management of pesticides, they should be consulted wherever possible.

When the required data is beyond the scope of local pesticide users, the required information (Table 2) can be gathered by searching sources such as the Ministry for Agriculture and Rural Development (MARD), Plant Protection Departments (PPD) and the Internet. When accurate information is not readily available (a frequent occurrence in this project and a common challenge in Vietnam), a field survey and some simple analyses should be done.

Soil characterisation can be conducted in the laboratory following the comprehensive set of methods published by the Soil Science Society of America (Klute and Page 1982; Sparks, 1996; Dane, 2002). The amount of organic matter in soil is considered to be one of the most important characteristics deciding the fate and transport of most (non-ionic) pesticides. A good determination of organic matter content is therefore required for any desktop modelling of pesticide behaviour. If Part 3 of *Methods of Soil Analysis* (Sparks, 1996) is not available, the Loss-On-Ignition approach—a relatively simple and inexpensive technique, although requiring a muffle furnace—can be used to estimate the percentage of organic matter in local soil (details provided in Appendix 1).

3.3 Identifying hazards and formulating problems

Hazard identification involves identifying the chemicals in use and determining the impacts they could have on the local environment or on the quality of local farm produce. Problem formulation involves defining and stating the objectives and scope of the risk assessment. The 'introduction' and 'aims' of a risk assessment report should contain a short description of the problem and the specific hazard(s).

The identification and problem formulation processes provide a link between the regulatory or management goals and the risk assessment (Norton et al., 1992). Based on the legal requirements or management goals, the standards (i.e. the levels of protection of an ecosystem or its produce) can be identified for various aspects including the ecosystem, human health, nearby farming systems, and the quality of farm produce. Different standards can be defined for different circumstances. The level of protection should be directly related to the value of the commodity being managed. Good, well-managed farming practices take account of all these aspects while still producing a profit.

It is sometimes difficult to make clear distinctions between field site characterisation, hazard identification and problem formulation, as all these processes are required to begin the risk assessment procedure.

Example

Ninh Thuan is the largest grape growing area in Vietnam. The biodiversity of this region is rich and varied, so it is necessary to protect the area's ecosystems as well as to assure quality of the grapes produced.

Several insecticides and fungicides are used as the grapes are grown. A Risk Assessment (RA) can identify how the chemicals in use might impact on the environment, and determine whether chemical residues in the grapes might prevent their sale. The objectives of the RA would be to raise the level of farmer/community awareness, to identify which standards are at highest risk and to compare the relative risk of the different chemicals being used.

Appropriate management strategies can then be suggested to ensure long-term sustainability and profitability of the farming practice and the region.

3.4 Risk characterisation

3.4.1 The need for exposure and effect data

Once the hazard has been defined and the problem formulated, it is necessary to establish **exposure characterisation** (the amount of chemical being used) and **effect characterisation** (what effects might occur at a predicted range of concentrations). These characterisations are based on exposure, toxicity or other effect data that can be collected from field studies and literature searches. For informed decision-making, good exposure and effect data must be collected.

3.4.2 Data collection and requirements

Before the hazards are characterised, good data sets must be collected for the two fundamental elements of the assessment, **exposure (e)** and **effect (E)**. Data collection for these two elements should be linked so that compatibility between toxicity and exposure pathways can be maintained when necessary, for example in terms of ecological risk assessment (Norton et al., 1992).

3.4.3 Exposure (e) characterisation

Collect exposure data by field sampling, by modelling the information collected during the field investigation (see case studies for examples), or by a combination of both methods.

Exposure: The concentration or amount of toxicant available to cause an **effect** (damage) eg the concentration of pesticide within the ecosystem, as a result of farming practices, that is available to harm native species. Exposure may also be defined as the concentration of pesticide within produce that is considered to indicate contamination (i.e. above a prescribed limit).

Exposure can be determined in several ways, including analysis of environmental samples, modelling or the use of adopted data (the last being the least desirable for risk assessment). An objective of exposure characterisation is to evaluate the distribution of pesticides within the various environmental compartments to determine concentration. The time from pesticide application—taking into account the associated persistence of a chemical in the ecosystem—affects the risk of contamination. The exposure routes for produce and off-target organisms also need to be carefully considered.

The only way of ensuring an accurate assessment is to obtain high-quality field or commodity data (using data from a similar study will provide a risk assessment that is not area-specific). Accuracy and cost-effectiveness are greatest when exposure data is collected from both an analysis of field samples and modelling, for example, by combining desktop modelling with selective field sampling for validation.

Modelling is a mathematical desk-top approach used to create data based on the chemical properties and previously observed behaviour of a given pesticide. However, simplifications and assumptions made during calculations can limit modelling approaches. Thus, although modelling is useful for predicting likely pesticide fate, especially when resources are limited, **modelling should be validated using field data**. A well planned study will include a combination of modelling and field sampling or monitoring to maximise cost-effectiveness and accuracy.

Choose a model to provide data either for a preliminary risk assessment or to add to limited field data.

Several mathematical models are available that predict the environmental fate and concentration of pesticides, including CREAMS (Knisel, 1980), EXAMS II (Burns, 1990) and PRZM (Mullins et al., 1993) for determining predominantly runoff information, while multimedia models such as ChemCAN, SIMPLEBOX, CalTOX, EcoFATE and Fugacity I, II and III (Mackay, 2001) provide an understanding of the distribution of pesticide into different environmental phases. Many of these models can be readily downloaded from websites of USEPA (www.epa.gov) or the Canadian Environmental Modelling Centre (www.trentu.ca/cemc/welcome.html).

3

In the project reported in this book, the approach for determining environmental concentrations of pesticides was based on the Fugacity model (Mackay, 2001), which has an obvious advantage over single media models as it calculates the concentrations of residues in all environmental compartments. This approach is detailed in the case studies (Part B, Section 5).

The data obtained from modelling pesticide application (rate of pesticide application and the area to which it was applied) is useful for assessing a large number of chemicals, and can be used to focus field sampling and monitoring of persistent chemicals. In addition, modelling is the only possible way to predict the fate of new chemicals not yet in use (Mackay,

Table 3. Important pesticide properties required to model pesticide fate and transport

Pesticide property	Label (units)	Brief description
Water solubility	Sol.(mg L^{-1})	The amount of pesticide that can dissolve in pure water (a guide to solubility in natural waters)
Binding coefficients/ sorption data[a]	$K_{OC}/K_{OW}/K_d$ (Log scale)	To determine the amount of pesticide partitioned to organic matter, organic carbon or soil; may be obtained from the literature or determined experimentally (K_d)
Half-life	$t_{1/2}$ (days)	A guide to the longevity or persistence of a chemical in environmental compartments (soil, water, vegetation and air)
Vapour pressure	Pa ($mmHg^{-1}$)	To indicate the extent of vaporisation of a chemical into air after application
pH, pKa	(pH units)	Can be a guide to the form (non-ionic or ionised/polarised) of a pesticide in the environment.
Bioconcentration Factor	BCF	A determination (often algorithmic) of the potential for a chemical to accumulate in higher biological orders
Application data	Rate (kg ha^{-1} or L ha^{-1})	This data may have been collected in the field assessment; recommended rates should appear on container labels

[a] Inaccurate binding coefficients are a cause for discrepancy between modelled data and field data. Values obtained from the literature may not represent the region being studied: when accurate information is required, it would be prudent to conduct the simple sorption (Kd) experiments using the soil type/s included in the study.

2001; Sanchez-Bayo et al., 2002). A modelling approach was especially appropriate in this project, because exposure data was unavailable and difficult to obtain. Although calculations of exposure are overestimated in many cases, it is good practice to conduct the assessment based on the worst-case scenario (Sanchez-Bayo et al., 2002). Any overestimation can be corrected by validation using real data or used to provide a safety margin for management practices.

Collect pesticide data that describes the properties of the pesticides being used to model the fate and transport of pesticides.

Several key pesticide properties (physical and chemical characteristics) are required to model the fate and transport of a pesticide (Table 3), although the specific data requirements are prescribed by the specific model being used. Any modelling approach that does not include these pesticide characteristics is probably too simplistic.

Thus, physical-chemical properties for the insecticide endosulfan, identified from the literature (Table 4), are appropriate for use in modelling, but could be improved by conducting some simple site-specific tests.

One of the largest discrepancies in pesticide modelling occurs in obtaining accurate distribution coefficients, which are used to measure and report the behaviour of a pesticide.

Table 4. Physical-chemical properties[a] of endosulfan; provided as an example of the data requirement for fugacity modelling (Mackay, 2001)

Chemical	Endosulfan
Mol. Wt.	406.9
Solubility	0.33 mg L^{-1}
Henry's Const.	1.48 (α), 0.07 (β)
log K_{OW}	4.76[a]
$t_{1/2}$ Soil	50[b] days
$t_{1/2}$ Veg.	5[b] days
$t_{1/2}$ Water	35[b] days
BCF[c]	4.9
BCF[d]	2740.9

[a] Tomlin, 1997, unless otherwise indicated;
[b] Howard and Meylan, 1997;
[c] $BCF=0.607+0.893\log K_{OW}$ (Chiou *et al.*, 1977);
[d] $BCF=0.048K_{OW}$ (Mackay and Paterson, 1982)

Thus K_d is the representation of the partitioning of organic solutes between water and soil or sediment, also referred to as an adsorption isotherm. The measured K_d is site-specific and varies directly with temperature, pH, the chemical and physical nature of the soil, and the specific organic chemical. This means there are too many variables to record K_d values for all environmental conditions. Therefore the more 'reportable' parameters K_{OW} and K_{OM} are derived to enable better prediction of the fate of organics. When using models to calculate environmental concentrations, errors and

uncertainties should be identified and reported for the experimental values used for modelling input (Mackay, 2001; Baskaran, 2002), and all assumptions should be detailed in the modelling report so that the level of uncertainty within the risk assessment process can be considered when making management decisions.

3.4.4 Analysis of environmental samples

The concentrations of pesticides can be determined by analysis of field samples. When conducted following quality assurance standards with quality control (Section 4), such site-specific field data is the best data for risk assessment, providing the best basis on which to select safer pesticides.

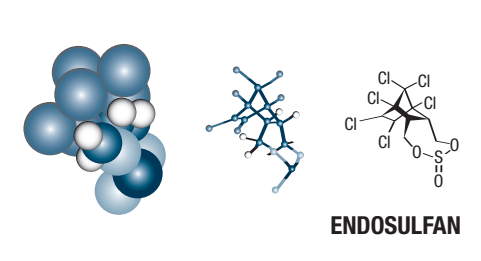
Gather pesticide exposure data: concentration data can be obtained by collecting and analysing field samples

The process of sampling and analysis needs to be well planned. Sample analysis requires specialised skills and equipment (detailed in Section 4), so it is usually carried out by an appropriate laboratory or by those proficient in the use of enzyme-linked immunosorbent assays (ELISA). In the context of exposure characterisation, the purpose of a field-survey is to collect information regarding pesticide applications for the areas being studied. As already described, this data can be used in modelling. From our experiences in Vietnam, collecting data on pesticide application from field sites is sometimes difficult, as farmers do not record their crop protection practices, so it is important to validate the information on application practices by field sampling and analysis.

It is important to specify the level of quality control (QC) and the degree of quality assurance (QA) available for collection and analysis of field samples (see Section 4 for details). There are many prescribed sampling procedures. The analytical team must establish a plan appropriate to the objectives and scope of the study. To obtain good QC and QA for field work and laboratory analysis, a set of standard operating procedures should be created and followed by all collaborating researchers. For example, the procedures should specify the form of log book to be used for data collection and all methodologies to be used.

For several reasons, analysis of samples is best carried out by a specialist laboratory, which will have established QC and QA procedures and will produce the best quality data. Using an analytical laboratory can also save time, especially when compared to the need for 'in-house' development and validation of analytical methods before sample analysis can occur. Having samples analysed by an independent third party also adds an element of impartiality to the project. However, one drawback with outsourcing analytical services may be the expense, so this must be included in the project's budget from the outset.

Participants in risk management workshop luncheon, University of Agriculture and Forestry (Nong Lam University).



Space-filling model of endosulfan

In Vietnam, the Plant Protection Departments in Hanoi and Ho Chi Minh City can offer advice and analytical expertise regarding pesticide analysis.

Instrumental analytical methods

Processes such as gas chromatography (GC) and high performance liquid chromatography (HPLC) can be used to separate pesticide compounds from interfering substances. Using specific detectors, such as electron capture (ECD) for organochlorines, these techniques identify and measure the amounts of the pesticides that have been separated. Pesticide molecules can be specifically identified through mass spectrometry (MS). Methods for instrumental analysis of pesticides can be obtained from handbooks of the Association of Official Analytical Chemists (AOAC, 2000) or from the British Pharmacopoeia guidelines. (If necessary, these methods can be modified and adapted for local use, but any changes to standard analytical methods must be correctly validated, with the relevant evidence included in the risk assessment report.) Although instrumental analytical methods are precise and accurate, they are time-consuming and expensive, requiring highly skilled technical staff and expensive equipment. Nevertheless, a set of samples should be analysed using instrumental techniques to validate and confirm other techniques such as modelling or ELISA.

ELISA

Enzyme-linked immunosorbent assays (ELISA) provide rapid immunodiagnostic analysis based on sensitive and highly specific antibodies, and are capable of screening a large number of samples for pesticide residues, showing which samples are contaminated. ELISA tests are simple and cost-effective (Hammock and Mumma, 1980; Skerritt, 1995; Lee and Kennedy, 2001). Appropriate methodology and discussion were provided in the manuals of workshops conducted in Vietnam at the Post Harvest Technology Institute (PHTI) in March 2002 and at the University of Agriculture and Forestry in July 2002.

Staff trained at these workshops can develop new ELISA test kits and are able to conduct training in this analytical technology. ELISA is especially useful for conducting screening tests, for example to check produce going to market, possibly reducing costs. New ELISAs are being developed within Vietnam: contact the Sub-Institute for Agricultural Engineering and Post Harvest Technology (SIAEP) in Ho Chi Minh City (formerly the PHTI) for updated information.

This book includes examples of the use of ELISA data, validated by instrumental methods (Fig 7.2). The exposure data for endosulfan in southern and northern Vietnam, used for the risk assessments, were obtained by both ELISA and GC methods (Bui et al., 2003; Pham et al., 2003). These examples show that a combination of analytical techniques can overcome the limitations of a single approach.

Surrogate data

Measurements at field sites are not always possible, especially for new pesticides undergoing preliminary assessment. Only modelled data may be available, probably overestimated because of the assumptions made during the modelling process. Therefore, availability of data from other application scenarios is desirable. For example, there may have been previous exposure studies at the field site, perhaps conducted by other research institutions or universities, that can be used for risk assessment purposes (Bui, 1998a, 1998b, 1998c, 1999, 2002). Such data can be obtained from the literature after peer review, and can be used either to support the modelled data or to perform a preliminary risk assessment, with appropriate checking. The methods used for data collection should be appropriate for the purpose and all QC and QA considerations should be reported.

3.4.5 Effect (E) characterisation

Select the 'effect' significant for the purpose under study. Determine and collect the 'endpoint' values that define the significance of the effect, using available literature or experimentation to collect these data.

The purpose of a risk assessment is to determine whether the activities being conducted produce a risk (or, as discussed, an 'exposure') that will produce an undesirable **effect**. Management goals can be established by allocating values appropriate to achieve best practice. This stage of the risk assessment thus defines qualities by giving values **('endpoints')** that are desirable for protection.

The effect value is the value, or range of values, where an undesirable outcome would occur, given sufficient **exposure**. For example, if we define our hazard assessment as a dose of pesticide that would kill half of a test population of a particular species (i.e. reaching an LD_{50}), then the effect value is the concentration of that pesticide at which that proportion of species

would be killed. Using the risk assessment approach described in this book, we can then determine whether our practice is likely to result in the exposure value becoming larger than the effect value, in which case the undesirable outcome is likely.

Effect values can be chosen for any factor that is considered the focus of the risk assessment. It is thus the effect that defines the risk assessment process. In the case of an ecological risk assessment, the effect concentration would be a range of ecological endpoints. For the management of residues in agricultural produce, the effect concentrations would be the Maximum Residue Limit (MRL) values or other management guidelines. This adaptability demonstrates the major advantage of quantitative risk assessment—the process can be used to assess, regulate and manage many situations. The challenge is how to quantify, meaningfully, the undesirable effect.

Ecotoxicity characterisation / ecological risk assessment: toxicity data

Toxicity data consists of all available data on the toxicity of the chemicals under consideration to the range of non-target organisms present in the relevant area.

Endpoints used in the field of ecotoxicology include:

- Lethal Dose (50%) (LD_{50})—the dose at which 50% of the test species is killed. LD_{50} values are determined in laboratory experiments and are most applicable to terrestrial species.
- Lethal Concentration (50%) (LC_{50})—the concentration at which 50% of the test species is killed. LC_{50} values are used for amphibious aquatic species, and are determined in laboratory experiments.
- No Observed Effect Level (NOEL)—this is the highest concentration that has been added to an experimental system without any effects (i.e. changes in growth, reproduction, activity, feeding) being observed.
- Lowest Observed Effect Level (LOEL)—this is the concentration at which effects of some kind (eg in growth, reproduction, activity, feeding) were first observed. The LOEL is specific to a particular ecosystem aspect (eg reproduction). In some cases differences between NOEL and LOEL values may be minimal.

Toxicity data (eg for endosulfan—Table 5) can be found in *The Pesticide Manual* (Tomlin, 1997), the *Extension Toxicology Network* (EXTOXNET, 2004), *AQUIRE* (USEPA, 2004), *Handbook of Physical Properties of Organic Compounds* (Howard and Meylan, 1997), as well as in journal articles.

However, data acquired from these databases has come from studies performed outside Vietnam and, depending upon the species under consideration, it may not be appropriate for use in Vietnam. Where local Vietnamese toxicological data is lacking, the overseas data can be used if the conditions and species in Vietnam can be assumed to be similar. In general, however, it is important that, whenever possible,

studies on the toxicity of pesticides to species specific to Vietnam should be carried out: such studies would verify any assumptions and ensure appropriate management for Vietnamese agricultural practices.

Biodiversity

Biodiversity is an indicator of the health of an ecosystem (Altieri, 1999). Biodiversity data describe the number and identity of species present in a given ecosystem or, for selected taxa, in agricultural environments. However, it is not possible to assess the health of an ecosystem through biodiversity values alone. The complex interactions and functions of different species are not fully understood, and precise characterisation is difficult.

Importantly, the toxicity value for one species does not provide protection for the entire genus or population in a given ecosystem. For risk assessment, therefore, it is desirable to collect as many toxicity endpoints as possible.

Information about biodiversity can be found through field survey, or from the relevant authorities, the literature or the Internet. When considering the biodiversity of field sites, species per taxa (S) and the total number of species in an ecosystem (N) should be considered (Sanchez-Bayo et al., 2002). In our Vietnamese project, especially for some regions, this information was limited: estimates of biodiversity for a field site could therefore be based on the available information for a larger region.

Table 5. Toxicity of endosulfan to a selection of ecological species; reported by class

Species	Endosulfan[a]			
	Endpoint	Lowest	Highest	Units
Mammals	acute LD_{50}	70	77	mg kg^{-1}
	dermal LD_{50}	360	2250	mg kg^{-1}
	inhalation LC_{50}	0.0126	0.0345	mg L^{-1}
Birds	acute LD_{50}	220	810	mg kg^{-1}
Reptiles	acute LD_{50}	na	na	mg kg^{-1}
Frogs	acute LC_{50}	2	12	mg L^{-1}
Fish	acute LC_{50}	0.3	5085	mg L^{-1}
Crustaceans	acute LC_{50}	7	7000	mg L^{-1}
Shell-fish	acute LC_{50}	na	na	mg L^{-1}

[a]Tomlin (1997), na: not available

Safety factor method

Add a safety factor; multiply the exposure figure by 10 to increase sensitivity.

This approach is only used when there is a lack of readily available data. This approach does not take into account local variables. This approach is used predominantly when no other characterisations are available and is accepted by the USEPA as a first tier approach. (Safety factors can be used for simple risk reduction, as discussed in subsequent sections.) Another approach is to use limited toxicity data collection in combination with a model to produce a specific dose-response curve (Model Dose Response Curve).

Use a dose response model if necessary

The third approach—when there are sufficient data points and no assumptions as to the dose response—is to use all the toxicity data together. The data must be of high quality and the units must be similar (or converted if necessary). This approach to risk assessment is repeatedly used within the literature and some examples are given below: it also leads into probabilistic risk assessment, by far the most useful risk management tool (discussed in detail in subsequent sections).

Other effect concentrations

The adaptability of risk assessment is such that values other than ecotoxicological values can be used as **effect** (E) concentrations to assess different hazards. In the case of monitoring for trade risks, the MRL values can be substituted and the probability of exposure determined. Many variations are possible: the prerequisite is to define meaningful endpoints, or **effect** guidelines. This book presents several examples of the adaptability of risk assessment (for example, see equations 2 and 3 in the following section).

3.5 Risk assessment

Given that risk is the probability of a prescribed undesired effect (Suter, 1993), ecotoxicological risk assessment is the characterisation of risk from chemicals that act via toxicological mechanisms, conducted in the ecological context (Solomon, 1996).

The best risk assessments are conducted as a series of tiers (Solomon, 2000). The simplest tier should be applied first. If the results suggested a potential risk, further tiers of risk assessment can be applied.

There are many options for risk characterisation and deciding whether the risk is acceptable. The choices depend upon field site, availability of data and the target for management—ecosystem protection, produce quality, human health or a combination of these.

What is acceptable risk?
Unfortunately, there is no easy answer to this question. 'Acceptable risk' is associated with aspects such as cost of pesticide, profitability of the pesticide-using industry, the sensitivity of the area where pesticides are being used, the available alternatives, the profitability of a particular farm, 'survival' and perceptions of supplying essential food for the family. The management of risk depends on classifying practices as unacceptable. It is usually governments—as regulators—that make decisions, based upon various forms of information. All management and regulation require decisions to be made as to the degree of risk that is acceptable in pesticide use. In other words, a qualitative judgement must be made, and acceptable risk should be clearly defined for all concerned.

3.5.1 The hazard quotient approach

The starting point of hazard characterisation involves formulating a **Hazard Quotient (HQ)**, as adopted by the US EPA (Urban and Cook, 1986). The data necessary to formulate a hazard quotient has already been described. The quotient can be described as the proportion of exposure compared to effect. This approach can be considered as the first real tier in the risk assessment process.

Determine/calculate the hazard quotient as exposure divided by effect. A value greater than one indicates that the exposure might be sufficient to cause the effect.

Equation 1

$$HQ = \frac{\text{Exposure concentration}}{\text{Effect concentration}}$$

The actual effect is determined by real exposure: the characterisation of the hazard will therefore depend on the assumptions that have been included. For example, if the toxicity value being used is overprotective (say 10 times more sensitive, as previously discussed), a HQ greater than one may not indicate that the hazard will occur, but rather should attract attention and encourage further investigative action, to improve the assessment.

Table 6 provides a guide to interpretation and expression of the hazard categories for the first tier quotient (Urban and Cook, 1986).

The most common use of the HQ is to screen a series of pesticides or practices. The pesticides that return a high HQ—greater than 0.1 (Table 24)—require more information to be collected to characterise the hazard in more depth. (In terms of risk assessment, the process would move to a higher tier.)

Table 6. Presumption of hazard based on Hazard Quotient (HQ) values for non-endangered species

HQ	Presumption
<0.1	No hazard (10x safety factor)
0.1-0.5	Hazard may be mitigated by restricted use (2x safety factor)
> 0.5	Unacceptable Risk (more detailed assessment required)

A note of caution regarding scoring systems: to provide a quantitative measure, risk assessments should always be based on a quotient. Scoring systems—where each quality is given a score and summed or multiplied—can lose the important characteristics, and thus lose sensitivity. Scoring approaches are generally arbitrary, and not based on field data and good scientific rigour, thereby making them more difficult to use for rational management and selection of safer pesticides.

The HQ approach can be expressed in many ways, depending on the regulatory or management goal and available information.

Equation 2—a quotient for use when the risk assessment process aims at managing pesticide residues in produce or other commodities:

$$HQ = \frac{\text{Exposure Concentration}}{\text{Maximum Residue Limit } (MRL)}$$

Equation 3—a quotient for use when the risk assessment process focuses on human health

$$HQ = \frac{\text{Exposure Concentration}}{\text{Acceptable Daily Intake } (ADI)}$$

Equation 4—a quotient for use when the risk assessment process is focused on ecosystem protection, where several parameters of effect concentration can be used

$$HQ = \frac{\text{Exposure Concentration}}{\text{LD50 or LC50 or NOEL}}$$

- Remember—the value of exposure concentration can be measured or modelled. While the highest value can be used to represent the worst-case scenario, the worst case is a very rare occurrence. The median values (or maybe the average values, depending on the spread of data) are more realistic and are normally used to represent the compartment as a whole.

- The value of effect or endpoint concentrations —including MRL values, ADI, LD_{50}, LC_{50}, NOEL—are available in the literature such as *The Pesticide Manual* (Tomlin, 1997), or from the websites of agencies such as FAO (www.fao.org), WHO (www.who.org) or EPA (www.epa.org).

In the case of part 2 of the worked example below, the management of endosulfan could be reviewed, by either improving practices, reducing the amount of endosulfan applied, or choosing a different chemical. Once changes have been made, another risk assessment should be carried out to test the benefit of the changes.

Validation should form an integral part of the risk assessment process, so that feedback is used to continually improve pesticide use practice.

Interpretation of the hazard quotient can be simplified by applying a two-fold safety factor to the hazard value (Equation 5), which results in a ratio that generates a presumption of acceptable hazard for all HQ<1.

Equation 5

$$HQ = \frac{\text{Exposure concentration}}{0.5 \times \text{Effect concentration}}$$

Worked example—endosulfan

1. The maximum observed concentration of endosulfan residues in grapes is 100 µg kg^{-1}, and the FAO (www.fao.org) prescribed MRL of endosulfan in grapes is 2000 µg kg^{-1}. Using Equation 2, the HQ for assessing the management of produce is 100/2000 = 0.05. In this example, therefore, the HQ is less than one, so there appears to be no risk of exceeding the Codex MRL trade value.
2. Analysis of a series of samples showed that the concentration of endosulfan in grapes was above 2000 µg/kg (the FAO-prescribed MRL, as above) in 0.5% of the samples (that is, in 5 samples out of 1000). Based on this set of observations, the probability of exceeding the Codex MRL value (would be 0.5%. Therefore, using endosulfan in this way (both in quantity and practice) poses a risk.
3. If the maximum concentration of endosulfan residues in grapes is 100 µg kg^{-1}, and 2000 µg kg^{-1} is the Codex prescribed MRL of endosulfan in grapes, the HQ for produce is 100/(0.5 x 2000) = 0.1 [Equation 5]. The outcome is the same as for Example 1, the calculation showing that there is no hazard of exceeding the prescribed MRL value.

Results with HQ>1 are considered to have exceeded a level of concern at whatever hazard is targeted; human health, ecological species or produce (Urban and Cook, 1986).

This method shows the sensitivity of the HQ approach. Management of the pesticides can be assessed by the residues remaining in the produce at market. We have demonstrated the potential for limited scaling of risk, or level of concern, of a specific use of pesticide or management option. When conducting desktop modelling a 'sensitivity assessment' should be conducted, and also used in risk assessment.

A sensitivity assessment allows adjustment of parameters to determine how much would need to be changed in order for the practice to become acceptable or unacceptable. Usually, in risk assessment, we focus on adjusting the environmental exposure, as the effect endpoints are often finite.

Consider such questions as: Is the chemical easily replaced with a less risky chemical? Was this chemical a cheaper option? The answers to these questions determine the options available for management. If there are no alternative chemicals that are of equal or lower price, then effort must be to ensure there are no residues detected at concentrations above the prescribed limits.

A feature of the hazard quotient method is that the HQs that are generated may not be measures of real risk, but are rather measures of levels of concern (USEPA, 1989; Bartell, 1996). Two other limitations weaken its utility, particularly in the ecological risk assessment process. First, HQs are not population-based, and it is difficult to integrate biodiversity into HQ assessments. Second, HQs have a limit arising from the record of dose-response testing with the animal model, where linearity in response is not necessarily valid.

However, this approach is considered appropriate for initial assessment (tier 1) where there is a lack of information, as in Vietnam. Some approaches do incorporate biodiversity into HQ methods (Sanchez-Bayo *et al.*, 2002), but, these may be impractical in some situations. However, a probabilistic approach can overcome some of the limitations of the HQ approach.

3.5.2 Probabilistic risk assessment

When a range of values is available for both exposure data and toxicological effects, probabilistic risk assessment is a desirable addition to the first tier of risk assessment. When probability information is used in a risk assessment, a better understanding of the risk can be obtained. By this, we mean that we can start to understand how often or likely a hazard may occur or how severe the consequence. Backed with such insight, better management can be achieved. Probabilistic approaches take into account the frequency of occurrence and can provide a better understanding of uncertainty. The probability of attaining a desired level of protection can be calculated and management practices developed to ensure ongoing best management.

The principle of the probabilistic approach has been well described (Cardwell et al., 1993; Klaine et al., 1996; Solomon, 1996 and Solomon et al., 2000). As with the quotient approach, the probabilistic approach requires two data sets; *exposure* and *toxicity* data. The main difference is that a range of data is used rather than a single endpoint. The data range is assessed to provide a frequency, the basis of any probabilities. For example, if we have one 'high value' in 100 samples, then our probability of detecting 'high values' is 1 in 100, or 1%. This is an example of a single probability, where we focus only on the frequency of exposure. The probabilistic risk assessment approach has a framework that uses double probability, or a combined probability, taking into account the frequencies of both exposure and toxicity.

Collect and collate toxicology data for a range of species. Ensure that the endpoints are comparable (for example, all dose responses to 50% of the population, either EC50 and LD50, or all NOEC values).

As for the HQ method, there are several sources of these data, including *The Pesticide Manual* (Tomlin, 1997), the Extension Toxicology Network (EXTOXNET), AQUIRE (USEPA, 2004), *The Handbook of Physical Properties of Organic Compounds* (Howard and Meylan, 1997), articles from the literature, as well as toxicological response lists published by ecotoxicology researchers.

Note: Ensure that the set of exposure data (usually presented as concentrations (mg kg^{-1} or µg L^{-1}), correspond to the units for the toxicology data and that both are in the same range.

Toxicology data for endosulfan (Tomlin, 1997—Table 7) indicate the minimum amount of data required for a meaningful attempt at using this approach. One could argue that there are too few species included and that the assessment may not be as thorough as necessary for management purposes. Remember that an assessment is 'only as good as the data it uses'. The person who is managing the risk must decide on the quality of the assessment and make appropriate decisions. To illustrate an approach to selecting safer pesticides, however, this example is adequate.

Collect and collate *exposure* data. The best data is a comprehensive set of specific local values, obtained using a focused sampling regime.

The risk assessment will reflect the data. If the exposure data is obtained from only one practice (maybe from one field or farm), then only this practice will be assessed. If the data is collected over time, then the assessment will reflect the practice during the relevant time period. Thus we can compare and contrast different practices, time periods and pesticides by collecting and

Table 7. Selected toxicology data for endosulfan (Tomlin, 1997)

Species	Toxicity data (mg kg^{-1} or mg L^{-1})
rat	70 (acute oral LD_{50})
dog	77 (acute oral LD_{50})
mallard duck	205 (acute oral LD_{50})
ring-necked pheasant	620 (acute oral LD_{50})
golden orfe	0.002 (LD_{50}-96h)
daphnia	0.075 (LD_{50}-48h)
algae	0.56 (EC_{50}-72h)

grouping the exposure data to reflect each aspect under study. For a general assessment, the data should include values for a range of practices over time.

Modelled data is not as useful as collected data, unless a range of scenarios are modelled, to provide a range of potential environmental concentrations. For probabilistic risk assessment, modelling is the best way to determine where the sampling resources are best used. To ensure the most meaningful assessments, frequency distributions and their associated probabilities should only be obtained from real data.

Our Hoc Mon case study provides an example of exposure data for endosulfan residues in water (Table 8), presented as a cumulative distribution: 20% of the samples were below the detection limit, and all the samples were below 0.014 mg L^{-1}.

Plot the two sets of data on the same axes, as a cumulative log-normal distribution (Figs 3.2 and 3.3).

Fig 3.2 (after Solomon et al., 2000) shows the dual plot of cumulative *exposure* and cumulative *effect*. Where there is an overlap of concentration between exposure and effect, there is risk of realising a hazard. In this case, at 55 *concentration units*— which represents 95% of all exposure concentrations (left axis, Fig 3.2)— 10% of the species are exposed at the toxic level (right axis, Fig 3.2). Further interpretations can be made as desired.

As with any level of *exposure* (concentration), there is an associated percentage *effect* that can be determined (Fig 3.2). Conversely, a percentage

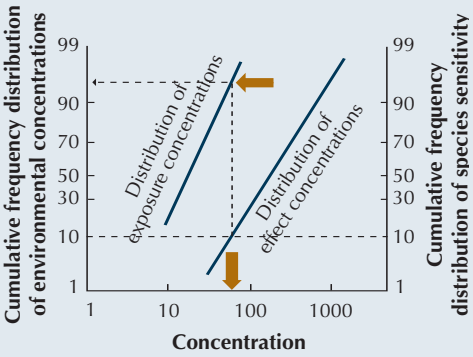
Table 8. Exposure data for endosulfan residues in water in Hoc Mon presented as cumulative distribution

Concentration (mg L^{-1})	Cumulative frequency (%)
0.000	20
0.001	60
0.003	65
0.004	70
0.006	80
0.010	85
0.011	90
0.013	95
0.014	100

value of ecosystem protection can be determined from the corresponding exposure concentration. Using the same example, if we wanted to protect 10% of species, we would need to ensure there were no environmental exposures above 55 (Fig 3.2).

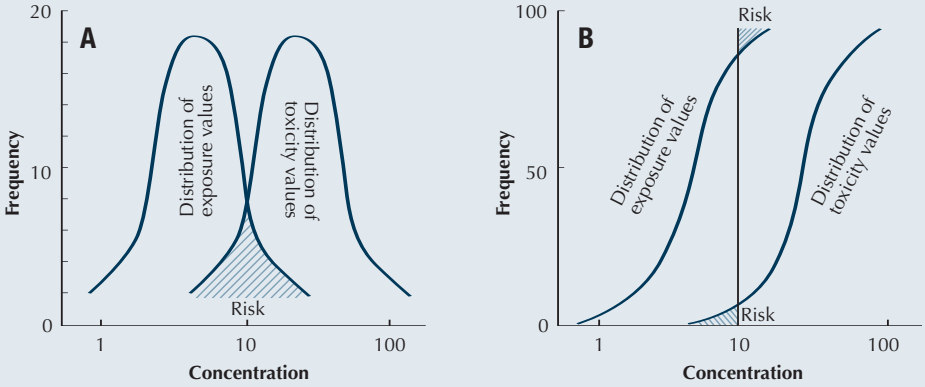
Arrange the data into the log cumulative form to enable a meaningful comparison and combination of the data.

Figure 3.2. Presentation of exposure and toxicology data as linear probability distributions (after Solomon *et al.*, 2000)



The explanation for the effectiveness of the dual probability approach can be observed in Figure 3.2a, below (after Solomon *et al., 2000*). The overlap of the *exposure* and toxicity (*effect*) distributions show the regions of risk where the hazard could be realised.

Figure 3.2a: Relationship between effect and exposure distributions expressed as log-normal distributions (A) and cumulative log-normal distributions (B) (after Solomon *et al, 2000.*)



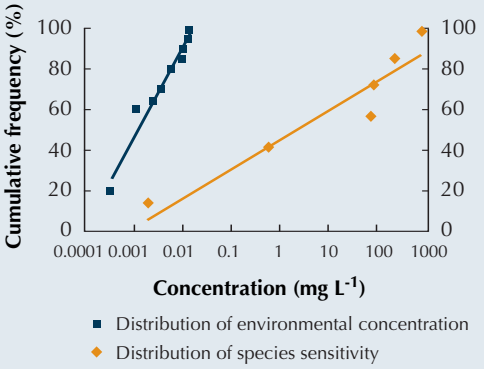
As an example, the endosulfan data (Tables 7 and 8) can be presented as linear probability distributions (Fig 3.3), allowing identification of the probability of occurrence for a particular level of effect.

The probabilistic risk assessment framework thus requires the generation of joint probability functions of the exceeded data. In Vietnam, not all our work advanced to this stage. However, the joint probability function can be done either by solving the functions describing the probability of exceeding both an exposure and an effect concentration (Solomon *et al*., 2000), or by using fitted regression models (ECOFRAM, 1999). The result is a joint probability curve, or exceeded profile curve, which describes the probability of exceeding the concentration associated with a particular degree of effect.

This probabilistic approach can be used for decision-making. For example, when a certain concentration of pesticide is applied, the expected exposure can be determined, as can the percentage of species that would be affected in this situation. Again using the Hoc Mon case study as an example, approximately 20% of species are affected by the current distribution of endosulfan residues, assuming that the obtained toxicity data covered all species in the Hoc Mon area (Fig 3.3).

It was very demanding to apply the probabilistic risk assessment approach in Vietnam, as it required information about exposure data and toxicity data not yet readily available. However, as more adequate data emerges, this approach will provide better insight into the risks associated with pesticide use. The case studies in this book (Sections 6, 7 and 8) describe how the probabilistic approach was applied to our Vietnamese project, within the limits of available information.

Figure 3.3. Probability distributions of exposure and toxicology data of endosulfan



3.5.3 Ecological Relative Risk (EcoRR)

Risk assessment methodology is so flexible that, once the site-specific information has been collated, it is suited to all field sites and agricultural practices. The fundamental Hazard Quotient approach can be adjusted and developed for specific management purposes. One such development, Ecological Relative Risk (EcoRR—Sanchez-Bayo et al., 2002), compares several pesticides to assess the relative risk

of pesticide use to the adjacent ecosystem. Relative assessments are useful for improving management practices, although they do not necessarily reflect actual risk.

EcoRR is estimated as the quotient of exposure and ecotoxicity, including a factor of probability and persistence. Biodiversity is taken into account by estimating ecotoxicity for species with limited available data (Sanchez-Bayo et al., 2002). EcoRR methodology thus provides another approach to risk assessment.

Exposure assessment

The module of exposure assessment for the EcoRR assessment is calculated separately for each environmental compartment (air, soil, vegetation, groundwater, surface water and sediment).

In each environmental compartment, the dose of residues in each affected area, the probability of exposure, and persistence in a certain environmental compartment (indicated by the half-life of a chemical and bioaccumulation in organisms) are combined to give a single value:

Equation 6

$$\text{Exposure (x)} = D \times P \times t_{1/2} \times BCF$$

D: the dose;

P: the probability of exposure to a compartment;

$t_{1/2}$: the half-life of a chemical in each compartment;

BCF: a bioconcentration factor.

The stepwise procedure to calculate the exposure component of EcoRR scores is detailed by Sanchez-Bayo et al. (2002).

The residue doses are obtained by converting the predicted environmental concentrations (PECs).

Equation 7

$$D = PEC \times \frac{Vol}{Area}$$

Vol: the volume of matrix (air, soil, etc.) for each compartment

Area: the area in hectares of the corresponding affected zone

Ecotoxicology assessment

Ecosystem toxicology is assessed as a composite of the ecological relationships among species, expressed in simplified mathematical terms. A mathematical model can be established to include biodiversity of the field site and toxicology to different taxa (Sanchez-Bayo et al., 2002). A stepwise procedure to calculate the ecotoxicity component of EcoRR scores has also been developed (Sanchez-Bayo et al., 2002).

Equation 8

$$\text{Ecotoxicity (Ecotox)} = \sum_{i=1}^{m} \frac{\text{Tgmtaxa}_i / (S_i / N)}{N}$$

Tgm taxai: LC_{50} or LD_{50} geometric mean of each taxon

Si: the number of species of a taxon

N: the total number of species of all taxa considered.

Relative risk assessment

The EcoRR scores for each compartment are calculated by dividing the exposure values by the corresponding ecotoxicity values. The total EcoRR for a particular area is calculated as the sum of EcoRR scores for each compartment, with the EcoRR scores then interpreted in terms of risk (Table 9).

The risk assessment process using the EcoRR approach has been described in detail by Sanchez-Bayo et al. (2002) and in the manual produced for Workshop 1 during this project (Post Harvest Technology Institute, March 2002—Le Van To et al., 2002). This same approach was recently applied to the Australian cotton industry (Kennedy et al., 2004). The Vietnamese case studies in Part B also apply this approach to risk assessment.

Table 9. Risk ranking based on the EcoRR scores

Ranking categories	EcoRR
Very high risk	>1000
High risk	100-1000
Medium risk	10-100
Low risk	1-10
Negligible	<1

Based on the literature and current applications, the EcoRR approach provides a good way of quantifying and comparing the relative risk among different hazardous chemicals applied to field sites, and is readily applied to Vietnamese scenarios, thereby providing information of pesticide use management.

4 Monitoring, validation and feedback

A vital aspect of the selection of safer pesticides is good quality feedback. In this sense, feedback means all additional information that can be used to improve the assessment process, such as field data (including traceback from contaminated produce), additional data from the literature, or improved understanding of the processes involved in pesticide transport (allowing better assumptions to be made). The best type of feedback is site-specific field data collected during a focused field study. The risk assessment process will identify situations where the quality of data is poor, drawing attention to the need for additional data.

This section describes the key components of the feedback system, including monitoring, validation, and collection of information after a change in management practice. These processes, regulated by quality controls, ensure that the data collection process is appropriate and specific for the task at hand. Such regulation is especially important when conducting field studies or surveys.

Section 5 focuses on the management of pesticides. Once a management change has been made, it is necessary to determine whether the change has reduced the risk. For example, if half the amount of a particular pesticide is applied, does this new application rate reduce the risk sufficiently (as determined by the risk assessment)? Or, if a a replacement chemical is used instead of a high risk chemical, does the replacement provide a more favourable risk profile? Thus, two sets of data—collected before and after the management change—must be compared. An ongoing process of feedback can continually improve the selection and use of pesticides.

4.1 Quality assurance and quality control

The process of collecting field samples and their subsequent analysis is 'analytical chemistry'. All actions required to complete an analytical task effectively and efficiently are covered by the term **quality assurance** (QA). So, emphasis is placed on *planning* all stages—from field to

laboratory—in a sampling regime. Moreover, quality can only be assured with extensive **quality control** (QC) measures in place, to monitor performance and eliminate any causes of unsatisfactory performance.

A critical aspect of the risk assessment process is to have good quality data to validate any required assumptions. High quality is ensured by incorporating appropriate QA and QC into all aspects of data collection.

Plan the complete analytical process—sample collection, sample preservation, transport, instrumental analysis and data analysis.

4.2 Monitoring

'To monitor' is defined as 'to watch and check a situation carefully for a period of time in order to discover something about it' (Cambridge University Press, 2004 http://dictionary.cambridge.org). This is a literal definition of monitoring as used in environmental science; we 'watch and check' the environmental fate of pesticides applied to crops. Monitoring includes the processes of planning, sampling, transport, sample preparation, analysis, data interpretation and presentation.

4.2.1 Sampling and sample handling

The variety of substances and matrices that can be sampled is too wide-ranging to have an exact procedure, so there are no strictly prescribed procedures for sampling. However, there are many published guidelines aimed at ensuring a true representation of the distribution of the substance being sampled. A sampling protocol should be developed for each field study: the analytical team must develop a complete plan, best presented as a flow diagram.

Collect samples for analysis that provide the best representation of the matrix (or material being sampled)

The two major components to be considered when planning a sampling protocol are the analyte (the substance that an analysis aims to identify/quantify) and the matrix (the material in which the analyte is contained). A sampling regime must consider the aims of the project, and be sensitive to both the analyte and the matrix. The analyte could include metals, biological products, or pesticides, while the environmental matrix can be biota (living species), water, soil, and air (or a mixture of these).

Statistical considerations are also important when planning a sampling regime. Significance refers to the reproducibility of the result and the level of confidence that the data is a true representation of the matrix being sampled, both temporally (over time) and spatially (over the area). Pesticides in the environment or in produce are usually not uniformly or thoroughly mixed into the matrix. Therefore, an adequate number of replicates must be collected and consideration given to using a composite sampling

regime, sufficient to allow standard errors and significant differences to be estimated.

Sampling regimes

Often the choice of sampling regime depends on available funding. Large sampling and analysis regimes, potentially able to give a very detailed understanding of the environmental presence of a chemical, can be expensive.

The choice of sampling program or regime should take into account the potential for distribution and the information required. For example, one may need to know how much chemical of interest is present across a region or how much is being released from a single source. Different sampling regimes would be needed in these cases; a larger area would probably be suited to composite sampling to limit the number of samples required to determine the extent of contamination.

Ensuring good quality data

The quality of data depends upon the success of six major activities:

1. Formulating the particular objectives for a sampling program
2. Collecting representative samples
3. Proper sampling handling techniques and (if necessary) sample preservation
4. Adhering to an adequate chain of custody and sample identification
5. Participating in QA/QC in the field, verifying that the recommended procedures have been followed
6. Properly analysing the sample, including the use of authentic standards, the method of standard additions and recovery from sample matrixes to an acceptable level (better than 80%).

Well-designed and well-implemented sampling programs are vital to pollution control. There are three phases in environmental sampling: collection, field treatment (transport) and storage. The quality of samples and sampling must be maintained throughout all three phases to ensure a high quality sample for analysis.

Sampling techniques

The nature of the sample and the substance to be monitored will dictate the choice of sampling technique. There are four different sample types that can be used within a sampling regime: grab samples, composite samples, duplicates and replicates, and split samples. The choice of sample type will depend on the desired outcome of the project.

Grab samples—An individual sample collected at a particular time and place, useful for obtaining a 'snapshot' of the conditions present at the time of sampling. Depending upon the consistency of the source, a grab sample may represent the entire source.

Composite samples—A thorough mixture of several grab samples, which may have been

collected at the same point at different times or at different places at the same time. A composite sample is useful for averaging a source or for obtaining a representative sample when mixing is not prevalent. Grab samples combined to form a composite should be of the same volume and collected at regular intervals so as not to skew representation within the sample. A composite sample should be well mixed before instrumental analysis.

Duplicates and replicates—Two (duplicate) or more (replicate) samples collected over space or time. Duplicates and replicates are collected to check the precision of the sampling process and can be used to assess variation. For environmental sampling, replicates can be used to indicate real variation between samples.

Split samples—Split samples are taken to check analytical performance. After collection, the sample is mixed well and then half the sample is placed into a container identical to the first. Both samples can then be analysed (and should yield the same results).

Tools and containers—The choice and condition of sampling equipment is vital in maintaining sample quality. Sample contamination is a major issue to consider when choosing an appropriate material in which to collect and store samples. Losses of sample contents to the sample container must also be minimised. Risks of loss or contamination generally increase with increased handling. Sample containers must also be cleaned adequately, to ensure that all possible sources of contamination are eliminated (see suggested cleaning regime for pesticide sampling equipment and containers).

Reporting and archiving

An important aspect of analytical work is to report the project well. Reporting involves the translation of the analytical information into an understandable and functional format.

Cleaning regime for pesticide sampling equipment

- Soak item in a pyro-negative solution (high alkaline).
- Wash with hot soapy tap water and scrub with a brush.
- Rinse thoroughly with hot tap water.
- Rinse thoroughly with deionised water.
- Where there is a risk of existing contamination, triple rinse with pesticide-grade solvent (once with acetone, then with hexane or isopropanol) but, in general, use new containers or minimise the use of hazardous solvents.
- Air-dry completely.
- Store in sealed container or wrap in aluminium foil for storage or transportation.

Good analytical reporting should include the following elements:

- Identification of the end user
- The objective of the study
- The sampling strategy and sampling techniques, the staff involved and the sample location(s)
- Sampling details (including date of sampling, date of arrival and storage conditions)
- Description of the analytical procedures, QC measures, and indications of how and where this information can be retrieved (identification of staff involved is important)
- Analytical data with information on the methods, and including performance indicators (eg precision, sensitivity, limit of detection)
- Evaluation/interpretation of the results in terms of their analytical significance, in response to the initial objectives of the study
- Questions and possible unsolved problems that may have arisen from the study.

Sample preservation

Once a sample is taken from its original matrix, it is subject to different chemical and physical conditions. As a result, the sample's residue content can deviate from that occurring *in situ*. Without measures to prevent such change, the analysis will not provide appropriate information about the sample. Relevant

Table 10. Minimising potential problems associated with sample preservation

Potential problem	Solution
Volatilisation (loss of sample to air)	Collect sample with no head space, limiting contact with air
Adsorption and absorption (most commonly this involves metals with glass surfaces and pesticides with plastic containers)	Eliminate problem by using plastic for metal samples and glass for pesticides (unless otherwise directed)
Diffusion (some volatile organics can diffuse through plastic)	Use Teflon containers and seal
Precipitation (due to change in sample conditions eg pH)	Stabilise metal oxides or hydroxides by adding HNO_3
Photochemical changes (light-catalysed reactions)	Use amber-coloured glass for collection and transport away from light
Microbial and chemical degradation	Minimise by using low temperature, preservatives or a changed pH

conditions include exposure to light (may cause photochemical reactions), changes in temperature (may affect temperature-dependent kinetics) and changes in dissolved gases. Taking a sample from water can increase the sample's dissolved oxygen concentration: the introduction of oxygen to an anoxic sample can initiate oxidation, or alter the pH of the sample.

General practices for minimising changes to samples

The actual act of sampling can change the sample, altering analysis results. Sampling and storage techniques must therefore aim to minimise the physical and chemical changes to a sample (Table 10).

4.3 Validation of risk assessment

As explained in Section 3, the first tier of a risk assessment involves a largely theoretical approach, using calculations based on the best data available, including real analytical data where available. The risk assessment framework identifies situations where more data is required (where there are no data or where the available data are not appropriate).

When actual data are not available, risk assessments usually make assumptions regarding the properties of chemicals. All such assumptions should include a safety margin, to address a 'worst-case' scenario.

Underestimating the level of 'risk' is the worst possible outcome of a risk assessment and must be avoided.

The importance of risk assessment assumptions makes it highly desirable that they are validated in the field or by focused experiments. Changes in management practices can only be assessed by on-going monitoring (possibly becoming less frequent as improvements are made).

Primary monitoring is directed at target chemicals, and involves analytical methods that measure the relevant concentration in produce or the environment, or the likely exposure dose. The CARD Workshops 1 and 2 (Le Van To et al., 2002; Bui Cach Tuyen et al., 2002) provided details of monitoring techniques that use ELISA technology, which enables more rapid testing than instrumental methods such as gas-liquid chromatography (GLC) and high performance liquid chromatograph (HPLC).

Secondary monitoring is more concerned with confirming the predicted impacts of pesticides, as in ecotoxicology. While attention is drawn to the importance of these secondary monitoring approaches, they are specialist fields outside the scope of this book and are therefore not considered further in this context.

Only real data and correct information of good quality can reduce the risk determined by a risk assessment.

4.4 Characteristics of ELISA (enzyme -linked immunosorbent assay)

In the project that initiated this book (Section 1), the process of risk assessment was integrated with the application of enzyme-linked immunosorbent assays (ELISA) for pesticide analysis. ELISA provides accurate, rapid and relatively inexpensive tests for pesticides in produce and the environment. ELISA is very flexible and can be used for detecting both specific chemicals and classes of chemicals, such as the cyclodienes—as with the endosulfan ELISA test used in our Vietnamese project.

Quantitative analysis by ELISA requires knowledge of the specificity of the test to a particular chemical or analyte, as it is helpful to be sure that, in the samples of produce or environmental materials, there is only one analyte to which the ELISA is sensitive. For screening purposes, however, ELISA can be used in a semi-quantitative way, to establish which positively testing samples should be subjected to confirmation analysis using GLC or HPLC.

ELISA is characterised by the following features:

Excellent sensitivity, which can sometimes exceed that achieved with instrumental methods. During their design, ELISA tests are usually adjusted to provide a particular range of sensitivity, which may be set at its highest in the range of the maximum residue level (MRL).

Minimal clean-up of samples. For water samples, no pre-treatment is usually necessary to conduct ELISA analysis, other than dilution if the concentration is too high or there are interfering compounds present.

Rapid throughput. With ELISA, hundreds of analyses can be performed in a few days, many more than are possible using procedures that require solvent extraction and clean-up from interfering materials.

Low cost. Only the simplest laboratory equipment is required. A working laboratory can be equipped with funding of about $AUD 5000 (for pipettors (automatic pippettes), plastic-ware and a simple colorimeter). Using ELISA in a qualitative fashion is even more cost-effective.

Relative ease of training. Training expert analysts for GLC and HPLC is an intensive process, whereas laboratory personnel with minimal experience can be trained in ELISA techniques in a few days.

Special design. Each ELISA must be specifically developed, which can take some months (see below).

Unreliability in some circumstances (eg if there are strong matrix effects). Some of the advantages of speed and simplicity may be lost if special procedures are needed to overcome matrix effects.

4.5 How ELISA works

The ELISA process depends on specific immunological reactions between antibody molecules, an analyte and an enzyme reagent. A chemical with a structure that mimics a particular pesticide (a hapten) is linked to a larger protein and injected into an animal such as a rabbit. Such a large molecule causes the animal to produce a specific antibody, which can be extracted, purified and used in an analytical assay to give high specificity.

Full details of competitive ELISA tests for endosulfan, carbaryl and DDT are given in the Workshop 1 Manual (Van To et al., 2002—details available from SIAEP, Ho Chi Minh City). A full description of the development of the ELISA test for endosulfan will be available soon (Trang et al., in press).

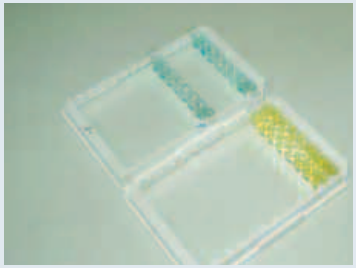
However, several characteristics of ELISA—specificity and sensitivity of the antibody, and matrix effects—must be considered so that the data they have generated can be understood.

Antibody specificity is a function of the hapten used to mimic the pesticide, to which the antibody is raised as a protein-conjugate. The host animal (rabbit) may influence the specificity. The more specific the antibody, the more it is possible to design a quantitative assay.

The sensitivity of the antibody determines the useful concentration range of the assay. Sensitivity is expressed by the IC_{50}, a concentration of the analyte (pesticide) that gives 50% inhibition of colour development in the competitive assay. In this format, full colour development means that there is no pesticide present in a sample.

Sampling stream water for pesticide runoff in Ninh Thuan province.

Sampling well water in a Ninh Thuan vineyard.



ELISA reactions in immuno-strip wells.

Matrix effects. It is important to determine whether these are present in the medium being extracted for analysis. Matrix effects usually tend to decrease the maximum colour possible

and to shift the analytical curve towards a higher IC_{50} value. These effects are usually overcome by dilution of the sample, or by constructing the standard curve using standards made up in the same extraction matrix.

The best test of whether an ELISA is performing well is the shape of the standard curve included with each set of analyses. This should indicate the correct IC_{50} value, both in solvent alone and in an extract of the product or environmental sample known to be uncontaminated.

4.6 Validation of ELISA data using instrumental methods

Analytical data obtained using ELISA methods must be subjected to independent confirmation using alternative analytical methods. These will usually include the officially approved analytical procedures, such as those approved by the Association of Official Analytical Chemists (AOAC) or other internationally recognised agencies. An extensive list of AOAC-approved methods is available (www.aoac.org).

Validation can be achieved by analysing a proportion of the samples by an instrumental analytical method such as GLC, following extraction and clean-up if necessary. As routine QC, it is also suggested that 10% of positive ELISA samples should be analysed by an independent method, without knowledge of the ELISA result. (With experience, it may be possible to reduce this proportion to 5%.)

Independent Validation

The Centre of Analytical Services and Experimentation at Ho Chi Minh City has experience in providing independent validation of ELISA results: contact SIAEP (formerly PHTI).

Although validation can be conducted by the same analytical service that conducts the ELISA, this will not carry the same weight as an independent validation without knowledge of the previous results. Where ELISA is used by a network of testing personnel, it will in any case be necessary to refer the analytical program to a well-equipped and independent analytical laboratory.

However, ELISA should never be used without some degree of independent confirmation of the analytical results.

The role of the laboratory providing analytical validation is to provide regular feedback to those conducting the ELISA analyses. These results can then be used to improve the standard of the analyses. Suppliers of ELISA kits are often willing to provide advice to optimise the tests, to ensure that ELISA products are employed effectively and used only under appropriate conditions. However, ELISA suppliers cannot take responsibility for cases where kits have been misused.

Risk management

5

Risk management is an approach to enable farmers and their advisers, resource managers, government agencies, industry and regulators to assess, and subsequently manage, the risk of chemical use. The purpose of risk management is to lower the risk of hazardous chemicals in farm produce and the environment.

For management to be effective in minimising the adverse impact of agricultural pesticides in the environment, farmers should be advised which compartments are most at risk when using a particular chemical, and how to take precautionary action.

In addition to conducting risk assessment using the approaches previously explained, this CARD project also used the concept of the Pesticide Inventory, Risk Assessment and Management System (PIRAMS) model (under development—S. Baskaran, pers. comm.), which offers a simple approach to risk management (Section 5.3).

5.1 Integrated pest management

Several practices can be included in a farming system to reduce the impact of pesticides on the environment and human heath. Integrated pest management (IPM) is a multi-disciplinary approach that practically and effectively manages pests whilst maintaining human and ecosystem health (Smith et al. 1976). This book has focused on risk assessment techniques to allow selection of safer pesticides, a key philosophy of IPM. (In this context, other IPM strategies will not be discussed. For more information on IPM see Dent (1995) and Maradia et al. (2003). Within Vietnam, several NGOs are assisting with the integration of IPM into farming communities.

There are five key IPM approaches with regard to pesticide use:

Use safer pesticides. (As this book shows, safer pesticides *can* be selected logically). Use pesticides that pose less risk to the sensitive values being managed.

Use less pesticide, subject to pest pressure only. Do not use pesticides unnecessarily.

Support beneficial insects, allowing them refuge. Do not use 'hard' chemicals early in the season; 'soft' (more selective) pesticides reduce the impact on beneficial insects.

Adopt appropriate agronomic practices such as low-till farming regimes and adequate rotation of crops. Explore alternatives to pesticide use.

Consider the use of genetically modified (GM) varieties some of which have been shown to reduce the amount of pesticide needed for production, while other varieties lower the risk to the environment by allowing different pesticides to be used. More flexibility means that better choices can be made.

5.2 Remediation options

The methods available for remediation are as varied as combinations of the polluted matrices and the materials causing pollution. In fact, the options available for remediation depend on two factors; firstly the matrix of the system to be remediated (that is soil, water or air) and secondly, whether the remediation is to be undertaken *in situ* or *ex situ*. Many remediation techniques are not suited to farming environments. In addition, the concentrations of contaminant are often insufficient to warrant intensive clean-

Table 11. Remediation techniques suitable for chemical contamination in farming systems

Technique	Details
Separation/ sedimentation	Gravitational settling or centrifugation of insoluble compounds
Bioremediation	Engineering to optimise biodegradation by providing an adequate supply of electron acceptors and minimising mass transfer
Filtration	Gravitational or pressurised filtering through sand, microfilters or ultrafilters
Phytoremediation	The use of plants to concentrate or degrade contaminants. Mechanisms include phytoextraction, phytostabilisation or enhanced biodegradation
Dissolved air flotation	Pressurised air is pushed through water and carries oily or suspended material to top for skimming and collection
Carbon adsorption	Adsorbs organic compounds and some inorganic compounds from waters
Ion exchange	Removal of metal ions from water via ion exchange resins
Air sparging	Coupled with soil vapour extraction, *in situ* uses for ground water

Example

The PIRAMS model (provided as an Excel spreadsheet during Workshop 2 held at the University of Agriculture and Forestry, July 2002) was applied to the pesticides being used in the Ninh Thuan grape growing area (Table 13), with all parameters obtained from field survey (see case studies for more detail) and The Pesticide Manual (Tomlin, 1997).

up. In general, the more transport and energy needed to dispose of the contamination, the higher the costs. It is better to take precautions and avoid heavy contamination.

Sellers (1999) gives a comprehensive list of remediation techniques for environmental pollutants: Table 11 lists those suitable for remediation within farming systems.

5.3 PIRAMS model parameters and data requirements

PIRAMS has an action- and output-focused integrated system approach, intended to help resource managers, government agencies, industry and regulators to assess the risk and risk management of chemicals.

The four factors considered in the PIRAMS approach are food crops, surface water, ground water and spray-drift (Table 12). These factors

Dr Le Van To's market-oriented response to pesticide management.

SIAEP teacher Nguyen Thu Trang giving instruction in ELISA pesticide analysis in Danang, 2003.

SIAEP teacher Nguyen Thu Trang giving instruction in ELISA pesticide analysis in Hanoi, 2004.

Teachers Nguyen Thu Trang and Le Van To at Hanoi workshop, 2004.

Table 12. Potential hazards

	Definition of risk	Variables considered
Food crops	The potential of a pesticide to reach food crops through application, irrigation of pesticide contaminated water and other sources to harm consumers.	Crop cover; rate of application; site and time of chemical application; droplet size: pesticide half-life; withholding period; toxicity to humans.
Surface water	The potential of a pesticide to reach surface water body through runoff from agricultural fields or spray drift and to organisms.	Proximity to water body; soil organic matter; soil texture; crop cover; irrigation practices; amount and position relative to application; droplet size; pesticide persistence; and toxicity to aquatic organisms and humans.
Groundwater	The potential of a pesticide to reach groundwater through leaching and to affect its potential use as a source of drinking water for humans.	Soil organic matter; soil texture; crop cover; depth to water table; irrigation practices; amount and position of application; pesticide sorption; persistence of chemical; and toxicity to humans.
Spray-drift	The potential of a pesticide to volatilise and to contaminate air, water bodies, food and human exposure.	Proximity to sensitive areas; pesticide volatility; wind speed; amount and position of application; droplet size; pesticide persistence; toxicity to humans.

Table 13. PIRAMS risk categories for the Ninh Thuan grape growing area

Chemicals	Risk for various categories				
	Farm worker	Surface water	Spray drift	Ground water	Food
abamectin	medium	medium	medium	medium	medium
endosulfan	high	high	medium	medium	high
cypermethrin	medium	medium	medium	medium	medium
chlordane	medium	medium	medium	medium	medium
fenvalerate	medium	medium	medium	medium	high
methidathion	medium	high	medium	medium	medium
methamidophos	medium	medium	medium	medium	medium

Table 14. Managing ground and boom spray-drift

Factors	Methods to reduce risks of hand-sprayed and tractor boom spray drift
Wind speed/air stability	Spray in the morning when there is a steady wind (< 20 kmh^{-1}), low temperature (15-25°C) and moderate humidity.
Droplet size	Set the boom spray to deliver most droplets in the 300-600 micrometer range.
Release height	Lower the boom spray height using low drift nozzle.

are considered to pose potentially hazardous situations in farming.

When calculating risk, a numerical rating (scale of 1–5) is assigned for each given set of parameters.Thus a score of 1 is assigned when a pesticide has a low toxicity or minimal impact on the input variable; and a score of 3–5 when it is highly toxic or has a major negative environmental impact.

The user chooses the most appropriate rating (from 1 to 5) for each parameter and the total score is calculated for each chemical; from a combination of all assigned ratings. The higher the index score, the greater the risk of chemical use. The output can provide the risk of one chemical for various categories (risk for spray drift, surface water, groundwater, food and human exposure) or of many chemicals for one category.

5.4 Risk management strategies

The output from the PIRAMS model can provide managers with useful strategies. The PIRAMS model identifies pesticides that have low, medium or high risk, and so can reduce the impact of high-risk pesticides in farm produce and the environment.

Example

With endosulfan, risk to farm workers decreased from high to medium when we increased the buffer zone area and proximity to the field (Table 17).

In comparison to other countries, Vietnam has reduced risk because aerial spraying is not used. However, Vietnam lacks ecotoxicology and exposure information for local species, and also has farmers with low levels of education — both factors that limit effective risk management.

In combination with Integrated Pest Management (IPM) and suitable pesticide use policies (for example, a complete ban or limited use of very hazardous chemicals), the management strategies from the PIRAMS model are applicable to Vietnamese situations. Tables 14, 15 and

Table 15. Managing pesticide entry into surface water

Entry route/factors	Methods to reduce pesticide entry to surface water
Spray drift	Offset enough buffer distances in the sensitive areas such as rivers, lakes or ponds Manage vegetation (eg. hedges) near water ways
	Adopt low drift technologies such as good weather condition, lower release height, deliver optimum droplet size
	Lower the boom spray height (from 500 to 300 mm) using low drift nozzle
Runoff/surface flow	Manage soil surface eg adoption of minimum tillage practice
	Buffer zones with various surface treatments eg grass strips
	Reduce drain intensity; improved irrigation practices can reduce drain leaving the farm
	Optimisation of application rates
	Target timing of application; check the weather details
	Adopt IPM and IFS practices
	Retention of runoff. Ideally no irrigation water runoff should leave the farm
Monitoring	Establish a monitoring program (water and soil samples) during the main cropping season

Table 16. Managing pesticide entry into food

Factors/entry route	Methods to reduce pesticide entry to food
Spray drift	Offset enough buffer distances in sensitive areas
	Manage vegetation (eg. hedges) near water ways
	Adopt low drift technologies such as good weather conditions, lower release height, delivery of optimum droplet size etc.
Chemicals	Reduce application rates or combination of products
	Harvesting of produce after exceeding the withholding period
	Adopt Integrated Pest Management (IPM) practices

Table 17. Managing occupational health and safety risks associated with farm chemicals

Factors/Entry route	Methods to reduce pesticide exposure to farm workers
Spray drift	Offset enough buffer distances in the sensitive areas
	Adopt low drift technologies such as good weather condition, lower release height, deliver optimum droplet size etc.
	Advance information about aerial spraying and provide protective clothing to farm workers
	Adopt minimum 24 h time to re-enter the farm
Chemicals	Choose chemicals which have low acute, oral and dermal toxicity and wide spectrum activity
	Reduce application rates or combination of products
	Adopt Integrated Pest Management (IPM) practices
	Apply chemicals in accordance with label requirements
	Maintain farm chemicals register and record of pesticide usage
Chemical handling	Establish safe systems for pesticides transport, storage and application
	Always use protective clothing including gloves, mask, glasses and long clothes covering all exposed skin
	Mix pesticides in well ventilated areas

16 outline several management strategies that can reduce the risks associated with agricultural pesticide use. These strategies are focused on simple changes of practice that could be effectively adopted with appropriate education. Spray-drift (Table 14) can be affected by wind speed during spraying, droplet size and the release height. Reducing the entry of pesticides into surface waters (Table 15) is achieved by reducing spray drift and by reducing the flow of contaminated water off farm.

It is important to manage the possibility of pesticide residues entering food and farm produce, as well as the occupational health and safety of chemical users. The risks of food contamination can be reduced by ensuring all withholding periods are met and by adopting IPM strategies (Table 15). Additionally, much care must be taken to ensure that everyone who handles pesticides is protected from contamination (Table 17). It is good practice for people who use pesticides to always wear gloves and long clothes as protection against accidental spills, and to wash well before eating or drinking.

PART B

Case studies

Integrated field research projects were conducted at three sites in Vietnam: Van Noi (in the Red River Delta), Ninh Thuan province (in Central Region), and Hoc Mon (near Ho Chi Minh City). These field projects illustrate how the integrated approach (detailed in Part A) can be used for risk assessment in Vietnamese situations, and make the collected data available to a wider audience.

To illustrate the methods presented in Part A, all following section numbers correspond to the detailed methods and the risk assessment flow chart (Figure 3.1) For example, methods of field site characterisation can be found in Section 3.2, and examples of completed characterisations can be found in Sections 6.2, 7.2 and 8.2 of the case studies respectively.

6 Case study at Van Noi

6.1 Background

The Van Noi field site is a cultivated area near Ha Noi where market vegetables are grown. Van Noi village belongs to the Dong Anh district, one of five suburban districts of Ha Noi (the others being Gia Lam, Tu Liem, Thanh Tri and Soc Son). Dong Anh's agricultural area comprises some 10,100 ha, occupying 23% of the total agricultural area of Ha Noi city. The Dong Anh district supplies a wide range of produce, including cabbage, green cabbage, cauliflower, green pepper, aubergine, tomato, and pear shaped melon.

6.2 Field site characterisation

Like most agricultural areas in Vietnam, the Van Noi farm is not isolated from habitation: farmers' houses and roads are close by (Fig 6.1). This common situation limits local animal life, and the exercise of ecological risk assessment is limited to impacts on humans (farm workers), household pets, cattle and some local seasonal birds.

6.2.1 Field site description

The field site comprised several small adjacent paddies (5 ha total area), with mainly loam soils. The irrigation system consisted of two parallel 1 m wide channels (680 m total length), with levees around the paddies. All runoff water from flooding or irrigation is usually contained within the channels, which are well separated from nearby river ecosystems.

6.2.2 Field site investigation

Data about the Van Noi field site were collected from Lang Meteorological Station and local investigations (Table 18). The pesticides used in Van Noi (Table 19) can be divided into four categories—pyrethroids, organophosphorous, carbamates and bio-pesticides—of which the most popularly used are abamectin, permethrin, cypermethrin, methamidophos, acephate and fipronil. These pesticides account for more than 75% of all chemicals used on the site.

Figure 6.1. Map showing location of Van Noi field site

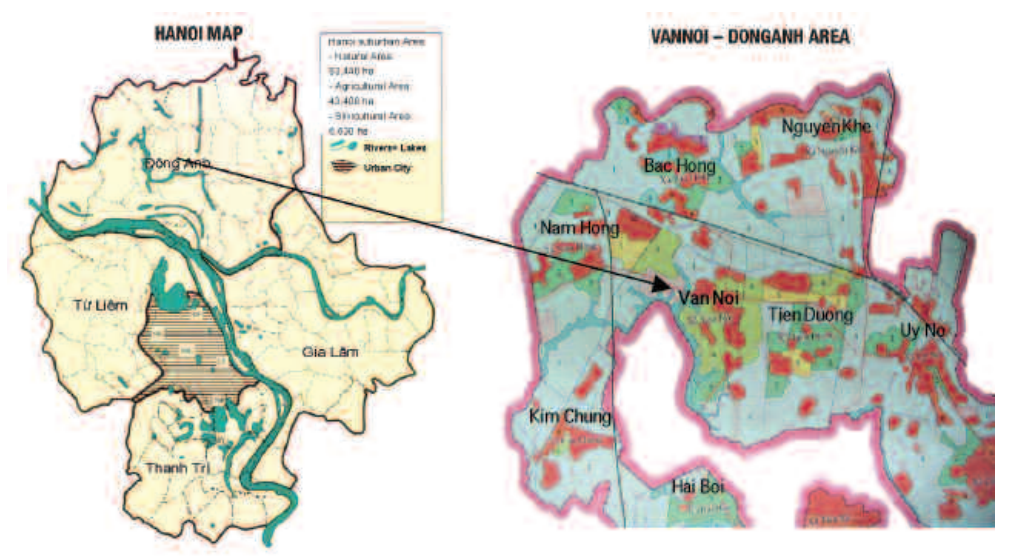


Table 18. Information about the field site (Lang Meteorological Station)

Type of data	Description	Value (average)
Meteorology of field site	Rainfall	140 mm/month
	Temperature	25°–37° C
	Number of storms	7
Pesticide use	Type of chemicals	4 categories
	Rates of application	1.43 kg ai ha^{-1}
	Timing of application	11
Water use	Volume of water use in irrigation	0.173 ML ha^{-1}
	Description of the water system	Two perpendicular channels; each 1m wide by 680 m length
Soil type	Organic carbon	2%
	Clay content	20%

Table 19. Most commonly used pesticides in Van Noi in 2002 (Le Thi Kim Oanh, 2003)

Chemical	Percentage (%)
Abamectin	33.1
Acephate	5.7
Cypermethrin	11.5
Fipronil	5.7
Methamidophos*	7.2
Permethrin	14.4

* banned chemical

6.3 Hazard identification

Every year, there are many cases of food poisoning in Vietnam. In 1997, Vietnam reported 6421 people suffering from food poisoning, of whom 46 died. In urban areas during 1999, there were 1256 cases of food poisoning, resulting in 42 deaths. Reportedly, the main cause was a lack of basic knowledge about pesticide use: for example, farmers harvested their vegetables just a few days after spraying, which resulted in high levels of pesticide residues in crops and potential harm to the consumers of those crops (Nguyen Xuan Thanh, 2002). To validate risk assessments of pesticide contamination, therefore, it is necessary to obtain pesticide data, including actual concentrations, predicted worst-case concentration, ecotoxicity, and chemical use patterns.

6.4 Risk characterisation

6.4.1 Exposure characterisation

Exposure characterisation was made by environmental sampling and modelling. The concentrations of endosulfan in samples from Van Noi's environment and farm produce were obtained by ELISA (Table 20).

Apart from actual site-specific measurements, it is also possible to use the fugacity model (described in Mackay, 2001 and Baskaran, 2002) to calculate the environmental concentrations of pesticides applied in Van Noi. This method estimates the concentration of chemicals based on their predicted distribution among the different compartments, given their solubility in each phase or compartment (Table 21). A spreadsheet can be prepared to make such calculations routine, inputs vary according to particular chemicals or site-specific features (examples of such spreadsheets can be obtained from the authors).

6.4.2 Ecotoxicity

Toxicity data

Toxicity data of pesticides used in Van Noi (Table 22) were taken from *The Pesticide Manual* (Tomlin, 1997) and the Extension Toxicology Network (EXTOXNET).

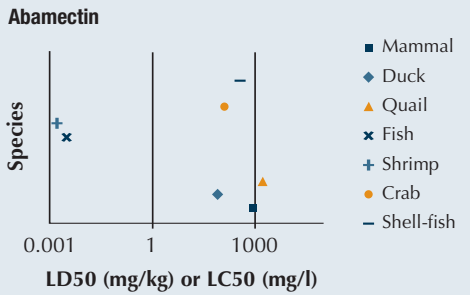
Table 20. Endosulfan (cyclodienes) in environmental and produce samples

Samples	Number	Range of data	Average	% positive samples
Water	50	0-11.9 µg L^{-1}	2.7 µg L^{-1}	63
Soil	50	0-1,200 ng g^{-1}	122.5 ng g^{-1}	78
Vegetable	100	0-370 ng g^{-1}	62.4 ng g^{-1}	36

Table 21. Predicted concentration of pesticides by using fugacity model

Pesticides	Water (µg L^{-1})	Soil (µg kg^{-1})	Vegetable (µg kg^{-1})
Abamectin	$< 10^{-3}$	5.3	1463
Permethrin	$< 10^{-3}$	159.7	4451
Cypermethrin	$< 10^{-3}$	56.2	3682
Methamidophos	115.3	0.9	7.1
Acephate	59.7	1.4	4.2
Fipronil	1.72	23.8	29.3
Endosulfan	$< 10^{-3}$	5.8	480

Figure 6.2. Ecotoxicology data for abamectin



Biodiversity

An Internet-based literature review of Vietnam's biodiversity showed that there are:

- 275 mammal species, 800 bird species, 180 reptile species, 80 amphibian species, 5500 insect species and 12,000 plant species
- in fresh water ecosystems, 1402 species of algae (259 genera in 9 phyla), 782 species of aquatic invertebrates, 52 species of shrimps and crabs; 48 species of other crustaceans (4 genera), and 544 fish species in 288 genera.

Table 22. Properties and toxicity of chemicals (Tomlin, 1997; EXTOXNET)

Properties of chemical		abamectin	permethrin	cypermethrin	methamidophos	endosulfan
MW		873.1	391.3	416.3	141.1	406.9
H		3.50×10^{-05}	1.42×10^{-01}	0.025	1.62×10^{-06}	1.48
Kow(logP)		4.5	6.1	6.6	-0.8	4.74
$t_{1/2}$ soil		7	34	8	4.8	50
$t_{1/2}$ sediment		21	38	12	12	70
$t_{1/2}$ vegetation		0.21	10	1	4.95	5
$t_{1/2}$ water		0.5	4.6	50	27	4
BCF (Chiou)		4.61	6.05	6.50	-0.11	4.84
BCF (Mackay)		1449.58	60428.42	191091.44	0.0076	2637.80
Toxicity[a]						
Mammals	acute LD_{50} (mg kg^{-1})	10	2215	2200	20	160
	dermal LD_{50} (mg kg^{-1})	2000	2500	4920	130	–
	inhalation LC_{50} (mg L^{-1})	–	23.5	2.5	0.2	21 (1h) 8 (4h)
Birds	acute LD_{50} (mgkg^{-1})	84.6(duck)	3000(chicken)	10000(duck)	29.5(duck)	31 (mallard)
		2000 (quail)	13500 (quail)	2000 (chicken)	10.5 (quail)	80 (pheasants)
Reptiles	acute LD_{50} (mg kg^{-1})					
Frogs	acute LC_{50} (mg L^{-1})					
Fish	acute LC_{50} (mg L^{-1})	0.0032	0.0025	0.0069	40	1.5
Crustacean	acute LC_{50} (mg L^{-1})	0.0016 (shrimp)		0.0002	0.22 ng L^{-1}	
		153 (crab)				
Shell fish	acute LC_{50} (mg L^{-1})	430				
Algae	acute LC_{50} (mg L^{-1})				178	

[a] Tomlin (1997); gaps in the literature can be seen clearly by vacant spaces within the table.

Table 23. Characterisation of biodiversity in Van Noi

Compartments on Farm	Air	Soil	Vegetation	Sediment	Water	Water
Exposure route	*Inhalation*	*Contact*	*Ingestion*	*Contact/ Ingestion*	*Aquatic*	*Ingestion*
Mammals	4	4	1	1	0	3
Birds	3	1	1	1	0	3
Reptiles	2	1	0	1	1	0
Frogs	2	1	0	2	2	0
Fish	0	0	0	2	2	0
Crustaceans	0	0	0	2	5	0
Shell-fish	0	0	0	5	2	0
Algae	0	0	0	0	2	0
Taxa (N)	11	7	2	14	14	6

Biodiversity information specific to the Van Noi area was limited, so for the project purposes it was considered as similar to that of the Ha Noi region (Table 23).

6.5 Risk assessment

6.5.1 Hazard quotient approach

To address the risk assessment aims for farm produce or commodities and human health, the Hazard Quotient (HQ) method was used (Section 3.5.1). Both real data and model data were used to calculate the HQ (Table 24).

In summary, the HQ estimation showed:

- HQ < 0.1 (no hazard): acephate and methamidophos
- HQ from 0.1 to 0.5 (hazard): endosulfan
- HQ > 0.5 (unacceptable risk): permethrin, cypermethrin and abamectin

Based on the modelling, abamectin presented the highest risk, which accords with the pesticide's high-calculated concentration as well as its very high toxicity. However, more adapted models may be required for more precise assessment.

Table 24. Hazard quotient results for pesticides in produce samples

Compound	Real data		Model data
	Average conc.	Max conc.	
Endosulfan	0.06 (62.4/1000)	0.36 (356.8/1000)	0.48 (480/1000)[a]
Abamectin			73.5 (1463/20)[b]
Permethrin			0.9 (4451/5000)[a]
Cypermethrin			7.4 (3682/500)[c]
Methamidophos			0.01 (7.1/500)[a]
Acephate			0.002 (4.2/2000)[a]
Fipronil			(29.3/na)

[a] Codex MRL of cabbage (head); [b] tomatoes; [c] MRL of beans

6.5.2 Probabilistic risk assessment approach

Probabilistic risk assessment model (PRA) should be applied when there are available data ranges, including toxicology data for a chosen range of species (end point and metric) and a set of exposure data (environmental concentrations).

Cumulative log-normal distributions of these two data sets were plotted on the same axes, then the exposure and toxicity distributions were converted to dual straight-lines (Fig. 6.3). The final step was to generate a joint probability function of exceedance data by solving functions describing the probability of exceeding both an exposure and an effect concentration (Fig. 6.4). This may also be completed by fitting regression models (ECOFRAM).

The resultant joint probability curve (Fig. 6.4) provides an aid to decision-making. The joint probability functions show that the risk is highest for endosulfan in the soil environment. The risk is lowest for endosulfan in water environment because of lower residue concentrations in this phase. The results are similar to those given by EcoRR modelling.

6.5.3 Ecological Relative Risk

For endosulfan, the comparative study between data simulated by fugacity and analytical results by ELISA showed that the model overestimates the concentration in plants (Table 25). The measure concentration in soil is much higher than modelled, which shows the importance of field studies to obtain a good representation of environmental concentrations. Differences between the two sets of concentrations do not seem to induce any important change in the degree of risk in vegetation. However, because

Figure 6.3: Exposure and toxicity data as linear probability distribution

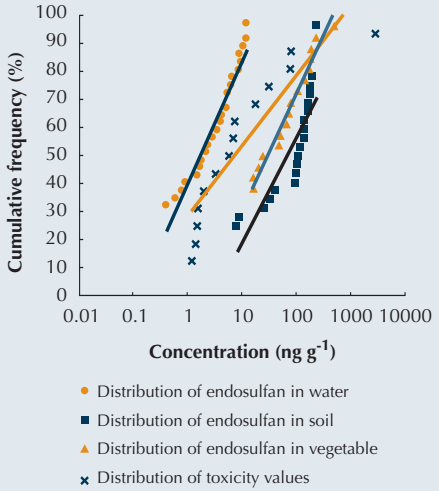


Figure 6.4: Joint probability function of exceedance data

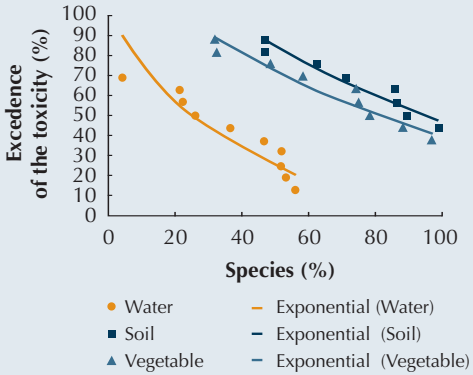


Table 25. Modelled distribution of endosulfan (fugacity model) compared with ELISA-measured data

	Calculated data		Measured data	
	Conc. (ppb)	EcoRR score	Conc. (ppb)	EcoRR score
Air	1.36	221	na	na
Soil	5.8	15	122.5	314
Vegetation	480	43	62.4	12
Water	< 10-3	0	2.7	< 1

of the persistence of endosulfan in soil, its residues place the score in the high risk range.

The result of the EcoRR approach (Figs 6.5a, 6.5b and 6.6) clearly indicate the differences in risk described by the modelled and the real data. Based on the actual data, it would be essential to take action. There are differences among the various chemicals (Fig 6.7), with fipronil showing the highest overall risk score.

Figure 6.5a: Ecological relative risk scores of endosulfan in Van Noi (calculated data)

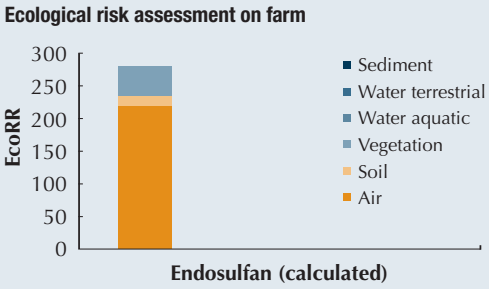


Figure 6.5b: Ecological relative risk scores of endosulfan in Van Noi (measured data)

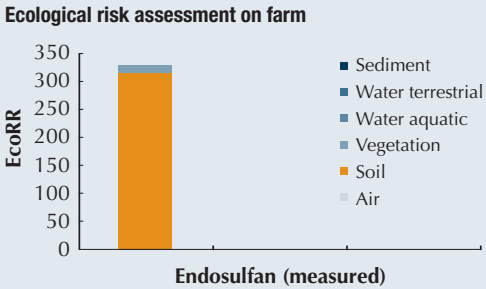
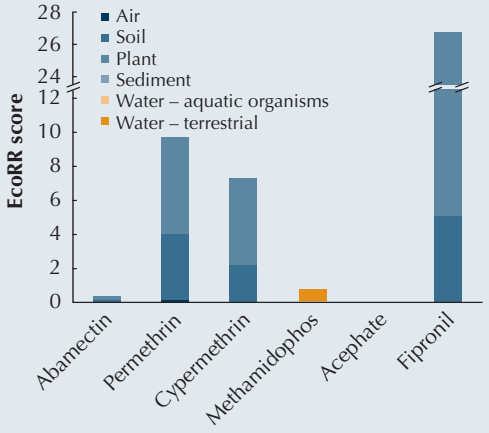


Figure 6.6: Ecological relative risk scores of the most used pesticides in Van Noi



6.6 Risk management

The Pesticide Inventory, Risk Assessment and Management System (PIRAMS) was used to indicate management actions (as described in Section 5.3). The data specific to Van Noi was used in the PIRAMS model to assess risk of a chemical for various categories (Table 26).

The PIRAMS model identified the following key management strategies:

- Choose pesticides that have less leaching potential; low acute, oral and dermal toxicity; and wide spectrum activity.
- Apply chemicals in accordance with label requirements.
- Offset enough buffer distances in the sensitive areas, and manage vegetation near waterways.

Table 26. Result of PIRAM model for the most commonly used pesticides in Van Noi in 2002

Pesticide Name	Farm Worker Score	Surface Water Score	Spray Drift Score	Ground Water Score	Food Score
Abamectin	19 (M)	21 (M)	21 (M)	21 (M)	20 (M)
Acephate	20 (M)	22 (M)	21 (M)	22 (M)	21 (H)
Cypermethrin	19 (M)	25 (M)	21 (M)	23 (M)	20 (M)
Endosulfan	22 (H)	21 (M)	24 (M)	18 (L)	20 (M)
Fipronil	19 (M)	24 (M)	21 (M)	22 (M)	21 (H)
Methamidophos	22 (H)	21 (M)	24 (M)	22 (M)	20 (M)
Permethrin	21 (H)	23 (M)	23 (M)	21 (M)	21 (H)

L: Low, M: Medium, H: High

Vegetables in Hoc Mon district near Ho Chi Minh City.

UAF's CARD project team in their base laboratory.

From left to right: Nguyen Thi Thu Trang, Phung Vo Cam Hong, Le Do Hien, Tran Thi Lan Huong, Bui Cach Tuyen.

- Do not spray during unstable conditions.
- Use higher volumes of water carriers to ensure adequate coverage of targets.
- Optimise application rates (reduce application rates or combinations of products).
- Adopt a minimum delay of 24 hours before re-entering the farm.
- Harvest farm produce only after exceeding the withholding period.
- Establish safe systems for pesticide transport, storage and application.
- Adopt IPM and IFS practices.

After adopting these general practices, further field monitoring could be used to ensure beneficial changes.

7 Case study at Ninh Thuan

7.1 Introduction to the Ninh Thuan region

Ninh Thuan, located at the southern end of Central Vietnam, is the country's largest grape growing area, occupying 90% of the total grape production area of some 2400 ha (Le Quang 2000). The biodiversity of this province is relatively rich and varied, with 93 species of birds alone recorded (Eames and Nguyen Cu, 1994). The sea turtle *Helonia mydas*, regarded as an ecologically sensitive species, can also be found here. The Nui Chua Nature Reserve is located nearby.

7.2 Field site characterisation

The field site, about 10 km from the coast (Fig 7.1), is part of Ninh Thuan's grape production area. The site consists of 31 fields totalling 200 ha of irrigated vineyards, surrounded by residential areas and areas cultivated for dragon fruit, rice and cotton. The site's meteorological data (Table 27) and soil data (Table 28) are available.

Figure 7.1. Map of Ninh Thuan province

7.2.1 Supplementary irrigation

According to Ninh Thuan farmers, irrigation (only necessary in the dry season) is one of the main inputs ensuring high grape productivity and quality. Farmers have often used the flooding method of irrigation on the surface of grape beds. The quantity of water and the irrigation frequency, together with inorganic fertiliser application, are the most important practices of all the field operations. Vineyards are usually

Table 27. Average meteorological data at Nha Ho station 1998 (after Le Quang, 2000)

Month	Temperature (ºC)			Relative humidity (%)	Sunshine hours/ month	Rainfall (mm)	Rainy days/ month
	Mean	Max.	Min.				
January	24.4	33.5	16.3	72	213.6	7.7	1
February	24.8	35.2	17.3	72	225.6	2.4	1
March	26.1	36.5	18.0	75	286.6	7.8	1
April	27.7	36.8	20.4	76	236.9	12.1	2
May	28.2	39.0	19.9	79	198.4	77.1	10
June	28.4	40.5	22.2	79	218.9	66.4	11
July	28.2	39.6	21.9	76	183.2	74.7	9
August	28.2	39.5	21.2	78	205.9	149.1	10
September	27.0	37.7	20.8	82	141.4	169.8	14
October	26.6	34.5	19.3	84	169.5	150.4	15
November	26.0	34.5	17.7	84	136.4	140.1	15
December	24.9	34.0	16.4	80	129.5	55.0	8

Table 28. Properties of soil in Ninh Thuan grape growing area

Parameters	Value
Soil texture[a]	Sandy-clay-loam
Average organic carbon[b]	1.5%
Average clay content[b]	24%
Average sand content	55%
Average silk content	31%
Bulk density (g cm^{-3})	1.2

[a] Soil type was classified using the USDA classification scheme (Klute and Page, 1986)

[b] Analysed by methods indicated in Dane (2002)

irrigated according to a 10–15-day schedule, but in sandy soils irrigation is more frequent, usually every 5–7 days.

7.2.2 Chemical use

Information about local chemical use was gathered by a user survey, which identified seven insecticides (Table 29) and five fungicides (metalaxyl, mancozeb, hexaconazole, triadimenol, diniconazole) and a sixth — chlorothalonil (not considered in this risk assessment) in use at the site.

Table 29. Insecticides and their uses in the field

Chemical	Type	Rate a.i. (L ha^{-1})	Withholding period (days)	Use (%)
Abamectin	Avermectin	0.3–0.6	3	8.8
Chlordane*	Cyclodiene organochlorine	0.1–0.3	na	2.0
Cypermethrin	Pyrethroid	0.3–1.5	7	27.7
Endosulfan	Cyclodiene organochlorine	0.6–1.5	14	28.3
Fenvalerate	Pyrethroid	0.3-1.5	14	23.3
Methamidophos*	Organophosphorus	0.3-0.6	na	3.2
Methidathion	Organophosphorus	0.6-1	7	6.7

* use in Vietnam is banned (Bui Si Doanh, 2002)

7.3 Problem formulation and hazard identification

Ninh Thuan is not only Vietnam's largest grape growing area, but also has a rich and varied biodiversity, so ecosystem protection is as important as the quality of farm products. Toxicity data and exposure data related to the insecticides used locally (Table 29) can be used to evaluate the risk that agricultural pesticides pose to local ecosystems.

The objectives of the risk assessment are to raise concerns, to identify which compartments are most at risk, to compare the relative risk of different chemicals applied at the site, and to suggest management strategies.

7.4 Risk characterisation

7.4.1 Exposure characterisation

Modelled data

Exposure data were calculated using the fugacity approach (Mackay, 2001). Fugacity II calculations were prepared in spreadsheet format and the required input data (Table 28) were entered for each chemical. The output data thus generated show the concentration and proportion of the chemical applied in each compartment (Table 30).

7.4.2 Measured data

Sampling

To obtain exposure data for endosulfan residues, field samples were collected, using the following procedures:

Table 30a. Chemical data of insecticides applied to the Ninh Thuan site

Chemical	abamectin	chlordane	cypermethrin	endosulfan	fenvalerate	methamidophos	methidathion
MW	873.1[a]	409.8[a]	416.3[a]	406.9[a]	419.9[a]	141.1[a]	302.3[a]
Solubility	0.007[a]	0.1[a]	0.004[a]	1[a]	<0.01[a]	>200[a]	200[a]
H	3.50E-05[a]	1.3[a]	0.0253313[a]	1.48[a]	$1.40x10^{-7}$[a]	$1.60x10^{-9}$[a]	$1.66x10^{-9}$[a]
$logK_{ow}$	4.5[a]	2.78[d]	6.6[a]	4.76[a]	5.01[a]	-0.8[a]	2.2[a]
$t_{1/2}$ S	7[c]	1460[c]	8[c]	50[b]	75[a]	4.8[c]	10.7[c]
$t_{1/2}$ V	0.21[c]	na	1[c]	5[b]	14[c]	4.95[c]	4.4[c]
$t_{1/2}$ W	0.5[c]	20[d]	0.21[c]	35[b]	21[c]	27[c]	18[a]
BCF[e]	4.6	3.1	6.5	4.9	5.1	-0.1	2.6
BCF[f]	1517.86	28.92	191091.44	2740.99	4911.81	0.01	7.61

[a]Tomlin, 1997; [b]Hornsby et al.,1996; [c]EXTOXNET; [d]EPA; [e]BCF=0.607+0.893$logK_{ow}$ (Chiou et al., 1997); [f]BCF=0.048K_{ow} (Mackay and Paterson, 1982); In the case of methamidophos, as logKow <0, when calculating BCF, logKow can be replaced by logKoc=0.48. Then, in that case, BCF[e]=1.04, BCF[f]=0.15.

Table 30b. Calculated concentration of pesticides in each compartment in a model grapevine farm (ppm)

	Air	Soil	Vegetation	Water	Aquatic biota	Sediment
Abamectin	$6.86x10^{-9}$	$7.15x10^{-4}$	$1.69\ x10^{-1}$	$5.83\ x10^{-6}$	$1.01\ x10^{-4}$	$7.16\ x10^{-5}$
Chlordane	$1.54x10^{-4}$	$1.65X10^{-6}$	$1.21x10^{-3}$	$2.16x10^{-5}$	$4.47x10^{-6}$	$1.22x10^{-5}$
Cypermethrin	$2.03x10^{-8}$	$3.38x10^{-2}$	1.90	$4.05x10^{-10}$	$4.59x10^{-5}$	$1.15x10^{-4}$
Endosufan	$7.88x10^{-3}$	$3.96x10^{-2}$	2.78	$4.19x10^{-5}$	$4.42x10^{-4}$	$2.25x10^{-3}$
Fenvalerate	$1.20x10^{-10}$	$4.15x10^{-2}$	1.56	$8.00x10^{-7}$	$2.95x10^{-5}$	$7.34x10^{-4}$
Methamidophos	$3.36x10^{-11}$	$3.17x10^{-5}$	$2.16x10^{-4}$	$5.11x10^{-3}$	$1.06x10^{-6}$	$5.34x10^{-5}$
Methidathion	$8.03x10^{-12}$	$5.85x10^{-3}$	$9.94x10^{-2}$	$3.31x10^{-4}$	$1.37x10^{-4}$	$1.43x10^{-3}$

Soil samples. In each small field (belonging to different farmers), five holes were made (one in the centre, four at the diagonals). Soil from these five holes was collected and mixed to form a composite (representative) sample. The soil samples were covered with aluminium foil, placed in plastic bags and kept in a freezer until analysis.

Water samples. Water samples were taken from the channels and the deep wells (the source of irrigation water). All samples were kept in clean brown glass bottles with inert caps, and stored in a refrigerator until analysis.

Grape samples. Grape samples were collected in the Ninh Thuan cultivation area at the same time as farmers were harvesting. Samples were kept in plastic bags, and transferred to the laboratory immediately, where they were chopped and stored in a freezer until analysis.

Analysis. Samples were analysed by ELISA and validated by GC following AOAC (2000) methods (Fig 7.2). Correlation between GC and ELISA results was very good, especially for water samples. Results from ELISA were usually higher than those from GC because of matrix effects and the presence of chlordane residue in some samples.

Results. The results of analysis (Table 31) were validated by GC (Table 32) and by GC/MS (by UAF and CASE).

Table 31. Exposure data for cyclodiene residues (α-endosulfan, β-endosulfan, endosulfan sulfate and chlordane) collected from Ninh Thuan grape cultivation area (by ELISA)

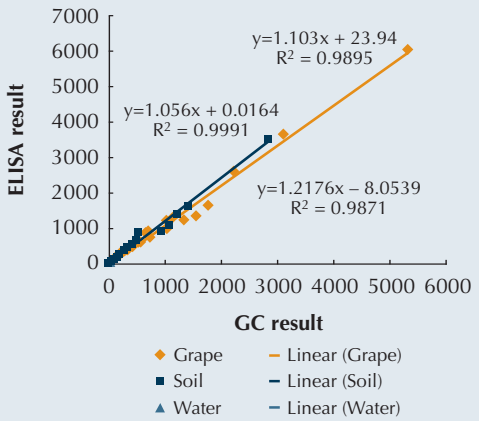
Compartment	Range of conc. (ppb)	Mean value (ppb)	% positive samples	Total number of samples
Soil (July 2003)	7–3600	554	100	22
Water (July 2003)*	0–12	3.3	90	20
Grape (from the site) (July 2003)	80–6000	771	100	38
Grape (from market) (October 2002)	0–1283	254	90	20

*In addition to surface water samples, two deep well samples were also collected. Water from these wells was probably used by people. Concentrations of endosulfan in the two samples were 30.5 and 48.5 ppb.

Table 32. Exposure data for endosulfan residues (a-endosulfan, b-endosulfan, endosulfan sulfate) collected from Ninh Thuan grape cultivation area (by GC)

Compartment	Range of conc. (ppb)	Mean value (ppb)	% positive samples	Total number of samples
Soil(July 2003)	5–2830	462	100	22
Water (July 2003)	0–11	3.2	90	20
Grape (from the site) (July 2003)	42–5319	632	100	38
Grape (from market) (October 2002)	Na	na	90	20

Fig. 7.2: Correlation between GC and ELISA



Data from other sources

Concentrations of fenvalerate and cypermethrin have been reported in grapes (Bui Cach Tuyen et al., 2002) and these data (Table 33) were used for this risk assessment.

7.4.3 Validation of the fugacity model

Pesticide concentrations calculated using the fugacity model were much higher than measured concentrations (Table 34). This was probably because the input data were for the worst-case scenario (highest application rate and assuming no degradation time), and the model assumed equilibrium conditions.

Table 33. Residues of fenvalerate and cypermethrin in grape samples from market, September 2000 (by GC)

Chemical	Range of conc. (ppb)	Mean value (ppb)	% positive samples	Total number of samples
Fenvalerate	0–1930	210	37	30
Cypermethrin	0–1590	84	37	30

Table 34. Predicted vs. measured concentration of endosulfan, cypermethrin and fenvalerate in grape

Compartment	Concentration of endosulfan (ppb)		Concentration of cypermethrin (ppb)		Concentration of fenvalerate (ppb)	
	calculated	measured	calculated	measured	calculated	measured
Grape	2780	771	2279	84	1560	210

Table 35. Toxicity data of insecticides applied to the Ninh Thuan site

Species	Toxicity	abamectin[a]		chlordane[a]		cypermethrin[a]		endosulfan[a]		fenvalerate[a]		methamidophos[a]		methidathion[a]	
	(mg kg^{-1} or mg L^{-1})	Lowest	Highest	Lowest	Lowest	Highest	Lowest	Highest	Lowest	Highest	Lowest	Highest	Highest	Lowest	Highest
Mammals															
	acute LD_{50}	10	13.6	133	70	77	451	na	20	50	25	80	649	138	4150
	dermal LD_{50}	2000	na	200	360	2250	1000	5000	130	na	200	1546	2000	2460	4920
	inhalation LC_{50}	na	na	0.56	0.0126	0.0345	101	na	0.2	na	3.6	na	200	2.5	na
Birds	acute LD_{50}	84.6	2000	83	220	810	1600	9932	10	29.5	23.6	28	795	2000	10000
Reptiles	acute LD_{50}	na	na	Na	na	na	na	na	na	na	na	na	na	na	na
Frogs	acute LC_{50}	na	na	Na	2	12	na	na	na	na	na	na	na	na	na
Fish	LC_{50} (96h)	0.0032	0.0096	0.04	0.3	5085	0.0036	na	40	47.7	0.002	0.01	0.09	0.00069	0.0024
Crustaceans	EC_{50} (48h)	0.00034	na	0.59	7	7000	na	na	0.27	na	na	na	na	0.00015	na
Aquatic Sp.	LC_{50} (96h)	0.000022	0.153	Na	0.56	na	na	na	178	na	na	na	na	na	na
Algae	LC_{50}	na	na	Na	0.006	0.02	0.004	0.001					na	na	na
ADI (mg kg^{-1})		0.002		0.0005		0.05									

[a] Tomlin, 1997; [b]Hornsby et al., 1996; [c]EXTOXNET; [d]EPA; [e]BCF=0.607+0.893logK$_{ow}$ (Chiou et al, 1997); [f]BCF=0.048K$_{ow}$ (Mackay and Paterson,1982); In the case of methamidophos, as logKow <0, when calculating BCF, logKow can be replaced by logKoc=0.48. Then, in that case, BCF^{e}=1.04, BCF^{f}=0.15.

7.4.4 Toxicity characterisation

Chemical and toxicity data of insecticides used at the site are presented in Tables 29, 35a and 35b.

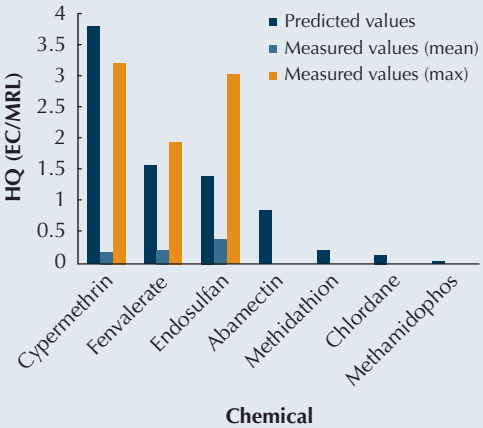
7.5 Risk assessment

7.5.1 Hazard quotient approach

Hazard Quotients (HQ) were obtained for the seven insecticides used for grape growing (Fig 7.3). Based on modelled concentration, cypermethrin, endosulfan, fenvalerate and abamectin were found to pose a high risk of exceeding MRL values, while the hazards related to methidathion, chlordane and methamidophos could be mitigated by restricted use. Based on measured concentration, calculated HQ values showed that the data were still acceptable.

Notably, chlordane and methamidophos are listed as pesticides banned from use in Vietnam (Bui Si Doanh, 2002). For the other insecticides that are allowed to be used on grapes, farmers tend to spray more than recommended.

Figure 7.3: Hazard quotient presented graphically for seven insecticides in grape using FOA MRL values



Therefore, the fruit should be monitored regularly to make sure the residues are lower than MRL values. ELISA was useful for screening a large number of samples in a short time.

Monitoring is especially important for endosulfan. Residues were detected in water in some deep wells (situated in fields) which could have been used for human consumption. The average concentration of endosulfan from two of these wells was 39.5 ppb, giving a hazard quotient value of HQ_{ADI}=6.58. This water should never be used for drinking, nor should it be used for irrigation. The source of contamination should be further investigated.

Vineyard in Ninh Thuan province, South central Vietnam.

Spraying pesticides in trellis vineyard in Ninh Thuan province.

Grapes on vines in Ninh Thuan province.

Grapes from Ninh Thuan showing surface residues. Observing the correct withholding period before marketing is essential.

Figure 7.4: Presentation of exposure and toxicology data as linearised probability distribution

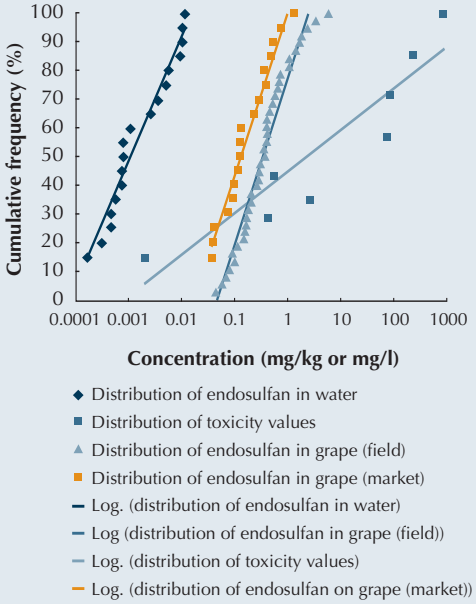
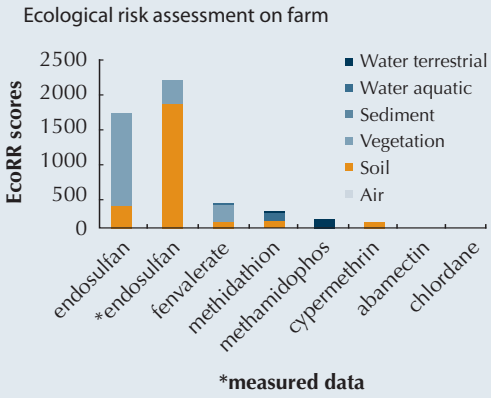


Figure 7.5: Ecological risk assessment on farm



7.5.2 Probabilistic risk assessment approach

Although there was a limit of readily available data, this case study attempted to apply a probabilistic risk assessment approach to endosulfan. The exposure data were determined from GC analysis of field samples, and plotted in log-normal distribution (Fig. 7.4).

Concentrations of endosulfan residues in water (Fig. 7.4) would affect approximately 15% of species, assuming that the toxicology data covers all species in the environment. In addition, about 94% of field samples collected during harvest, and all samples collected from the market, had residues lower than the MRL (Fig. 7.4).

7.5.3 Ecological Relative Risk (EcoRR)

EcoRR scores were calculated for the seven pesticides used in the Ninh Thuan region for five compartments (Fig. 7.5).

For most chemicals, the highest risk was identified on farm produce. The risk was high in water contaminated with methamidophos and methidathion, which are quite persistent in water. Endosulfan posed a very high risk, while fenvalerate, methamidophos and methidathion posed high risks, cypermethrin posed a medium risk and chlordane and abamectin posed low risks. EcoRR scores for endosulfan from measured data were much higher than the predicted ones, an outcome of the high endosulfan concentrations found in the soil.

Table 36. PIRAMS risk ratings for seven insecticides used in Ninh Thuan grape-growing area

Chemicals	Risk for various categories				
	farm worker	surface water	spray drift	ground water	food
abamectin	medium	medium	medium	medium	medium
chlordane	medium	medium	medium	medium	medium
cypermethrin	medium	medium	medium	medium	medium
endosulfan	high	medium	medium	medium	high
fenvalerate	medium	medium	medium	medium	high
methidathion	medium	high	medium	medium	medium
methamidophos	medium	high	medium	medium	medium

Many factors were considered when calculating EcoRR scores, including exposure and toxicity data, and proportion of use. All factors caused variations in score values. Persistence of a chemical in certain compartments is also an important factor in evaluating EcoRR scores. Chemicals are expected to have higher EcoRR scores in the compartment(s) where they have longer half-life, as seems to be the case with endosulfan, fenvalerate, methidathion and methamidophos. However, chlordane persists long-term in soil, for 4 to12 years (EXTOXNET, 2003), but demonstrated very low EcoRR scores. This is because this insecticide has been banned and its use was very limited.

Probabilities of exposure are lowest in the air compartment. Therefore, most insecticides pose a very low risk to air, especially as Vietnamese farmers spray only by hand, not with aircraft (posing a greater risk to farmers' health than to the environment).

EcoRR scores are not absolute risk values, but rather are relative measurements of environmental risk, which can be used for comparing risk among chemicals applied at the site (Sanchez-Bayo et al., 2002). The assessment provides good information for risk management to enable safer pesticides to be selected when there is a choice.

7.6 Risk management

Using the data obtained by survey and measurement, the PIRAMS model was used to determine the risk posed by each chemical for various categories and potential management strategies (Table 36).

There are several reasons why endosulfan and fenvalerate pose high risks to food. First, these

pesticides' application rates are normally higher than recommended. Second, farm produce is often harvested before the withholding period has finished — in this study, samples were taken when the grapes were being harvested, but endosulfan residues were very high (100% positive samples, 6% higher than MRL). Third, cultivation practices were not compatible with integrated pest management (IPM). In addition, the buffer distance was inadequate.

Using the PIRAMS model, it was observed that when the existing application rate was reduced to the recommended rate (a reduction of about half), the risk rating for food reduced to medium. PIRAMS scores also decrease when the withholding period is lengthened or cultivation practices are made more compatible with IPM. In summary, the management strategies already suggested (Table 14) can help to reduce risk. Similarly, risk posed by methidathion and methamidophos in the water could be reduced by applying identified good management strategies (Table 15).

Case study at Hoc Mon

8

8.1 Introduction to Hoc Mon

Hoc Mon cultivated area is located in a suburb of Ho Chi Minh City, about 28 km northwest of the city centre. The city has experienced rapid urban expansion during the last decade, so residential areas are now closer to cultivated areas. The Hoc Mon growing area supplies about 20–30% of vegetables consumed in Ho Chi Minh City.

8.2 Field site characterisation

The selected field site is part of the Hoc Mon cultivated area, and comprises 17.4 ha of irrigated vegetable-growing areas, surrounded by residential areas and cultivation areas (Fig. 8.1). Meteorological data (Table 37) and soil data (Table 38) are available.

8.2.1 Supplementary irrigation

Irrigation is necessary in the dry season but is not important in the wet season. Farmers often use the sprinkle method of irrigation, but it was difficult to ascertain the exact volumes of supplementary irrigation.

Figure 8.1. Map of the location of Hoc Mon

8.2.2 Chemical use

At the Hoc Mon field site, farmers use twelve insecticides (cypermethrin, fenobucarb, methidathion, cartap, fenvalerate, methomyl, permethrin, diazinon, rotenon, carbaryl, endosulfan and fipronil), three fungicides (metalaxyl, benomyl and difenconazol—Table 39), and two herbicides (glyphosate and paraquat).

Table 37. Average meteorological data in Hoc Mon (1998)

Month	Temperature (ºC)			Relative humidity (%)	Sunshine hours/ month	Rainfall (mm)
	Mean	Max.	Min.			
Jan	27.4	33.1	24.2	71	193	6
Feb	27.7	33.6	24.4	71	192	27
Mar	28.5	33.9	25.4	72	187	86
Apr	29.1	34.5	26.5	75	196	187
May	28.7	34.4	25.5	79	182	478
Jun	27.5	31.2	25.1	80	170	269
Jun	27.7	32.2	24.8	80	168	317
Aug	27.9	32.8	25.5	80	139	343
Sep	27.5	33.3	25.2	74	181	158
Oct	26.7	31.5	24.8	86	104	426
Nov	27.4	32.9	24.5	77	165	182
Dec	27	34.7	20.1	76	137	123

(Meteorological Centre of Southern Vietnam)

Table 38. Properties of soil in Hoc Mon vegetable-growing area

Parameters	Value
Soil texture[a]	Sandy-clay loam
Average organic carbon	2%
Average clay content	27%
Average sand content[b]	52%
Average silt content	19%
Bulk density	1.4
Average moisture	40%

[a]Soil type was classified using the USDA classification scheme (Klute and Page, 1986)

[b]Analysed by methods in Dane (2002)

8.3 Problem formulation and hazard identification

The Hoc Mon cultivated area is very close to residential areas. Buffer zones between cultivated areas and residential areas are very small. The percentage of farm produce going to market was significant, with almost one-third of all supply going to Ho Chi Minh City. It is therefore necessary to conduct a risk assessment based upon the quality of farm produce reaching consumers.

The objectives of the risk assessment were to raise concerns, to identify which environmental compartments were most at risk, to determine the quality of market produce, to compare the

Table 39. Main insecticides at Hoc Mon and their uses in the field

Chemical	Type	Rate ai (L ha^{-1})	Withholding (days) (recom.)	% farmers
Cypermethrin	Pyrethroid	0.3-1.5	7	61.82
Fenobucarb	Carbamate	0.6-1.5	7	50.61
Methidathion	Organophosphorus	0.3-1.5	7	30.91
Fenvalerate	Pyrethroid	0.3-1.5	14	23.64
Endosulfan	Organochlorine	0.1-0.6	14	12.6

Table 40. Calculated concentration of pesticides in each compartment in a model vegetable farm (all concentrations in ppm)

	Air	Soil	Vegetation	Water	Aquatic biota	Sediment
Endosulfan	$4.53x10^{-6}$	$1.95x10^{-2}$	$1.42x10^{-1}$	$5.40x10^{-6}$	$5.70x10^{-5}$	$2.48x10^{-4}$
Cypermethrin	$1.02x10^{-9}$	$1.45x10^{-2}$	$9.52x10^{-2}$	$6.74x10^{-11}$	$3.22x10^{-5}$	$1.64x10^{-5}$
Fenobucarb	$5.27x10^{-5}$	$5.62x10^{-2}$	$6.34x10^{-2}$	$1.90x10^{-4}$	$7.54x10^{-5}$	$2.05x10^{-3}$
Fenvalerate	$3.05x10^{-12}$	$9.04x10^{-3}$	$3.97x10^{-2}$	$3.97x10^{-8}$	$1.46x10^{-6}$	$4.17x10^{-5}$
Methidathion	$2.14x10^{-12}$	$4.98x10^{-3}$	$9.92x10^{-3}$	$2.38x10^{-4}$	$3.71x10^{-5}$	$8.30x10^{-4}$

relative risk of different chemicals applied at the site and to suggest some management strategies.

8.4 Risk characterisation

8.4.1 Exposure characterisation

Modelled data

One chemical at a time, all input data required to run the fugacity model (regarding compartments and chemicals) were entered onto an Excel spreadsheet, where calculations were performed in accordance with the multiphase fugacity approach (Mackay, 2001). The output showed the concentration and proportion of each chemical in each compartment (Table 40)

Measured data

To obtain exposure data for endosulfan residues, field samples were taken using standard sampling procedures. Samples were analysed by ELISA (Table 41) and validated by GC (AOAC, 2000). Eight groundwater and surface water samples all showed negative results (not included in Table 41).

Table 41. Exposure data for endosulfan residues (α-endosulfan, β-endosulfan, endosulfan sulfate) collected from Hoc Mon cultivated area (by ELISA)

Compartment	Range of conc. (ppb)	Mean value (ppb)	%RSD	% positive samples	Total number of samples
Soil (March 2002 & July 2003)	0–61	8	22.1	43	51
Water (March 2002 & July 2003)	0–13.5	1.5	4.3	68	50
Brassica sp. (from the site) (March 2002 & July 2003)	0–62	13	14.1	34	38
Brassica sp. (from market) (October 2002)	0–100	18	16.8	35	40

Table 42. Residues of fenobucarb and cypermethrin*

Chemical	Compartment	Range of conc. (ppb)	Mean value (ppb)	% positive samples	Total number of samples
Fenobucarb	Soil	7.6–13.8	10	100	5
	Water	6–16	10	100	5
	Brassica sp.	0–230	31	30	30
Cypermethrin	Soil	9.5–21	14	100	5
	Water	9–26	16	100	5
	Brassica sp.	0–560	43	37	30

* samples taken in 2001, analysed by GC

Data from other sources

Concentration of fenobucarb and cypermethrin in grapes have been reported from other studies (Bui Cach Tuyen et al., 2002; Phung Vo Cam Hong, 2002) and these data (Table 42) were used for this risk assessment).

8.4.2 Toxicity characterisation

Chemical data and toxicity data of the insecticides applied at the Hoc Mon site are presented in Tables 43 and 44.

Table 43. Chemical data of insecticides applied to the site

Chemical	cypermethrin	endosulfan	fenvalerate	fenobucarb	methidathion
MW	416.3[a]	406.9[a]	419.9[a]	207.3[a]	302.3[a]
Solubility	0.004[a]	1[a]	<0.01[a]	420[a]	200[a]
H	0.0253313[a]	1.48[a]	1.40×10^{-7}[a]	na	1.66×10^{-9}[a]
$\log K_{ow}$	6.6[a]	4.76[a]	5.01[a]	2.79[a]	2.2[a]
$t_{1/2}$ S	8[c]	50[b]	75[a]	11[c]	10.7[c]
$t_{1/2}$ V	1[c]	5[b]	14[c]	8[c]	4.4[c]
$t_{1/2}$ W	0.21[c]	35[b]	21[c]	21[c]	18[a]
BCF[e]	6.5	4.9	5.1	3.1	2.6
BCF[f]	191091.44	2740.99	4911.81	29.59	7.61

[a]Tomlin, 1997; [b]Hornsby et al.,1996; [c]EXTOXNET; [e]BCF=0.607+0.893$\log K_{ow}$ (Chiou et al., 1997); [f]BCF=0.048K_{ow} (Mackay and Paterson, 1982)

Table 44. Toxicity data of insecticides applied to the site

Species	Toxicity	Cypermethrin[a]		Endosulfan[a]		Fenvalerate[a]		Fenobucarb[a]		Methidathion[a]	
Concentration	(mg kg^{-1} or mg L^{-1})	lowest	highest	lowest	highest	lowest	highest	lowest	highest	lowest	highest
Mammals	Acute LD_{50}	138	4150	70	77	451	na	623	657	25	80
	dermal LD_{50}	2460	4920	360	2250	1000	5000	10250	na	200	1546
	inhalation LC_{50}	2.5	na	0.0126	0.0345	101	na	0.366	na	3.6	na
Birds	acute LD_{50}	2000	10000	220	810	1600	9932	323	5500	23.6	28
Reptiles	acute LD_{50}	na	na	na	na	na	na	na	na	na	na
Frogs	acute LC_{50}	na	na	2	12	na	na	na	na	na	na
Fish	LC_{50} (96h)	0.00069	0.0024	0.3	5085	0.0036	na	16	na	0.002	0.01
Crustaceans	EC_{50} (48h)	0.00015	na	7	7000	na	na	0.32	na	na	na
ADI (mg kg^{-1})		0.05		0.006		0.02		na		0.001	

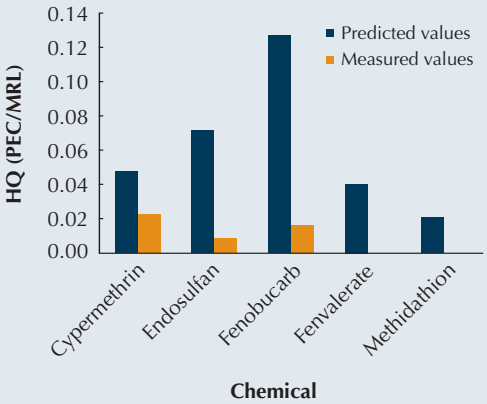
[a]Tomlin, 1997

8.5 Risk assessment

8.5.1 Hazard quotient approach

Hazard quotient (HQ) values for five main insecticides (Fig. 8.2) were based on the risk of FAO-prescribed MRL values being exceeded. Therefore, the assessment determines the risk of exceeding trade regulations. Based on the calculated concentration, all pesticides except fenobucarb were found to pose negligible risk. The risk related to fenobucarb could be mitigated by reducing its use. HQ values based on measured data were even lower.

Figure 8.2. Presumption hazard of insecticides based on Hazard Quotients for farm produce



8.5.2 Probabilistic risk assessment approach

Within the limits of the readily available information, this case study attempts to apply the probabilistic risk assessment approach for endosulfan. The approach used the exposure data derived from GC analysis. Data relating to endosulfan residues in water and toxicity have been plotted in log-normal distribution (Fig. 8.3). The concentrations of endosulfan residues found in water would affect approximately 14% of species (Fig. 8.2), assuming that the toxicology data cover all species in the environment.

Figure 8.3. Presentation of exposure and toxicology data as linearised probability distribution

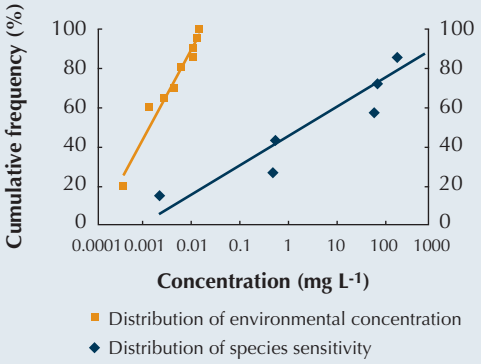
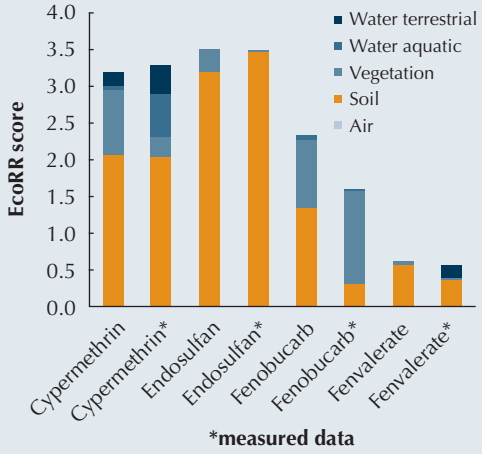


Figure 8.4. Ecological risk assessment on farm in Hoc Mon



8.5.3 Ecological Relative Risk (EcoRR)

EcoRR scores were calculated for five pesticides in five compartments (Fig. 8.4). Cypermethrin, endosulfan and fenobucarb posed low risk, while fenvalerate and methidathion posed negligible risk. Endosulfan—a chemical that has been restricted from use on leafy vegetables—showed the highest total risk.

Most of these chemicals are quite persistent in soil, so the highest risk occurred in soil. Risk was also high in vegetables contaminated with endosulfan, cypermethrin and fenobucarb. Persistence of a chemical in certain compartments is an important factor in evaluating EcoRR scores. Chemicals are expected to have higher EcoRR scores in the compartment where they have a longer half-life.

Exposure was lowest in the air compartment. Most insecticides pose a very low risk to air, especially as Vietnamese farmers spray only by hand, not with aircraft (posing a greater risk to farmers' health than to the environment).

Note that EcoRR scores do not reflect absolute risk, they are relative measurements of environmental risk, which can be used to compare risk among different chemicals.

Table 45. PIRAMS risk ratings for insecticides in Hoc Mon cultivation area

Chemicals	Risk for various categories				
	Farm worker	Surface water	Spray drift	Ground water	Food
cypermethrin	medium	medium	medium	medium	medium
endosulfan	medium	medium	medium	medium	medium
fenobucarb	medium	medium	medium	medium	medium
fenvalerate	medium	medium	medium	medium	medium
methidathion	medium	medium	medium	medium	low

8.6 Risk management

Data from survey and measurement were used in the PIRAMS model to determine the risk of each chemical in various situations (Table 45). When practices are improved—by reducing current application rate or increasing buffer areas, for example—the risk rating for farm workers decreases from medium to low. PIRAMS scores also decrease when the withholding period is lengthened or cultivation practices are made more compatible with integrated pest management. In summary, the management strategies previously suggested (Tables 14, 15, 16 and 17) would be helpful in reducing risk.

A project case study: horticultural production at Van Noi near Hanoi.

Irrigated horticulture at Van Noi near Hanoi.

8.7 Conclusion

In combination with risk assessment using the EcoRR model, probabilistic assessment and hazard quotient, the PIRAMS model indicates that current practices in Hoc Mon cause considerable risk to farm produce, human health and the environment. The risk posed by endosulfan is especially not acceptable. Although the previous study from city market samples did not give rise to any samples with residues higher than the MRL, the recent study raised concern about samples showing evidence of pesticide contamination. In particular, samples taken during harvesting had high concentration of endosulfan and its metabolites.

This risk assessment shows the need for regular monitoring for endosulfan residues and endosulfan metabolites in grapes before they are sold at market. To ensure good quality control, screening a large number of samples is important. This can be achieved using ELISA, with the results subsequently validated using GLC.

References

Altieri, M. A. 1999. The ecological role of biodiversity in agroecosystems, Agriculture, Ecosystems and Environment, 60, 81-96.

AOAC. 2000. Official Methods of Analysis of Aoac International, AOAC International, Arlington.

Bartell, S. M. 1996. Ecological/Environmental Risk Assessment Principles and Practices. *In* Risk Assessment and Management Handbook, (eds Kolluru R, Bartell S and Pitblado R), McGraw-Hill, New York.

Baskaran, S. 2002. Environmental Concentration of Pesticides in Cotton Production Systems: Risk Assesssment by Fugacity Modelling. *In* Environmental Protection and Risk Assessment of Organic Contaminants; (ed Kookana, R. S et al) Science Publishers. Enfield, USA.

Bui Cach Tuyen. 1998a. Monitoring pesticide residues in grapevine (*Vitis vinifera* L.) in Ninh Thuan and in Ho Chi Minh City market (In Vietnamese with English abstract). Journal of Agricultural Sciences and Technology (University of Agriculture and Forestry), 2, 30-32.

Bui Cach Tuyen. 1998b. Monitoring Monocrotophos and Cypermethrin residues in apple (*Ziziphus mauritiana*) in Ho Chi Minh City market and in the field (In Vietnamese with English abstract). Journal of Agricultural Sciences and Technology (University of Agriculture and Forestry), 3, 167-172.

Bui Cach Tuyen. 1998c. Monitoring Cypermethrin, Fenvalerate and Dimethoate residues in tea and tea products (*Thea sinesis*) (In Vietnamese with English abstract). Journal of Agricultural Sciences and Technology (University of Agriculture and Forestry), 3, 3-14.

Bui Cach Tuyen, 1999. Monitoring pesticide residues in *Psidium guajava* and *Eugenis* sp. in Ho Chi Minh City market and in the field (In Vietnamese with English abstract). Journal of Agricultural Sciences and Technology (University of Agriculture and Forestry), 6, 184-187.

Bui Cach Tuyen, Chu Pham Ngoc Son, Le Van To, Pham Hung Viet and Kennedy, Ivan R. 2002. AusAID CARD Workshop 2: Environmental Risk Assessment, Monitoring and Remedial Action for Pesticide Residues, University of Agriculture and Forestry, Ho Chi Minh City, July 2002.

Bui Cach Tuyen, Nguyen Thi Thu Trang, Le Do Hien and Phung Vo Cam Hong. 2004. Monitoring Endosulfan Residues of Produce in City Markets using ELISA. In preparation.

Bui Si Doanh. 2002. Situation report of use of plant protection chemicals and their residue in Viet Nam http://www.hcmuaf.edu.vn/CdHoiThao/%20ELISA-7-2002/BaocaoHoithao%201.pdf, Plant Protection Department, Vietnam.

Burns, L. A.,1990 Exposure analysis modeling system: User's guide for EXAMS II. Version 2.9.4, US EPA, Washington, DC, USA

Cardwell, R. D., Parkhurst, B. R., Warren-Hicks, W. and Volosin, J. S. 1993. Aquatic ecological risk. Water Environment and Technology, 5, 71-87.

Chiou, C. T., Peters, L. J. and Freed, V. H. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science, 206, 831-832.

Chiou, C. T., Freed, B. H., Schmedding, D. W. and Kohnert, K. L. 1977. Partition coefficients and bioaccumulation of selected organic chemicals, Environmental Science & Technology, 11, 475.

Dane, J. H. 2002. Methods of Soil Analysis: Part 4, Physical Methods, Soil Science Society of America, Madison, Wisconsin.

Dent, D. 1995. Integrated Pest Management, Chapman & Hall, London.

Eames, J. C. and Nguyen Cu. 1994. A management feasibility study of Thuong Da Nhim and Chu Yang Sin Nature Reserves on the Da Lat plateau, Vietnam, WWF Vietnam Programme and the Forest Inventory and Planning Institute.

ECOFRAM. 1999. ECOFRAM Aquatic and Terrestrial Final Draft Reports, USEPA.

EXTOXNET. 2004. The Extension Toxicology Network (EXTOXNET), Pesticide Information Profiles, University of California, Davis.

Hammock, B. D. and Mumma, R. O. 1980. Potential of immunochemical technology for pesticide analysis. *In* Pesticide Analytical Methodology, (eds. Harvey, J. Jr. and Zweig, G.), ACS Symposium Series 136, Washington DC, 321-352.

Howard, P. H. and Meylan, W. H. 1997. Handbook of Physical Properties of Organic Compounds, CRC Press, Boca Raton, Florida.

Kennedy, I.R., Sanchez-Bayo, F., Crossan, A.and Rose, M. 2004. Cotton pesticides in perspective: Risk management for produce and environmental protection. World Cotton Research Conference-3, Cotton Production for the New Millennium, (ed. Swanepoel, A.), Pretoria, South Africa. pp. 1047-1060.

Klaine, S. J., Cobb, G. P., Dickerson, R. L., Dixon, K. R., Kendal, R. J., Smith, E. E. and Solomon, K. R. 1996. An ecological risk assessment for the use of the biocide, dibromonitrilopropionamide (DBNPA) in industrial cooling systems, Environmental Toxicology and Chemistry, 15, 21-30.

Klute, A. and Page, A. L. 1982. Methods of Soil Analysis: Part 1 and 2, 2nd ed., American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin.

Knisel, A. 1980. CREAMS: a field-scale model for chemicals, runoff, and erosion from agricultural management systems, US Department of Agriculture, 1980.

Le Quang Quyen. 2000. Grape production in Vietnam. In, Grape Production in the Asia-Pacific Region, (eds. M. K. Papademetriou and F. J. Dent), Food and Agriculture Organization of the United Nations National Regional Office for Asia and the Pacific, Bangkok, Thailand.

Le Thi Kim Oanh, 2003. Research on influence of insecticides to density of some insect pests and their natural enemies on cruciferous crops at Ha noi and near provinces. Ph.D thesis in Ha noi Agriculture University 145 pp. (in Vietnamese).

Le Van To, Bui Cach Tuyen, Pham Hung Viet, Chu Pham Ngoc Son and Kennedy, Ivan R. 2002. AusAID CARD Workshop 1: Environmental Risk Assessment, Monitoring and Remedial Action for Pesticide Residues, Post Harvest Technology Institute, Ho Chi Minh City, March 2002.

Lee, N. A. and Kennedy, I. R. 2001. Environmental monitoring of pesticides by immunochemical techniques: validation, current status, and future perspectives. Journal Association Official Analytical Chemistry, 84, 1393-1406.

Mackay, D. 2001. Multimedia Environmental Models: The Fugacity Approach, second ed., Lewis, Michigan.

Mackay, D. and Paterson, S. 1982. Calculating Fugacity. Journal of Environmental Science and Technology, 15(9), 1006-1014.

Maredia, K. M., Dakouo, D. and Mota-Sanchez, D. 2003. Integrated Pest Management in the Global Arena, CABI Pub, Wallingford.

Mullins, J. A., Casel, R. F., Scarbrough, J. E. and Ivery, A. M. 1993. PRZM-2 a model for predicting pesticide rate in the crop root zone and unsaturated soil zones: program and user's manual, US EPA, Washington D.C.

Nguyen Thu Trang, Vo Thanh Hau, Bui Van Thin, Le Van To, Jeevan Khurana, Nanju Alice Lee. 2005. Development of an ELISA kit detecting cyclodiene pesticides in agricultural products in Vietnam, (in preparation).

Nguyen Xuan Thanh 2002. Impact assessment of water, soil environment and fertilizers to safe vegetable cultivation and adaptability of soil in safe vegetable planning regions in Hanoi. PhD thesis in Hanoi University of Science, Vietnam National University 146pp. (in Vietnamese).

Norton, S. B., Rodier, D. J., Gentile, J. H., van der Schalie, W. H., Wood, W. P. and Slimak, M. W. 1992. A framework for ecological risk assessment at the EPA. Environmental Toxicology and Chemistry 11, 1663-1672.

Pham Hung Viet, Le Van To, Bui Cach Tuyen, Chu Pham Ngoc Son and Kennedy, Ivan R. 2003. AusAID CARD Workshop 2: Environmental Risk Assessment, Monitoring and Remedial Action for Pesticide Residues, Hanoi University of Science, Hanoi, October 2003.

Pham Hung Viet, Pham Ngoc Ha, Nguyen Thi Van Hai, Phan Thu Thuy, Nguyen Minh Tue, Nguyen Ngoc Vinh and Ivan R. Kennedy. 2005. Employment of ELISA technology for determination of cyclodiene pesticides and for risk assessment, (in preparation).

Phung Vo Cam Hong 2002. Monitoring and assessing cypermethrin and fenobucarb residues in some types of vegetables in Ho Chi Minh City and in grape in Ninh Thuan. Masters thesis (in Vietnamese). University of Technology, Ho Chi Minh City.

Sanchez-Bayo, F., Baskaran, S. and Kennedy, I. R. 2002. Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture, Agriculture, Ecosystems and Environment, 91, 37-57.

Sellers, K. 1999. Fundamentals of Hazardous Waste Site Remediation, CRC Press LLC, Boca Raton, Florida.

Skerritt, J. H. 1995. Analytical aspects of immunoassays of agrochemicals. In New Frontiers in Agrochemical Immunoassay (eds. Kurtz, D. A., Skerritt, J.H. and Stanker, L. H.), AOAC International, Arlington.

Smith, R. F., Apple, J. L. and Bottrell, D. G. 1976. The origins of integrated pest management concepts for agricultural crops. In Integrated Pest Management (eds. J. L. Apple and R. F. Smith), Plenum Press, New York.

Solomon, K. R. 1996. Overview of recent developments in ecotoxicological risk assessment, Risk Analysis, 16, 627-33.

Solomon, K. R., Giesy, J. and Jones, P. 2000. Probabilistic risk assessment of agrochemicals in the environment. Crop Protection, 19, 649-655.

Sparks, D. L. 1996. Methods of Soil Analysis, Soil Science Society of America, American Society of Agronomy, Madison, Wisconsin.

Suter, G. W. 1993. Ecological Risk Assessment, Lewis, Boca Raton, Florida.

Tomlin, C. D. S. 1997. The Pesticide Manual, Eleventh ed., British Crop Protection Council, Surrey.

Urban, D. J. and Cook, N. J. 1986. Ecological risk assessment, Standard evaluation procedure of the Hazard Evaluation Division, US EPA Office of Pesticide Programs. Washington, D.C.

USEPA. 1989. Risk Assessment Guidance for Superfund, Volume I, Office of Emergency and Remedial Response. Washington, D.C.

USEPA. 2004. Toxicity Information Retrieval (AQUIRE), Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continental Ecology Division, Duluth, MN.

Appendix

Organic Matter: Loss-On-Ignition (LOI) Method

The following method has been reproduced from Soil Science Society of America Part 3 (Sparks, 1989), which is a modification of a method described by Ben-Dor and Banin (1989).

Apparatus required:

- Pyrex beakers or porcelain crucibles (20 mL)
- Muffle furnace (electrically heated, high temperature oven; Tmax ca. 1200ºC)
- Drying oven (105ºC)
- Analytical balance (± 0.1 mg)

Procedure

Heat beakers or crucibles in muffle furnace at 400ºC for 2 h, cool, and determine tare weight to 0.1 mg. Add 1 to 3 g of air dried soil ground to <0.4 mm to a tared beaker and heat at 105ºC for 24 h. Cool in a desiccator over $CaCl_2$ and determine the weight of beaker plus oven-dried sample to 0.1 mg. Obtain weight of oven-dried sample ($Weight_{105}$) by subtraction. Ignite samples in a muffle furnace at 400ºC for 16h. Cool beakers in a desiccator over $CaCl_2$ and determine the weight of beaker plus ignited sample to 0.1 mg. Obtain weight of ignited sample ($Weight_{400}$) by subtraction.

The LOI content of the sample is calculated as:

$$\text{LOI (\%)} = \frac{\text{Weight}_{105} - \text{Weight}_{400}}{\text{Weight}_{105}} \times 100$$

The organic matter content is assumed to equal the LOI in most surface soils. Variation can occur with small sample sizes. Therefore, ensure that the samples are well mixed and sufficient care is taken when measuring the weights. Hydrated minerals and carbonates within the soil can also reduce the accuracy of this approach. If a soil sample is known to contain a relatively large percentage of hydrated minerals, obtain the SSSA (part 3) methods and follow the procedure to remove these by HCl and HF. However, for routine analysis and a good estimation, the above methodology would usually suffice.

Part of Australia's development assistance program

www.aciar.gov.au