Organochlorine insecticide usage in the sugar industry of the Herbert and Burdekin River regions: chemical, biological, and risk assessments

Thesis submitted by

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Jo-Anne Cavanagh

Abstract

Despite widespread usage of organochlorine insecticides in the Queensland sugar industry from 1947 to 1987, there is remarkably little information on the use and environmental consequences of their usage. This thesis explores three aspects of organochlorine insecticide use in two significant sugarcane growing regions in North Queensland, the Herbert and Burdekin River regions. The first is the distribution of organochlorine insecticide residues in sugarcane soils and coastal and riverine sediments in both regions to assess the current distribution of organochlorine insecticide residues and provide information on historical inputs to coastal sediments. This information is combined with historical information regarding insecticide use in both regions to derive a mass balance for the applied insecticides. The second is the use of an enzyme assay (ethoxyresorufin *O*-deethylase, EROD) to assess the exposure of a common tropical estuarine fish species, *Acanthopagrus berda*, to a range of organic contaminants and provide a screening tool for exposure to organochlorine insecticide residues. The third aspect is the examination of the historical factors influencing risks associated with insect control in the sugar industry, with a particular emphasis of the risks associated with organochlorine insecticide use.

Easily detectable concentrations of organochlorine insecticide residues were found in the sugarcane soils of the Herbert and Burdekin River regions and reflected known application histories. Mass balance estimates indicate that currently less than 0.01% of the 3,900 tonnes of hexachlorocyclohexane, 40 tonnes of aldrin, and 46 tonnes of heptachlor applied to sugarcane in the Herbert and Burdekin regions since 1947 is estimated to remain in the soils of these regions. Low and variable concentrations were found in farm drains and creeks adjacent to sugarcane areas, suggesting some movement of organochlorine residues from the sugarcane fields is occurring. Fish collected from creeks draining sugarcane land and land minimally disturbed by anthropogenic activity generally showed a low level of enzyme induction and a low incidence of detection of organochlorine residues in fish tissue. An exception to this was fish collected from Cromarty Creek, which drains agricultural land in the Burdekin region. These fish showed enzyme induction comparable to that in fish collected from the urban catchment. Although the identity of the inducer is unknown, a town rubbish dump and/or recreational boating activity are suspected to be the sources.

No detectable residues were found in coastal estuarine sediments of either region. Together with known sediment transport processes, this absence suggests that no contamination of the Great Barrier Reef environment as a result of historical organochlorine insecticide application in the Herbert and Burdekin Regions is occurring.

Changes in insect control techniques in the sugar industry have been influenced directly or indirectly by research, changes in farming practices and government legislation, global environmental concerns and trade events. However, in the near future, insecticide usage in the Herbert and Burdekin regions is likely to be largely driven by regional issues related to the efficacy of control.

This thesis is dedicated to Patty, to whom I would have liked to have shown the final product.

Acknowledgments

When the light at the end of the thesis tunnel finally becomes blinding and life after the thesis (almost!) a reality, you realise how all-consuming the whole process of "the thesis" has been - and that so many different people have contributed in so many different ways to this period of your life. Where do you begin to thank them? These two pages are a simple token of my heart-felt thanks to everyone who shared some or all of this time with me - so many good friendships were formed and unique opportunities, both personally and professionally, were provided - and taken!

My supervisors not only provided the opportunity for me to start the thesis in the first place but also made invaluable contributions during the evolution of the thesis - the things which stick out in my mind are; Gregg and his emphasis on the "big picture" and challenge to "show me I'm wrong"; Kathy and her "you need to pay your dues with analytical chemistry" comment that finalised my decision to start the thesis, and her prompting to conduct the fish work; and Ross and his knowledge of soils when I didn't want to know anything about them, and discussions on university and thesis requirements when I really didn't want to know about those either.

Whilst canefarmers and the recreational fishing body don't necessarily see eye to eye on environmental issues, I was fortunate in that both groups gave their support to my project. Numerous farmers in the Herbert and Burdekin regions allowed me to sample their farms, answer my naive questions about farming practises, and provided insight into the environmental issues which concern them. The Herbert, Inkerman, Invicta and Ayr Cane Production boards were instrumental in providing the initial contact with farmers and were forever helpful with providing general information about current and historical farming practises. For this, I am especially grateful to Ron Kerkwyk and Don Williams who received the bulk of my queries, and Terry Hall and Rod Schulz who also took time to talk to me. These Production Boards also kindly allowed me access to historical records as did Andrew Johnson (CSIRO) and the Bureau of Sugar Experimental Stations, Brisbane. Vern Veitch (Sunfish) gave me insight into the recreational fishers' view of the sugar industry and the environmental issues that concern them. Additionally, he generously donated his time and use of his boat to come fishing with me - even when it was pouring rain, the mozzies were biting and the fish weren't....

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The time I have spent in Townsville has been some of the best years of my life, largely due to the people I have met and the friendships we made. The times spent at the Tully River were some of the most memorable with, in no particular order, Vicki, Marls, Anne, Richard, Zitch, Nick - all of whom convinced me at various times that sometimes I really did need to paddle, climb, ride, dance.... or just have fun. Other friends, both old and new, and near and far provided endless hours of fun, conversation and stress relief at various times (also in no particular order) - Fran, Kate, Jack, Katharine, Amanda, Mary, Thomas, Al, Gav, Sonya, Pete. A few people deserve a special mention; Jane - for providing the phone counselling service, and visiting me - even in the US; Sue - my ex-house and lab mate who managed to live and work with me for just over three years, putting up with my various frenzied outbursts of work to the exclusion of all else, both at home and in the lab, without killing me! and Irena, who had to live with me right at the very end and who was also a brilliant typo/formatting error picker-upperer.

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Dave - for being there as brothers are

Dad - my own personal reference librarian (every PhD student should have one!)

And both Mum and Dad, who put up with my numerous phone calls bemoaning the stress in my life because of the thesis, and then resigned themselves to my periodic absences during the times I remembered what life was about.

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List of publications and conference presentations arising from thesis work

Publications

Cavanagh, J.E., Burns, K.A., Brunskill, G.J., Ryan, D.A.J. Ryan and Ahokas, J. (2000). Induction of hepatic cytochrome P-450 1A in Pikey Bream (*Acanthopagrus berda*) collected from agricultural and urban catchments in far north Queensland. *Marine Pollution Bulletin* (In press).

Cavanagh, J.E. (2000) Comparison of the environmental regulation of land management in the Sugar Industry under the *Sugar Industry Act* 1991 (Qld), the Sugar Industry Bill 1999 and the *Integrated Planning Act* 1997 (Qld). *Environmental Planning and Law Journal*, **17(2)**, 118-125.

Cavanagh, J.E, Burns, K.A, Brunskill, G.J. and Coventry, R.J. (1999). Organochlorine pesticide residues in soils and sediments of the Herbert and Burdekin River regions - implications for contamination of the Great Barrier Reef. *Marine Pollution Bulletin* **39(1-12)**, 265-275.

Cavanagh, J. E. (1998). Organochlorine insecticides - the good, the bad, the ugly.... *Canegrower*, **20(12)**, 27.

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Conference Presentations

Environmental and economic sustainability of chemical usage in the North Queensland sugar industry. (Paper). **Cavanagh, J.E.**, Burns K.A., Brunskill G.J. and Coventry R. Australian Marine Science Association national conference Melbourne, Victoria, 7-9 July 1999.

Ecological risk assessment and the North Queensland sugar industry. **Cavanagh, J.E.**, Burns, K.A., Brunskill, G.J. and Coventry, R.J. (Poster). Australian Marine Science Association national conference Melbourne, Victoria, 7-9 July 1999.

Induction of mixed function oxidase (MFO) in Pikey Bream (Acanthropagrus berda) collected from agricultural and urban catchments in far North Queensland. (Paper) **Cavanagh, J.E.**, Burns K.A., Brunskill G.J., Coventry R.J., Ahokas, J. Sources, fates and consequences of pollutants in the Great Barrier Reef and Torres Strait. Townsville, Queensland, 29-30 June 1999.

Changing risks in pest control in the sugar industry - an historical perspective. **Cavanagh, J.E.**, Burns K.A., Brunskill G.J., and Coventry R.J. Sources, fates and consequences of

pollutants in the Great Barrier Reef and Torres Strait. Townsville, Queensland, 29-30 June 1999.

Environmental and economic sustainability of chemical usage in the North Queensland sugar industry. (Poster). **Cavanagh, J.E.**, Burns K.A., Brunskill G.J. and Coventry R. Envirotox '99 Geelong, Victoria, 7-10 February 1999.

Ecological risk assessment and the North Queensland sugar industry. **Cavanagh, J.E.**, Burns, K.A., Brunskill, G.J. and Coventry, R.J. (Paper). Envirotox '99 Geelong, Victoria, 7-10 February 1999.

Environmental and economic sustainability of chemical usage in the North Queensland sugar industry. (Poster). **Cavanagh, J.E.**, Burns K.A., Brunskill G.J. and Coventry R. Society for Risk analysis annual meeting, Phoenix, Arizona, 6-9 December 1998.

Organochlorine pesticide residues in caneland soils - implications for contamination of the near-shore marine environment. **Cavanagh, J.E.**, Burns, K.A., Brunskill, G.J. and Coventry, R.J. (Poster).Society for Environmental Toxicology and Chemistry, 19th Annual General Meeting, Charlotte, North Carolina, USA, 15-19 November 1998.

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Ecological risk assessment and the North Queensland sugar industry. **Cavanagh, J.E.**, Burns, K.A., Brunskill, G.J. and Coventry, R.J. (Poster) Modelling and measuring the vulnerability of ecosystems at regional scales for use in ecological risk assessment and risk management symposium, Washington, USA, 17-20 August 1998.

Organochlorine pesticide residues in soils and sediments of the Herbert and Burdekin River regions - implications for contamination of the Great Barrier Reef. **Cavanagh, J.E,** Burns, K.A, Brunskill, G.J. and Coventry, R.J. 2nd International Conference on Marine Pollution and Ecotoxicology. Kowloon, Hong Kong, 10-14 June 1998.

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Glossary

AIMS - Australian Institute of Marine Science

aldrin - organochlorine insecticide, see p.5

anthropogenic - human

ANZECC - Australia and New Zealand Environment Conservation Council

assignment - land assigned for sugarcane growing by industry bodies

BHC - Benzene hexachloride, commercial formulation of HCH

BNF - β-napthoflavone

BSES - Bureau of Sugar Experiment Stations

Cane Production Board - local sugar industry board, previously known as Cane Pest and Productivity Boards (1992-1999) or Cane Pest and Disease Control Boards (pre-1991).

ccs - commercial cane sugar content

chlordane - organochlorine insecticide, see p.5

chlorpyrifos - insecticide containing chlorine and phosphorous

cytochrome P-450 - enzymes involved in the metabolism of a range of organic substrates

DBOF - dibromo-octafluorobiphenyl, recovery standard used in organochlorine analyses

DDD - organochlorine insecticide, see p.5

DDE - organochlorine insecticide, see p.5

DDT - organochlorine insecticide, see p.5

dieldrin - organochlorine insecticide, see p.5

DoE - Department of the Environment

DPI - Department of Primary Industries

ECOD - ethoxycoumarin-O-deethylase

enantiomer - a pair of isomers that are non superposable mirror images

endosulfan - organochlorine insecticide

EOM - organic matter extracted from soil and sediment samples during soxhlet extraction with dichloromethane

EROD - ethoxyresorufin-*O*-deethylase

Gammexane - commercial formulation of HCH

half-life - time taken for half of the initial amount of a compound to disappear

HCH - hexachlorocyclohexane, a mixture of 1, 2, 3, 4, 5, 6- hexachlorocyclohexane isomers

heptachlor - organochlorine insecticide, see p.5

inducer - compound which causes enzyme induction

induction - increase in the rate of enzyme reaction through increased reaction rates or enzyme synthesis

isomer - compound with the same chemical formula, but different structure

Lorsban® - spray emulsion formulation of chlorpyrifos

NRA - National Registration Authority

OCN - octachloronapthalene, recovery standard used in organochlorine analyses

organochlorine - organic compound containing chlorine

organophosphate - organic compound containing phosphorous

P-450 1A - subfamily of cytochrome P-450 group of enzymes

PAH - polycyclic aromatic hydrocarbon

PCB - polychlorinated biphenyl

PCDD - polychlorinated-dibenzo-dioxin

PCDF - polychlorinated-dibenzo-furan

photo-isomer - structural isomer of a compound formed by reaction with sunlight

risk - probability of a detrimental outcome

SuSCon® - controlled release formulation of chlorpyrifos

TCDD - tetrachloro-dibenzo-dioxin

TCMX - tetrachloro-m-xylene, internal standard used for quantitation in organochlorine analyses

terrigenous - derived from land

trade-off - increase in non-target risk as a result of decreasing a target risk

UVF - Ultraviolet fluorescence, analytical technique used in semi-quantitative analysis of oil concentration

xenobiotic - synthetic chemical

"That we are living with changes set off in the past is obvious. That we choose to ignore this history is a stance that will not obliterate the effects of the past. It simply makes our analysis of the present less adequate."

Wasson, 1994.

Chapter 1: Introduction

1.1 Aims of this thesis

Insecticide usage in Australia is driven by the relative economic benefits of application in agricultural cropping systems compared with any associated environmental and human health impacts. The dominant crop in north Queensland is sugarcane and as such, the sugar industry is the major user of insecticides and other agricultural chemicals. Sugarcane is usually grown within 50 km of the coastline (Figure 1.1). The areal extent of sugarcane and close proximity to the Great Barrier Reef lagoon has given rise to concern about the possible effect of the sugar industry on the Great Barrier Reef and near-shore environments (e.g. Yellowlees, 1991; Hunter, 1992; Hunter *et al.*, 1996). Organochlorine insecticides have played a major role in the development of the Queensland sugar industry since their release in 1947. These insecticides, in particular DDT, have gained a notorious reputation globally since their introduction, due to persistence in the environment, detrimental effects on wildlife, wide-spread contamination of previously pristine environments and human health implications (e.g. Carson, 1962; Duursma and Marchand, 1974; Edwards, 1976; Smith 1991; Carey *et al.*, 1998). These problems contributed to the general banning of organochlorine insecticides[1] in Australian agriculture in 1987, and subsequent banning for all uses in 1996.

A historical perspective is useful for examining environmental change resulting from agricultural land-use change compared with the relative "natural" environmental change resulting from climatic fluctuations, and social factors (e.g. economic, human health) which drive land-use changes. This perspective can, in turn, provide directions for reducing detrimental environmental impact from specific land-use practices such as insecticide usage. In north Queensland, changes in insecticide usage patterns and related farming practices in the sugar industry have driven changes in associated environmental influences. A history of this influence might be provided by examination of organochlorine insecticide residue profiles in near-shore marine sediment cores collected from areas of known terrigenous deposition, and comparison with patterns of known usage. Knowledge of the distribution of organochlorine insecticide residues in the terrestrial and marine environments can also provide information on both the spatial extent of distribution, and exposure of biota, to organochlorine insecticide residues.

Currently, there is limited knowledge of the distribution of organochlorine insecticide residues in the soils and sediments of north Queensland; the relationship of organochlorine insecticide residue distribution to land-use; exposure of fish to organochlorine insecticide

[1] Unless otherwise specified, the use of organochlorine insecticides throughout this thesis refers to the "older generation" organochlorine insecticides such as DDT and heptachlor and does not include the endosulfans or chlorpyrifos, which are also organochlorine insecticides under the definitions used in the glossary.

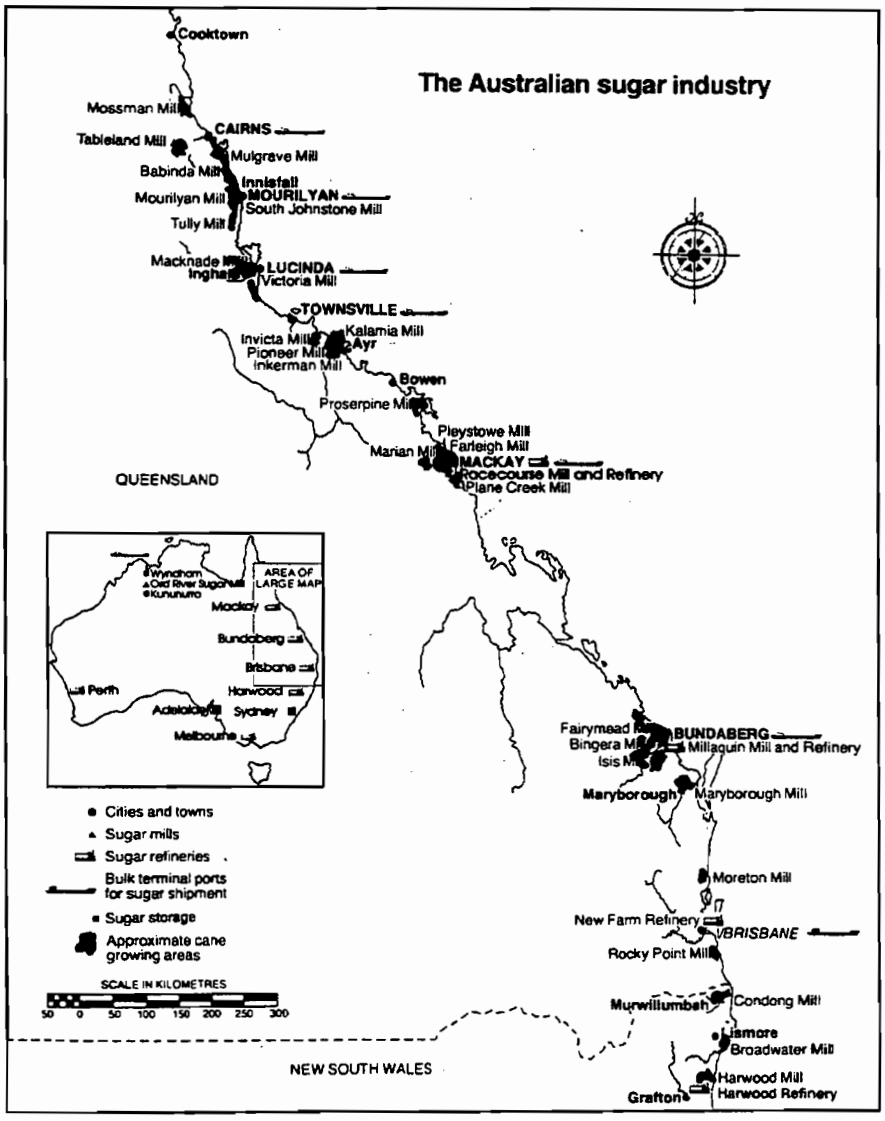


Figure 1.1. Location of sugarcane growing regions in Australia (Source: Australian Sugar Year Book 1999).

residues; and the economic and social factors that directly or indirectly drive insecticide usage. This thesis addresses some of these gaps in current knowledge by considering:

- the distribution of organochlorine insecticide residues in soils and sediments of the Herbert and Burdekin River regions (Figure 1.2);
- the relationship of organochlorine residue concentrations in soils to the known application history to derive a mass balance for organochlorine insecticide usage in these regions;
- organic contaminant exposure of fish collected from agricultural and urban stream catchments as a surrogate for biological exposure to organochlorine insecticide residues; and,
- the economic and social (primarily legislative) factors that have historically influenced insecticide usage in sugarcane farming in the Herbert and Burdekin River regions.

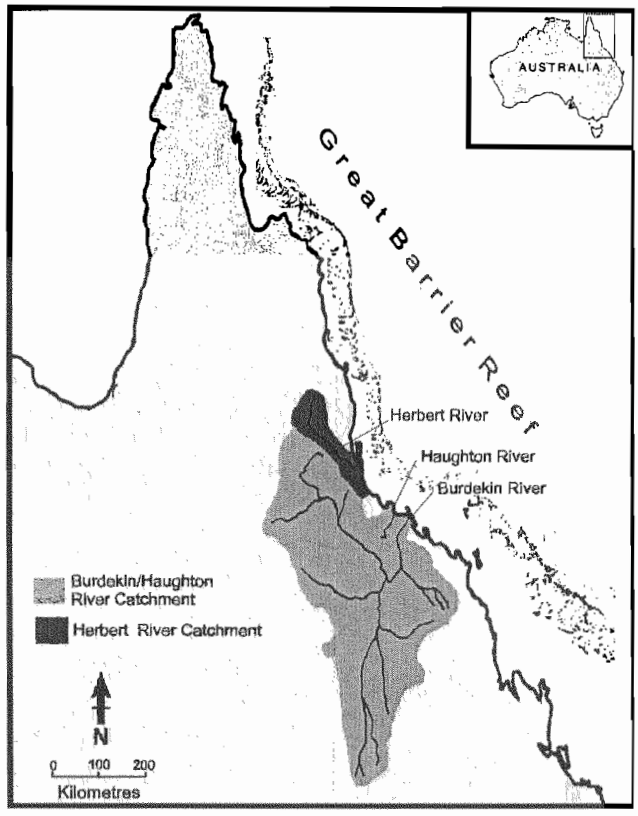


Figure 1.2. Location and size of the Herbert and Burdekin River catchments.

1.2 Organochlorine insecticides

Organochlorine insecticides were widely used globally for agricultural and public health reasons (e.g. malaria control) from the 1940s to 1960s (de Floriat, 1982; Madhun and Freed, 1990; Wargo, 1996). Growing evidence of detrimental environmental and human health impacts from the late 1960s resulted in banning wide-spread usage in many developed countries by the late 1970s (Edwards, 1976; Voldner and Li, 1995; Li, 1999). However, their efficacy, low cost and the lack of effective replacements has meant usage continues in many developing countries, primarily for public health reasons, despite global negotiations to reduce or eliminate usage (Renner, 1998a; Cooney, 1999). A wealth of literature is available on all aspects of organochlorine insecticide usage and effects (see for example Carson, 1962; Duursma and Marchand, 1974; Portmann, 1975; Edwards, 1976; Brown, 1978; Matsumara and Krishna Murti, 1982; Cheng, 1990; Smith, 1991; Carey *et al.*, 1998). This section provides a brief overview of aspects that are pertinent to this thesis.

1.2.1 Modes of action

Organochlorine insecticides act on the nervous system of animals. Acute effects of poisoning are characterised by tremors and nervous convulsions with death presumed to be ultimately caused by respiratory failure (Coats, 1982; Smith, 1991). The general mode of action is

through alteration of electro-physical properties of nerve cell membranes, although the exact mechanism for most organochlorine insecticides is not known (Brown, 1978; Smith, 1991; Carey *et al.*, 1998). The presence of chlorine in organochlorine insecticides has a limited effect on their general toxicity, for example through its contribution to persistence of the insecticides in the environment (Delzell *et al.*, 1994). A greater number of chlorine atoms generally results in greater environmental persistence (Delzell *et al.*, 1994). Poisoning occurs through ingestion, respiration or dermal absorption and is reversible if the source of poisoning is removed (Madhun and Freed, 1990; Smith, 1991). Organochlorine insecticides are acutely toxic to insects at relatively low concentrations, while higher concentrations are required for acute poisoning of other invertebrates and vertebrates (Edwards 1976; Madhun and Freed, 1990).

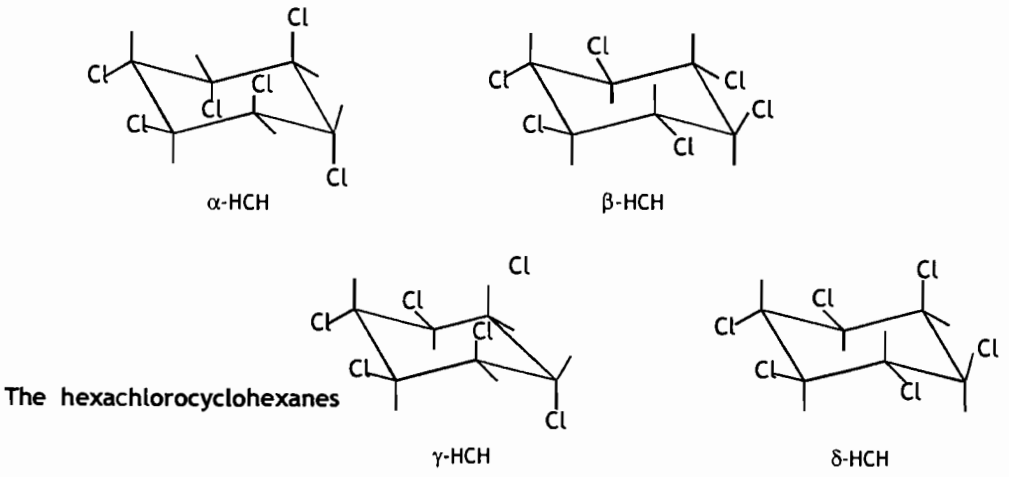
1.2.2 The physico-chemical aspects

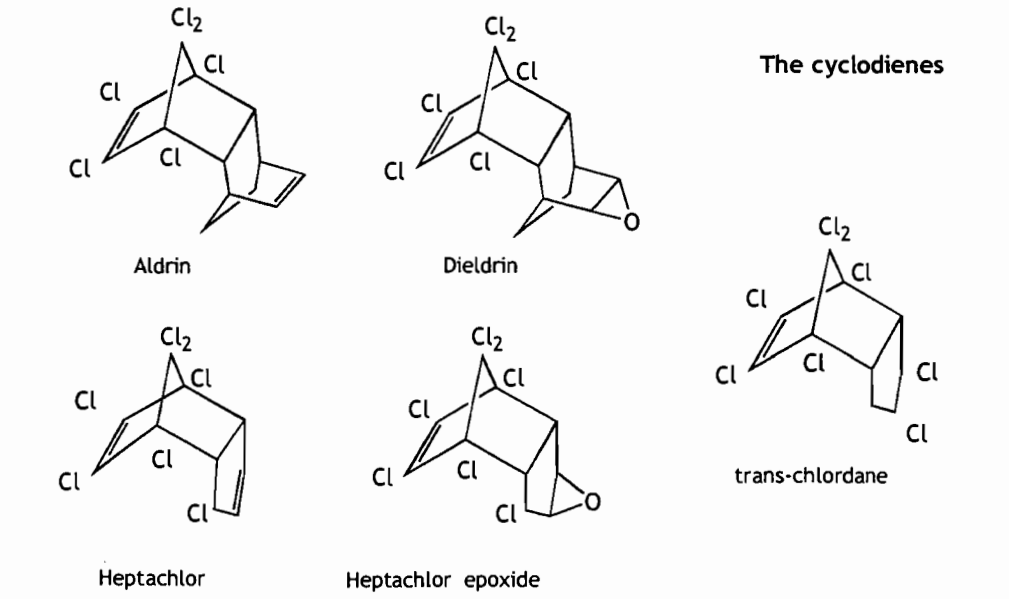
Organochlorine insecticides are generally slightly soluble in water, relatively highly soluble in lipid material and have a low vapour pressure. Structurally, they can be divided into five main groups;

- hexachlorocyclohexane (HCH),
- the cyclodienes (aldrin, dieldrin, heptachlor, cis- and trans-chlordane, endosulfan),
- DDT and analogues,
- toxaphene and related compounds,
- the caged structures: mirex and chlordecone.

HCH, aldrin, dieldrin, heptachlor, chlordanes, and DDTs form the focus of much of the work described in this thesis. Their structures are shown in Figure 1.3 and general physico-chemical properties are listed in Table 1.1. HCH is collectively used to describe eight isomers (denoted by α, β, γ, δ, ε, η, and θ; α-HCH exists in two enantiomeric forms) of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. The structures of α, β, γ and δ are shown in Figure 1.3. The γ-isomer, also known as lindane, is the isomer with the highest insecticidal activity. Formulations containing γ-isomer in a purified form (>99%) and technical mixtures of all isomers have been widely used as commercial insecticides. Technical formulations typically contain 60-70% α, 7-12% β, 10-12% γ, 6-10% δ, and 3-4% ε isomers (Willett *et al.*, 1998), and were often erroneously referred to as "benzene hexachloride".

Organochlorine insecticides may be removed from a particular environmental compartment by way of physical processes such as volatilisation, or sorption to and subsequent movement of eroded soil particles, degradation, or structural transformation. In the following section, degradation refers to the loss or incorporation of chemical elements (e.g. an oxygen atom) in the parent compound, while structural transformation refers to structural rearrangement of the parent compound.





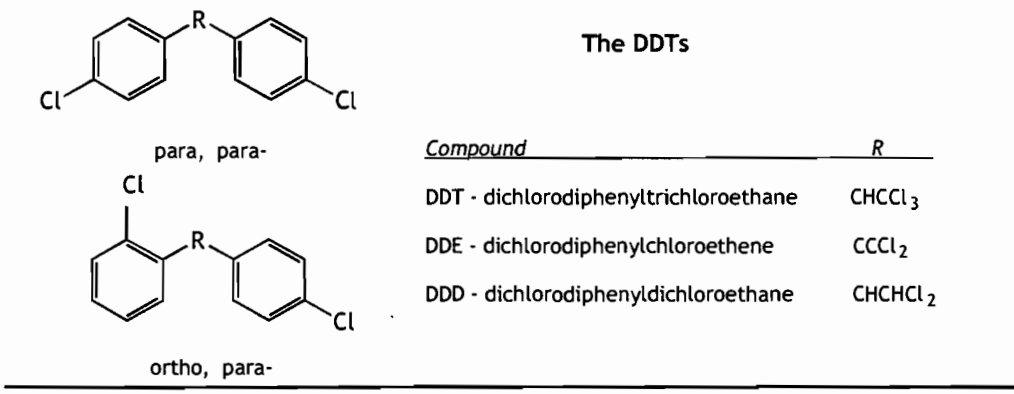


Figure 1.3. Structure of organochlorine compounds discussed in this thesis (Source: Smith, 1991; Willett *et al.*, 1998).

Table 1.1. Physico-chemical properties of organochlorine compounds discussed in this thesis (Source: compiled from Howard *et al.*, 1991; Mackay *et al.*, 1997).

Compound	Water solubility	Vapour Pressure	Henry's Law constant	K_{oc}	Soil env half-life
	(mg/l)	x 10^{-4}, Pa at 25°C	($Pa.m^3mol^{-1}$)	log K_{oc}	Days
α-HCH	1.5-10	1-2,270	0.2-2.2	3.8-4.1	14-135
β-HCH	0.05-5	0.4-272	0.05-0.12	3.5-3.9	14-124
γ-HCH (lindane)	2.2-10	7-213	0.005-1.5	1.1-4	266-400
δ-HCH	8-10	20-23	0.018-0.08	2.8	14-100
aldrin	0.01-0.2	8-750	1.4-91	2.6-6.2	43-590
dieldrin	0.02-2	0.2-8.9	0.02-5.8	3.9-5	49-1,000
heptachlor	0.006-.2	2,200-5,300	18-233	3.8-4.4	3-250
heptachlor epoxide	0.02-.2	3.5-450	3.3-395	2-4.3	33-552
chlordane	0.056-1.85	4.6-29	0.29-9.7	1.6-5.9	360-2,190
p,p'-DDT	0.001-0.46	0.2-18.7	0.86-7.3	3.9-6.8	173-3,300
p,p'-DDE	0.0011- 0.055	1.7-9.9	0.8-124	3.7-6.	1,000
p,p'-DDD	0.002-0.16	1-9	0.27-9	4.6-5.9	730

Organochlorine insecticides are considered to be persistent in the environment. A measure of their persistence is their environmental half-life, or the time it takes for half of the original amount present to be removed from a particular environmental compartment taking all degradation and loss mechanisms into consideration. Most organochlorine insecticides have soil environmental half-lives of greater than 20 days and more often in the order of 400 to greater than 1000 days in the soil, although this is highly dependent upon chemical and environmental conditions (Makcay *et al.*, 1997). In some cases, a parent compound is rapidly degraded to a product that is significantly more persistent in the environment (e.g. aldrin to dieldrin, heptachlor to heptachlor epoxide). In other cases, physical transport such as volatilisation, can determine the environmental half-life of particular compounds such as heptachlor, which is more volatile than other organochlorine compounds, in soils and sediments.

Organochlorine insecticides may undergo degradation or structural transformation by hydrolysis, oxidation, reduction or isomerisation. Hydrolysis and oxidation generally result in the incorporation of an oxygen atom into the parent compound, for example, epoxidation of aldrin and heptachlor to dieldrin and heptachlor epoxide respectively. In hydrolytic reactions the oxygen comes from water molecules. Reduction of organochlorine insecticides generally occurs due to dehalogenation, for example, removal of a chlorine atom from DDT forms DDD.

Isomerisation is a change in compound structure without the addition or removal of any elements, for example, transformation of α-HCH into γ-HCH, production of enantiomers and photoisomers of insecticides including dieldrin, α-HCH, chlordane, heptachlor, *o,p'*-DDT (Henderson and Crosby, 1967; Matsumara, 1982; Wolfe *et al.*, 1990, Aigner *et al.*, 1998). Compounds that are commonly found in the environment as a result of usage of particular organochlorine insecticides are shown in Table 1.2.

Table 1.2. Commonly detected environmental residues of selected organochlorine insecticides.

Insecticide applied	Residues commonly detected in environment
HCH	α-HCH, β-HCH, γ-HCH, δ-HCH
lindane	γ-HCH
aldrin	dieldrin
dieldrin	dieldrin
heptachlor	heptachlor epoxide
chlordane	cis-chlordane, trans-chlordane, heptachlor, heptachlor epoxide, cis-nonachlor, trans-nonachlor, oxychlordane
DDT, DDD	*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE , *p,p'*-DDD, *o,p'*-DDD

Degradation may occur as a result of biotic or abiotic processes. Biotic processes are the metabolic processes of microorganisms, plants and animals. Pesticides[2] in plants and animals are primarily metabolised to more innocuous compounds that are either excreted or stored. In contrast, microorganisms may utilize pesticides as a source of energy (Sethunathan *et al.*, 1982). Metabolism in all organisms generally occurs through enzyme activity, although in microorganisms some reactions can be non-enzymatically operated (e.g. reductive degradation of pesticides by flavoprotein-flavin cofactor systems; Matsumara, 1982). In animals, pesticides are primarily metabolised by a mixed function oxidase system in which cytochrome P-450 enzymes are the key enzymes (e.g. Dorough and Ballard, 1982; Guengerich, 1988). Similar systems are suggested to occur in plants and microorganisms (Matsumara, 1982; Shimabukuro *et al.*, 1982). Biotic processes are the only processes that produce enantiomers of certain insecticides (Aigner *et al.*, 1998; Iwata *et al.*, 1998).

Microbial processes are generally considered to dominate the pesticide transformation in soils and sediments (Wolfe *et al.*, 1990). However, under some conditions such as high sunlight or

[2] The following discussion is a more general discussion of pesticide degradation and is not necessarily specific for the organochlorine insecticides

below the root zone in soil, abiotic transformations may dominate the fate of pesticides. Soil or sediment pH, redox potential, temperature, soil composition, and sunlight can influence transformation reactions. Soil pH effects are generally related to hydrolysis and whether acid, alkaline or neutral hydrolysis occurs (Wolfe *et al.*, 1990). The redox potential of the soil and sediment will determine whether oxidation or reduction reactions will occur. Temperature influences the rate of reaction, with higher temperatures resulting in an increased rate of reaction. The mineral and organic composition of soil may also influence transformation reactions either directly or indirectly as a result of electrostatic interactions between minerals and adsorbed compounds (Wolfe *et al.*, 1990). The mineral content is dominated by clay minerals, which have a high surface area and charge density. However, many pesticides, including the organochlorine insecticides, are primarily associated with the organic fraction of soil or sediment due to their high lipid solubility (e.g. Karickhoff, 1984; Capel and Eisenreich, 1990; Schwarzenbach *et al.*, 1993). This may enhance or hinder transformation reactions (Wolfe *et al.*, 1990; Ghadiri and Rose, 1993). Photolysis refers generally to the process of transformation by sunlight (ultra-violet or visible light) and is the most significant abiotic influence on transformations that occur in surface and atmospheric environments. Sunlight is the only abiotic mechanism that produces isomers of different pesticides, for example photo-dieldrin and photo-heptachlor (Henderson and Crosby, 1967; Matsumara, 1982).

1.2.3 The cause of environmental concern

Environmental concerns stem from the exposure and subsequent ecological impact of organochlorine insecticides on non-target organisms, e.g. soil invertebrates, fish, birds, mammals. Non-target organisms may be exposed to organochlorine insecticides through ingestion or absorption from the surrounding environment. The relative importance of different pathways of exposure will depend on the ecology and physiology of different organisms. For example, accumulation of organochlorine residues in fish and aquatic organisms primarily results from absorption of residues present in the surrounding environment (Edwards, 1976; Brown, 1978; Gobas and Russel, 1991; Schrap, 1991). In contrast, ingestion (via treated grain or seed, or poisoned organisms such as earthworms or birds) is the most significant source of organochlorine residues for birds and terrestrial mammals (Edwards, 1976; Brown, 1978; Moriarty and Walker, 1987).

Historically, ecological concerns focused on mortality of wildlife (Carson, 1962; Brown, 1978). Numerous fish, birds and terrestrial mammals were killed as a result of poisoning by organochlorine insecticides during the 1960s when organochlorine insecticide were widely used in pest control programs (Edwards, 1976; Madhun and Freed, 1990). For example, Johnson (1973) estimated that in the period 1960 to 1970 more than 144 million fish had been killed by pesticides in 4,200 incidents in the US. Ninety-four species of birds were found dead or dying after DDT application to control Dutch Elm disease in the U.S. (Brown, 1978); ground

squirrel, cottontail rabbits, and muskrats were virtually eliminated during a control program in Illinois for Japanese beetles in which dieldrin was used (Scott *et al.*, 1959). In Australia, limited information is available, although fish kills as a result of organochlorine insecticide poisoning and egg-shell thinning in the peregrine falcon have occurred (Olsen and Olsen, 1979; Connell, 1993).

Concerns of residue accumulation and sub-lethal effects induced by residues also existed due to the detection of organochlorine insecticide residues in numerous organisms, including humans. Organochlorine residues accumulate in areas of high fat content such as fatty tissues and mammalian milk where, during storage, residues have a limited effect on the organism. During periods of starvation, fat and organochlorine residues are mobilised, which can then result in toxic effects (Edwards, 1976). Excretion of organochlorine residues that have accumulated in mammalian milk is a significant mechanism of removal for the mother. However, these residues are subsequently transferred to the off-spring, with potential detrimental effects. Numerous sub-lethal effects on target and non-target organisms have been observed including growth impairment or deformities, tumour growth, impairment of immune systems, and impairment of reproductive systems (Smith 1991; Madhun and Freed, 1990; Carey *et al.*, 1998). Other sub-lethal effects include suppression of immune response, which can lower resistance to disease and infection, or induction of immune response, which can cause hypersensitivity (Carey *et al.*, 1998). Dieldrin has been found to depress the immune system (Descortes, 1988; Wong *et al.*, 1992). Eggshell thinning in birds has been the most widely documented form of reproductive impairment (e.g. Ratcliffe, 1967). More recently, the focus of sub-lethal effects has been reproductive impairment by disruption of the endocrine system (Carey *et al.*, 1998). Disruption may occur by a number of different mechanisms including interference of neural activity related to stimulation or inhibition of hormone production, activation of hormone response by compounds that exhibit estrogenic behaviour, blockage of hormone response, or increased metabolic clearance of steroids through induction of the cytochrome P-450 system (Kupfer and Bulger, 1980). However, limited data is currently available as to the extent and the concentrations at which these effects might be observed in different species. Current concerns of the environmental impact of organochlorine insecticide residue concentrations has been renewed with the discovery that some residues can cause disruption of the endocrine system at low concentrations (e.g. Soto *et al.*, 1995; Silvestroni and Palleschi, 1999).

While considerable attention has been given to effects of organochlorine residues on fish, birds and terrestrial mammals, few studies have investigated the ecological impacts on soil and aquatic invertebrates and soil fertility. This is despite the known sensitivity of soil and certain aquatic invertebrates to organochlorine insecticides (Edwards, 1976). Studies on soil fauna suggested that soil invertebrates such as earthworms, slugs and snails were less susceptible to poisoning by organochlorine residues than insects although they concentrated

residues from the soil (Edwards, 1976). Studies on aquatic invertebrates have mainly focused on residues remaining in these organisms and their relationship to food chain accumulation. For example, crayfish, clams and oysters concentrate organochlorine insecticide residues from sediment and water (e.g. Edwards, 1976). Sub-lethal effects of exposure may also cause detrimental impacts on these organisms, which in turn may impact on higher trophic levels. However, little data are available to fully evaluate the ecological impact at this level.

1.2.4 The focus of environmental concerns

Environmental concerns exist at regional and global scales. Regional concerns are focused primarily on the consequences of movement of organochlorine insecticides from the point of application into adjacent terrestrial and aquatic ecosystems. This can occur through local volatilisation and re-deposition, movement through the food chain, and movement of organochlorine insecticides adsorbed on soil particles or direct input (e.g. spray drift) into aquatic systems. As such, regional effects are highly dependent on usage patterns and climatic conditions.

Volatilisation is generally considered to be the major mechanism of transport of many organochlorine insecticides from the point of application, particularly in tropical regions where the warmer temperatures enhance volatilisation (e.g. Spencer *et al.*, 1973, Racke *et al.*, 1997). However, few studies have examined the transport of organochlorine insecticides from tropical soils (Racke *et al.*, 1997).

Global environmental concerns stem largely from volatilisation and subsequent atmospheric transport of the organochlorine insecticides to areas remote from the sites of application. Atmospheric transport is the major mechanism for global re-distribution of organochlorine insecticide residues leading to contamination of wildlife and the environment in regions remote from usage such as the Arctic and Antarctic (e.g. George and Frear, 1966; Peterle, 1969; Norstrom, *et al.*, 1988; Joiris and Overloop, 1991; Barrie *et al.*, 1992; Tanabe *et al.*, 1994; Berg *et al.*, 1997; Court *et al.*, 1997; Bard, 1999). Movement of organochlorine residues from the point of application to the polar regions is suggested to occur either in a single "hop" (Bignert *et al.*, 1998), or a series of "hops", resulting from sequential volatilisation and deposition events related to the volatility of the individual compounds (Wania and Mackay, 1993; 1995; 1996). Sequential volatilisation and deposition forms a "global distillation" of organochlorine insecticides (Figure 1.4; Wania and Mackay, 1993; Wania and Mackay, 1996).

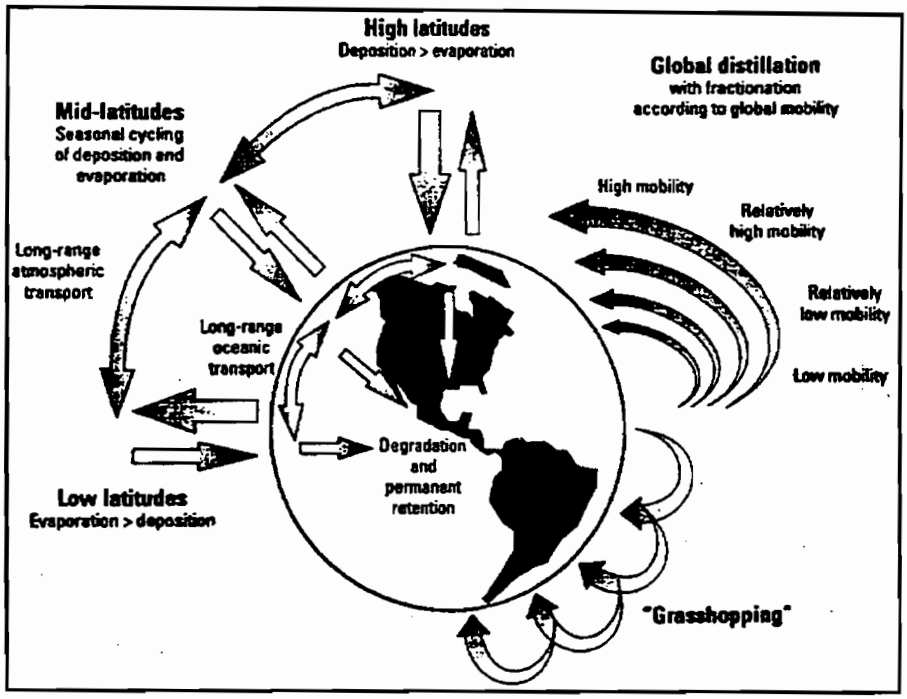


Figure 1.4. Global transport of persistent organic pollutants (Source: Wania and Mackay, 1996).

1.3 The Australian sugar industry, organochlorine insecticides and the Great Barrier Reef lagoon

1.3.1 The Australian sugar industry

Sugarcane was introduced into Australia with the First Fleet in 1788 (Easterby, 1931) and first grown in New South Wales in 1843 at Port Macquarie, and in Queensland around 1847 in the Brisbane Botanic gardens (Anon., 1972). However, it was not until 1862 that the first viable sugarcane plantation was established near Brisbane (Easterby, 1931; Queensland Sugar Corporation, 1996). Since then the industry has expanded considerably and now covers an area of approximately 532,000 ha along 2,100 km of coastal New South Wales and Queensland (Figure 1.1; Canegrowers, 1999).

The Australian sugar industry currently produces around 4.5% of the world's sugar and contributes around $4.7 billion each year to the Australian economy (Canegrowers, 1999). It is economically and socially important, being the nation's fifth largest rural industry in terms of gross value of production, the fourth largest export-earning agricultural industry with export sales around $1.7 billion, and employing 35,000 people directly and indirectly (Canegrowers, 1999). Approximately 85% of the sugar produced in Queensland is exported (Canegrowers, 1999).

Sugar is produced by crushing sugarcane and extracting the sugar during a milling process, creating an inter-dependence between the grower and miller to produce a marketable product. In recognition of this, payment of the grower and the miller is based on a cane price formula that allocates revenue to both parties. This formula is based on the commercial sugar content of sugarcane (ccs) and the price received for sugar (which is negotiated annually and is dependent on domestic and world sugar market demands). The maximum sugar content in sugarcane occurs when sugarcane matures at about 12-16 months, while damage to sugarcane by pests or climatic influences causes a decrease in sugar content. After harvest, delays before crushing can result in decreased sugar content and current recommendations are that cane is crushed within 16 hours of harvest (Canegrowers, 1999). This necessitates a close liaison between growers and millers for scheduling of harvesting and milling of cane.

Allocation of land for sugarcane growing (assignment) by organisations within the sugar industry places an obligation on the grower to supply cane to a mill and an obligation on the mill to accept the cane (King *et al.*, 1953). Assignment helps to ensure a mill is neither under-supplied nor over-supplied with sugarcane during a growing season. Currently, the area harvested for sugarcane is 85-100% of the assigned area. All sugar produced by the mills is purchased by a single buyer (currently the Queensland Sugar Corporation), which subsequently markets the sugar on the domestic and export markets. The inter-dependence of the grower and miller, and the purchase of all sugar produced by a single buyer, has resulted in a unique, highly structured industry, which provides a coordinated approach to research and its implementation.

Since the establishment of the Bureau of Sugar Experiment Stations (BSES) in 1900, extensive research into aspects of production and pest and disease control in sugarcane has been conducted. Additionally local boards were formed to oversee pest and disease control in different regions. Annual reports of research and production activities (e.g. Conference proceedings of local boards and of the Australian Society of Sugarcane Technologists, BSES reports) and Manuals of cane growing (Kerr and Bell, 1939; King *et al.*, 1953; King *et al.*, 1965) enabled the changes in farming practices, including pest control, over time to be followed.

1.3.1.1 The sugarcane cycle

Sugarcane is grown as a monoculture. In a typical sugarcane crop cycle, the same plant crop is harvested annually for 3-5 years, and occasionally for 8-12 years, before being ploughed out and the field allowed to lie fallow for a season (Figure 1.5). Sugarcane is generally planted in north Queensland during the dry season (March to September) by placing short segments of a sugarcane stalk (sett) end to end in furrows in a prepared field. Fungicides are generally applied to the sett just prior to planting. Fertiliser is placed at sett level at the time of

planting and immediately covered with a layer of soil (5-10 cm) to form a "half- open" furrow (Figure 1.6). Germination of sugarcane occurs and results in the formation of a "stool" of cane with both primary and secondary shoots. After the cane has stooled (approximately 2-3 months), the half-open furrow is filled in and soil mounded to form a hill ("hilling-up", Figure 1.6). This results in the cane sett being approximately 20-30 cm below the surface. Insecticides are primarily applied to the plant cane during field preparation, planting or in the half-open furrow just prior to "hilling-up". The cane matures in approximately 12-16 months and is then ready for harvest.

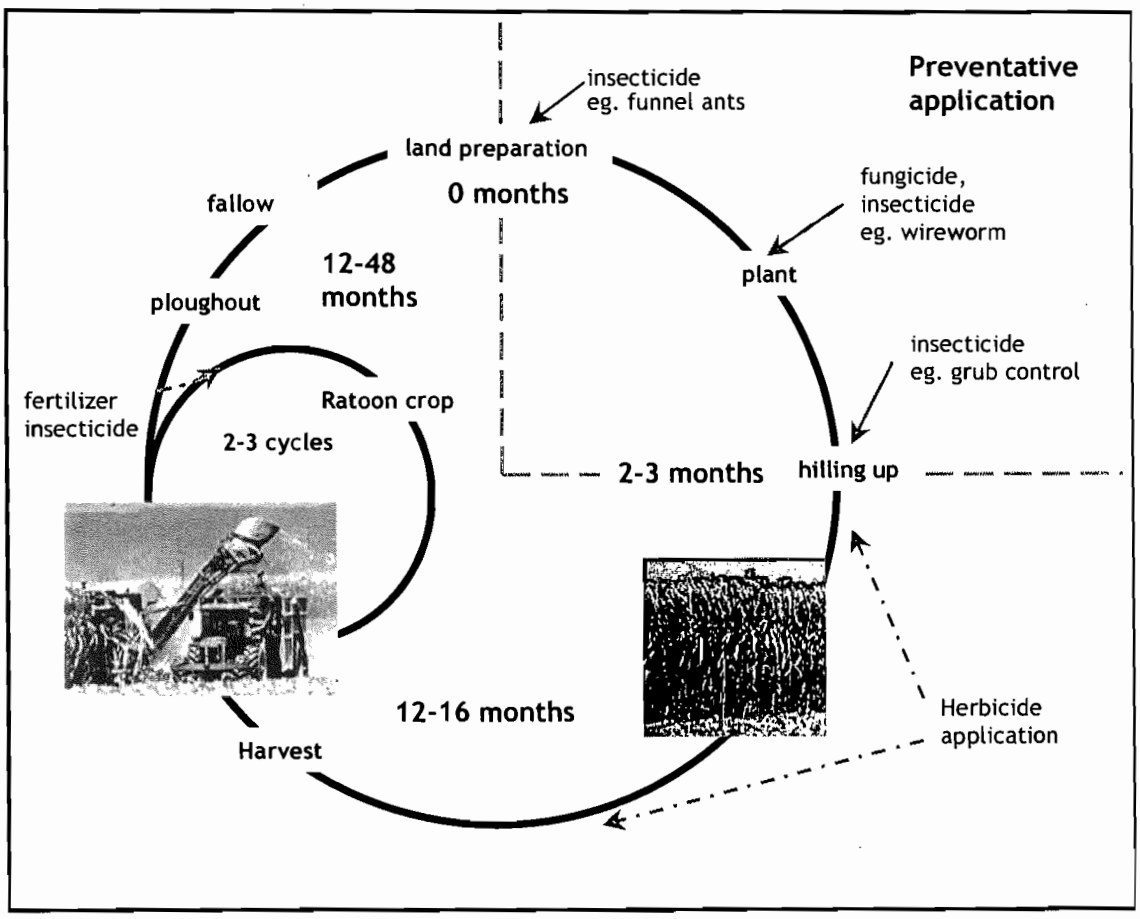


Figure 1.5. Illustration of the processes that occur during a sugarcane growing cycle (Source: compiled from Canegrowers, 1999).

Harvesting occurs from July to December. Two methods of harvesting are currently employed in the industry: burnt cane harvesting and green cane harvesting. Burnt cane harvesting entails burning of the cane field by a low intensity fire to remove excess foliage or "trash" immediately prior to harvest. No burning occurs in green cane harvesting. Post-harvest crop residues may be retained on the field to form a mulch layer or "trash blanket" that can reduce soil erosion and increase soil fertility. Cane is harvested by machinery that cuts cane stalks at ground level and into billets (~15 cm length) that are transported to the mill for

processing. The cane stumps remain in the ground and regrow. These "ratoon" crops are harvested again the following season after 12-16 months growth. The number of ratoon crops harvested from a given field depends on the productivity of the crop and the extent of disease or insect damage. Fertilisers, and occasionally insecticides, are applied to ratoon crops while herbicides are applied as required throughout the crop cycle. After the last ratoon crop is harvested, the field is ploughed and generally left to lie fallow for a season. Legumes or other crops may be planted to replenish the nitrogen content of soils during fallow periods or to break insect pest and disease cycles. Due to the cycle of ratooning cane, a typical farm may have 10-20% of its fields as recently planted cane, 10% as fallow fields, and the remainder under ratoon crops.

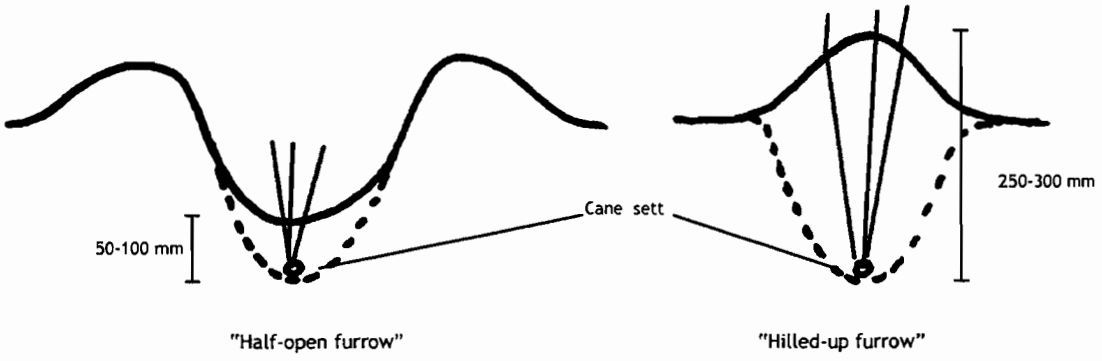


Figure 1.6. Cross-section of a plant furrow to illustrate the process of "hilling-up" during sugarcane planting.

1.3.2 Insects and organochlorine insecticides in the sugar industry

All major insect pests of sugarcane are indigenous to Australia and currently cause an estimated $10-15 M damage annually (BSES, 1993-1997). Insect pests may be divided into two broad groups: those that damage the root system, or young plant or ratoon shoots (soil pests) and those that damage the foliage or cane stalk (surface pests). Soil pests cause the most damage. Cane grubs, soldier fly larvae, wireworm and nematodes are the major pests. Nineteen different species of cane grub exist, however the greyback grub (*Dermolepida alborhirtum*) is the most important in north Queensland (Roberston *et al.*, 1995). Surface pests including locusts, grasshoppers, and cicadas may cause significant damage occasionally.

Organochlorine insecticides were significant in providing effective control of insect pests in sugarcane from 1948. "Gammexane," a commercial formulation of technical hexachlorocyclohexane (HCH) was the first organochlorine insecticide formulation available for commercial use. Technical HCH contained the α, β, γ, δ-HCH isomers in the approximate proportion of 70-75%, 5-7%, 13-15% and 6-8% respectively, and was often erroneously known as "Benzene hexachloride" (BHC). The first applications of technical HCH were so successful

in reducing cane grub damage that by 1949, a commercial formulation designed specifically for use in the sugar industry, was made available. This formulation contained approximately 20% technical HCH in rock phosphate dust. While other insecticides were trialed for cane grub control, these were found to be either not effective (chlordane, toxaphene, aldrin) or not effective against cane grub species other than the greyback grub (dieldrin, heptachlor) (Wilson, 1952; Wilson, 1958; Wilson, 1961; Smith, 1962; Hitchcock, 1964). This resulted in technical HCH formulations remaining the predominant chemical control for cane grubs until HCH was banned in 1987.

Technical HCH formulations were also effective against a number of other insect pests and were initially used to control wireworms. However, the usage of HCH formulations for wireworm was phased out when other insecticides became available due to phytotoxic effects of HCH on sugarcane. From the early 1950s, various organochlorine insecticides were trialed for control of different insect pests and by the early 1960s rates and methods of application were established (Table 1.3). Application of insecticides occurred in the half-open drill, as a broadcast dressing followed by immediate incorporation into the soil, or surface application (and no soil incorporation). Insecticides applied for soil pests are buried or incorporated in the soil and due to the process of ratooning, these insecticide placements are undisturbed for 3-5 years until the ratoon crop is ploughed out. HCH formulations were primarily technical HCH mixed in rock phosphate dust while lindane, aldrin, dieldrin and heptachlor were primarily used as spray emulsions. Organochlorine insecticides continued to be widely used in the sugar industry until 1987 when they were banned. Restricted usage of dieldrin for soldier fly control and heptachlor for funnel ant was permitted in some regions until 1991 and 1994 respectively (J. Steele, NRA, pers. comm.).

Table 1.3. Recommended method of insecticide application for different insect pests (Source: Mungomery, 1965).

Insect Pest	Insecticide				
	HCH	Dieldrin	Heptachlor	Lindane and Aldrin	DDT
All cane grub species	Half open furrow or Broadcast				
Greyback grub	Half open furrow	Half open furrow	Half open furrow	Half open furrow	
Wireworm				With fertiliser at planting	
Soldier fly	Broadcast	Broadcast			
Army worm	Surface				Surface
Grasshoppers/locusts	Surface				
Funnel ant			Broadcast		

1.3.3 Organochlorine insecticide residues in sugarcane lands

With continuously increasing area of sugarcane farming in north Queensland, concerns over the impact of land-use change, specifically increased sediment and chemical contaminant loads entering the Great Barrier Reef lagoon, have increased in recent years. Numerous studies have focused on aspects of nutrient and sediment transport to the reef (e.g. Yellowlees, 1991; Moss *et al.*, 1992; Pulsford 1993; Furnas *et al.*, 1995; Larcombe *et al.*, 1996) although comparatively few have examined the distribution of organic contaminants such as pesticides (McCloskey and Deubert, 1972; Olafson, 1978; Dyall and Johns, 1984; Hunter 1992; Rayment *et al.*, 1997) or petroleum hydrocarbons (Smith *et al.*, 1985; Sandström, 1988).

1.3.3.1 Physico-chemical aspects

Organochlorine insecticide residues are primarily transported from agricultural land to aquatic systems by adsorption on, and subsequent movement of, eroded soil particles (Karickoff, 1984; Leonard, 1990). Hence, factors influencing the amount and movement of soil eroded from sugarcane fields to, and within, aquatic systems will influence the distribution of residues in these systems. Farming practices, topography, and soil type play a significant role in soil erosion. Topography and soil types are important in determining soil erosion at a catchment scale. In catchments of similar topography and soil type, farming practices will be the dominant influence on soil erosion.

Soil erosion is manifested in river sediment loads. Substantial inherent climatic variability in tropical environments (e.g. floods, cyclonic events, extended dry periods) make it difficult to quantify annual changes in sediment loads. Most rivers entering the Great Barrier Reef lagoon have extreme high flow/low flow ratios and since sediment transport is partly a function of flow rate, the volume of sediment transported annually may be highly variable. Despite this, estimates of total increase in sediment flux since European settlement are placed at 2 to 5 times the natural flux (Moss *et al.*, 1992; Neil and Yu, 1996).

Chemical tracers, such as organochlorine insecticides or anthropogenic metals, can be used to identify sediment sources and provide a clearer picture of the contribution of specific land-use activities to sediment and contaminant loads. The use of dated sediment core profiles of contaminants has proven to be successful in plotting the history of human impacts on many lake and marine environments (e.g. Burns and Villenveuve, 1983; Gearing *et al.*, 1991; Sanders *et al.*, 1992; van Zoest and van Eck, 1993; Gerritse *et al.*, 1995; Hendy and Peake, 1996; Walker and Brunskill, 1996). Therefore, the widespread application of organochlorine insecticides to sugarcane land from the late 1940s to 1987 should provide good markers for sediment deposited during this time period.

In the present study, organochlorine insecticide residue profiles in sediment cores were examined to provide an assessment of the historical contribution of sugarcane growing to sediment export and depositional history. Furthermore, as organochlorine insecticides are more persistent than insecticides currently in use, the extent of their distribution in the marine sediments can provide a worst-case scenario for the distribution of current insecticides, assuming they are transported by the same mechanism. The distribution of organochlorine residues in sugarcane soils, in on-farm drains, creeks surrounding sugarcane land and coastal marine sediments were also examined to determine the extent of contamination resulting from historical application of organochlorine insecticides. The distribution of organochlorine residues in soils and marine sediments provided the basis for a mass balance of organochlorine insecticides used in the Herbert and Burdekin River regions.

1.3.3.2 Biological aspects

Few studies have investigated the biological aspects of chemical contaminants in the Great Barrier Reef lagoon. These studies have largely focused on chemical residues in biological tissue (e.g. von Westernhagen and Klumpp, 1995; Russell *et al.*, 1996; Rayment *et al.*, 1997) although Klumpp and von Westernhagen (1995) described abnormal development in fish larvae captured in coastal regions of the Great Barrier Reef lagoon.

One means of assessing biological exposure to chemical contaminants and potential detrimental effects is through the use of biochemical indicators or biomarkers. Biomarkers provide a screening tool for the identification of locations that may suffer detrimental impacts as a result of chemical contamination. Biomarkers have advantages over traditional methods of chemical monitoring of xenobiotic contaminants as they can provide faster and cheaper results in addition to providing a direct indication of biological effects. One particular biomarker that has received considerable attention for application in monitoring of organic contaminants in aquatic systems is cytochrome P-450 1A, which is a sub-family of the cytochrome P-450 enzymes. The cytochrome P-450 enzymes are the primary group of oxidative metabolic enzymes and catalyse a range of oxidative reactions on endogenous (e.g. steroids, hormones, fatty acids) and exogenous substrates (e.g. polycyclic aromatic hydrocarbons (PAH), halogenated aromatic hydrocarbons (HAH) such as biphenyls (PCB) and polychlorinated-dibenzo-*p*-dioxins/furans (PCDD/PCDF), and flavonoids). Induction of the enzymes occurs through either increased activity of the enzyme or increased synthesis of the enzyme, as a result of exposure to inducing agents. The P-450 1A sub-family is especially sensitive to induction by a range of organic contaminants, including PCDDs/PCDFs, PCBs, PAHs and some organochlorine pesticides (Payne *et al.*, 1987; Goksøyr and Förlin, 1992; Holdway *et al.*, 1995; Denison and Heath-Pagliuso, 1998). Induction of P-450 enzymes as a result of exposure to certain polychlorinated biphenyls has been shown to enhance metabolic clearance of steroids, resulting in delayed reproduction (Thomas, 1989).

In the present study, induction of cytochrome P-450 1A has been used to provide a screening tool to identify locations where fish have a high exposure to organic contaminants, and therefore are more likely to accumulate organochlorine insecticides if these were present in the environment.

1.3.4 Factors influencing insecticide usage in the sugar industry

At the most obvious level, control of insect pests is the major factor driving insecticide usage. However, the choice of the insecticide used and, indirectly, the method of control of an insect pest, are driven by a combination of environmental, economic, and social factors. Environmental factors include the distribution and persistence of insecticides in the environment, toxic effects of the insecticide on non-target organisms, and scale of use. Economic factors include the cost of insecticides, cost of alternate control measures, potential crop damage and value of the crop. Social factors include human health impacts of the insecticide on both the consumer and the farmer, legislative requirements, perceptions of the environmental and economic impact of insecticide usage, and the scale of the industry.

These factors may be considered in the context of risk, where risk is the probability of a detrimental outcome. What that outcome is, depends on the context in which risk is examined. For example, there is a risk that environmental impacts will occur as a result of insecticide usage; there is a different risk that a crop will be damaged if insecticides are not used. The magnitude of these risks is the result of a combination of factors including the chemical used, transport mechanisms, toxic effects on non-target organisms, the insect pest, and its potential to damage the crop. An individual farmer makes a decision to apply insecticides based on consideration and perception of the relative environmental, economic, and human health risks associated with application. This risk consideration is made not only at an individual farmer level, but also at an industry, national, and global level. The outcome of these considerations or risk trade-offs can impact directly and indirectly on the type of insecticide used, the amount used, and the method of insect control, resulting in significant cultural changes within the industry. Conversely, the outcome of risk trade-offs may not result in any change, and any environmental impacts resulting from insecticide usage may continue. Thus, in order to make informed decisions regarding future control of insect pests, it is important to identify the direct and indirect risks associated with insecticide usage and the risk trade-offs that must necessarily be made if changes occur. In the present study, the historical usage of organochlorine insecticides in sugarcane farming is used to identify the risks and risk trade-offs associated with insecticide usage in this industry.

1.4 Study sites

The Herbert and Burdekin River regions are two significant sugarcane growing regions in north-eastern Australia (Figure 1.2), which together produce approximately 30% of Australia's sugar (Canegrowers, 1999). Contrasting climatic conditions and farming practices provide an opportunity to examine the influence of these factors on the distribution of organochlorine insecticides in the sugarcane lands and surrounding aquatic environments of the two regions.

1.4.1 The Herbert River region

The Herbert River catchment drains an area of approximately 10,130 km^2 and is the largest river system located in Australia's sub-humid to humid tropical north-east (Figure 1.2; Johnson and Murray, 1997). The mean annual rainfall of 1,370 mm is strongly influenced by the incidence of cyclonic activity during the wet season (November to May). The Herbert River drains into the southern end of Hinchinbrook Channel where unusual tidal dynamics results in trapping of water and sediments contained in the water column in the inter-tidal and sub-tidal muds which line the channel (Wolanski *et al.*, 1990). Subsequent deposition of the majority of sediment from the Herbert River occurs in the deltaic, mangrove and near-shore mud bank deposits of the Hinchinbrook Channel and Missionary Bay at the northern end of Hinchinbrook Island (Brunskill, 1995). Extensive mangrove swamps have colonised the current distributary area of the Herbert River and Hinchinbrook Channel (Johnson and Murray, 1997) and strongly influence sediment dynamics.

Sugarcane is the dominant land-use on the coastal floodplain, currently covering an area of approximately 65,000 ha (ca. 6.5% of the total catchment area, Figure 1.7), while grazing is the predominant land-use in the upper catchment. The area of sugarcane has expanded considerably since being first grown in this region in the late 1860s (Figure 1.8). Some of the earliest areas used to grow sugarcane were the Macknade and Victoria regions located downstream of Ingham on the floodplain. This was followed by areas along the banks of the Herbert River extending up to Stone River and Abergowrie. The industry expanded around this core moving southwards towards Cattle Creek and further north to the Seymour River and Ripple Creek area. The sugarcane land of the Herbert region is relatively flat, with slopes generally less than 1% (Anon., 1999a). Conventional cultivation techniques were used until the introduction of green-cane harvesting around 1976. Since then green-cane harvesting has become increasingly widespread and now forms almost 100% of the harvest (R. Kerkwyk, Herbert Cane Production Board, pers. comm.).

Greyback grub and wireworm have been the most significant insect pests, with technical HCH formulations predominantly used for cane-grub control, and aldrin and lindane for wireworm control (Figures 1.9 and 1.10). Insecticides were applied infrequently for other insect pests such as armyworm, other cane grubs, and soldier fly.

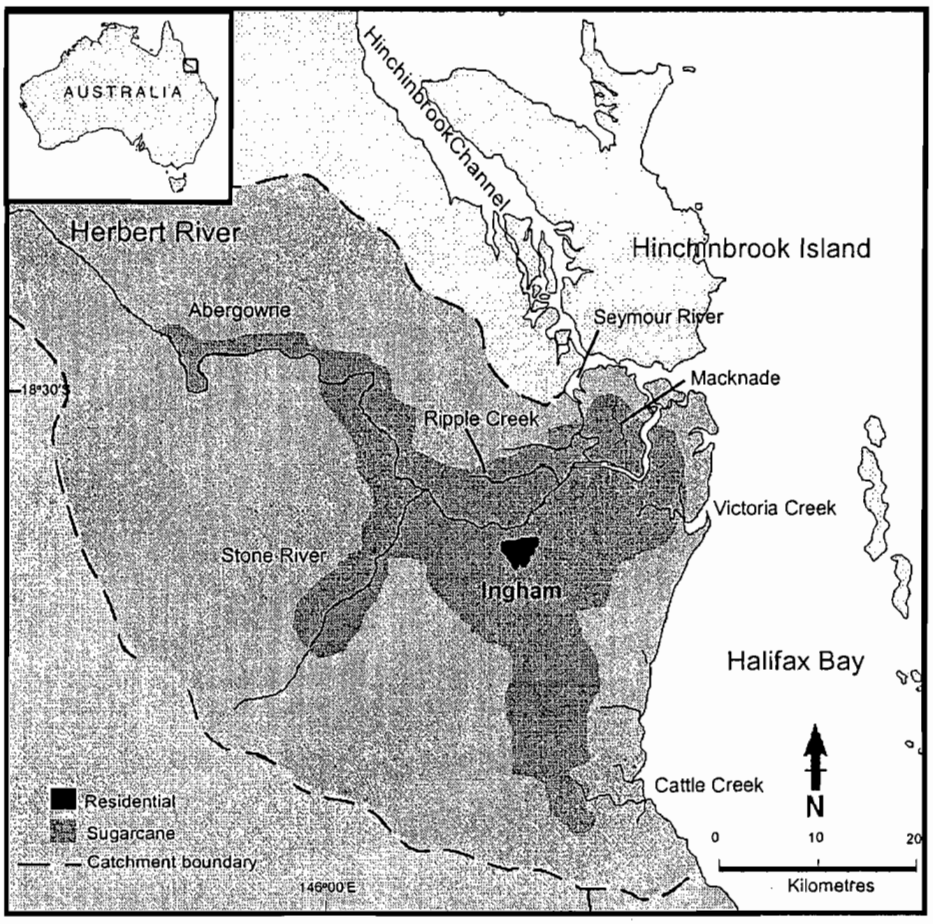


Figure 1.7. Current distribution of sugarcane in the Herbert region.

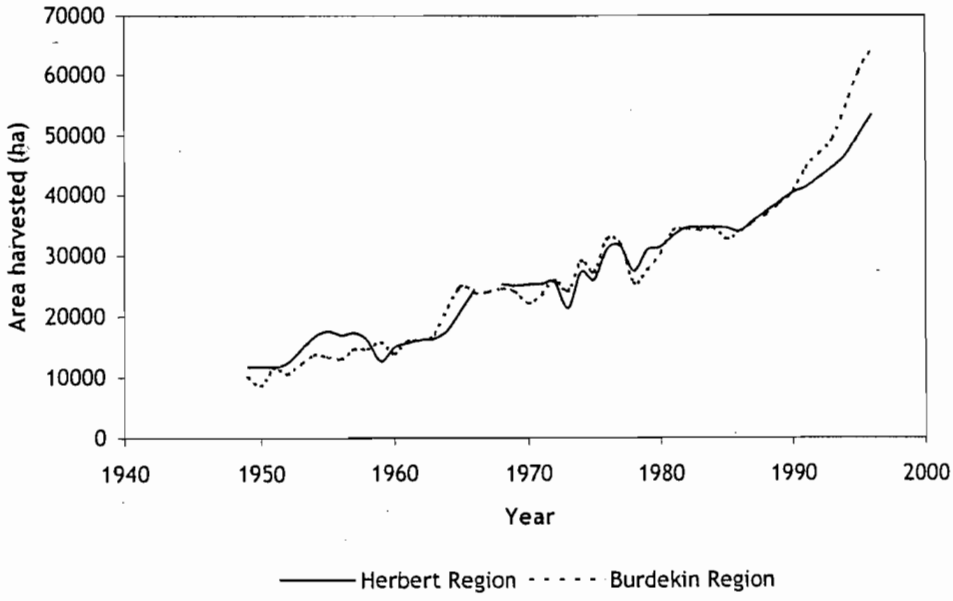


Figure 1.8. Area of land harvested for sugarcane in the Herbert and Burdekin regions (Source: compiled from BSES, 1947a-1996a).

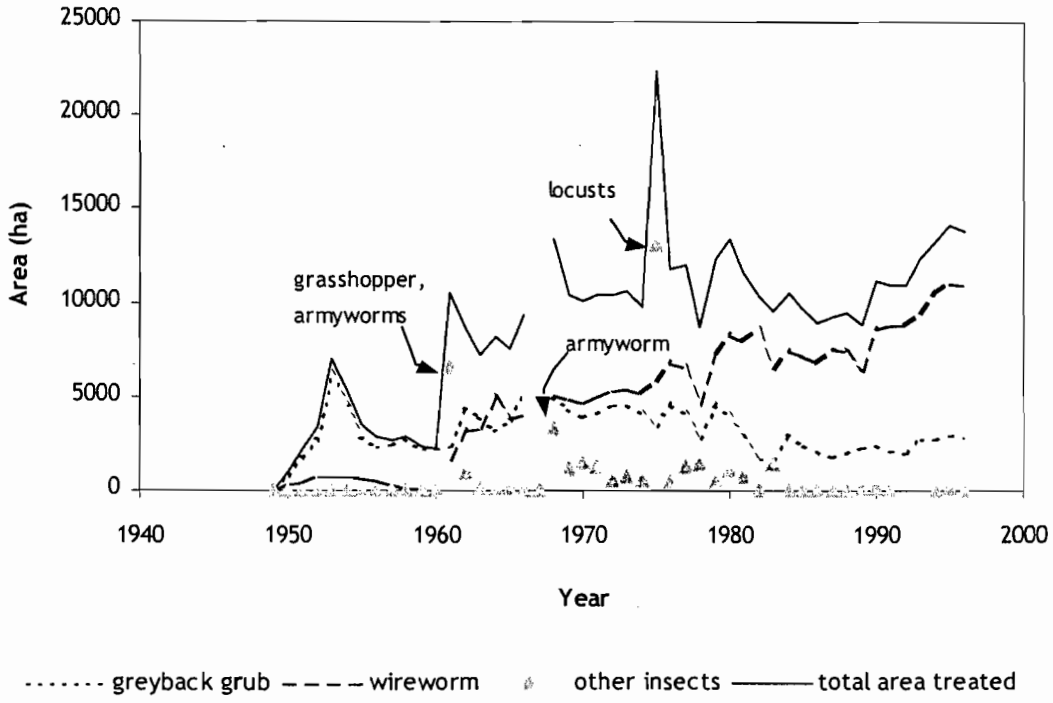


Figure 1.9. Area treated for different insect pests in the Herbert region (Source: compiled from BSES, 1947a-1996a).

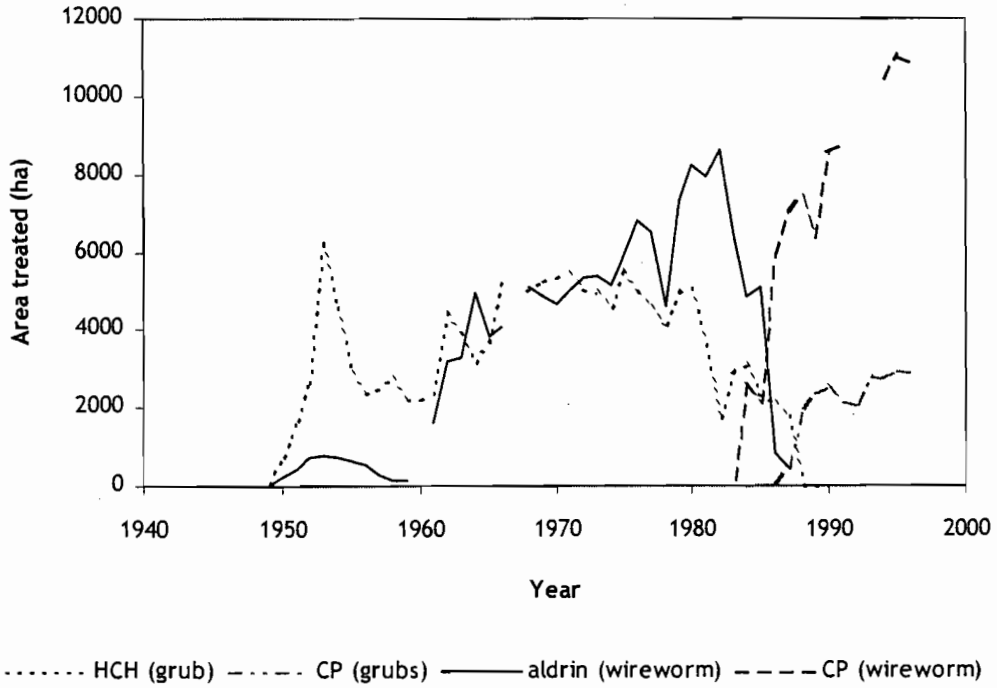


Figure 1.10. Area treated with different insecticides for different insect pests in the Herbert region (Source: compiled from BSES, 1947a-1996a). CP - chlorpyrifos formulations.

1.4.2 The Burdekin River region

The Burdekin River catchment drains an area of 129,860 km^2 and, together with the Haughton River system (3,650 km^2), is estimated to form the largest source of sediment to the Great Barrier Reef lagoon (Moss *et al.*, 1992; Neil and Yu, 1995). The Burdekin River catchment is situated in the seasonally dry tropics. Rainfall varies considerably across the catchment ranging from 2,770 mm per annum at Paluma Range to 400 mm at Bowie on the western margin, with the coastal flood-plain receiving an average of 1,100 mm (Anon., 1977). The lower rainfall in the Burdekin River coastal floodplain influences the type of inter-tidal wetland present in this area. In contrast to the extensive mangrove swamps in the Herbert River region, the intertidal wetlands of the Burdekin River region are characterised by mangrove creeks with narrow mangrove fringes surrounded by saline wetlands (Wolanski, 1990). Long-shore advection due to waves and current generated by south-east trade winds, distributes Burdekin River sediment from Cape Upstart to Cleveland Bay (Woolfe *et al.*, 1996) with significant deposition occurring in Bowling Green Bay (Woolfe and Larcombe, 1998; Brunskill *et al.*, 1998). Grain size analyses indicate that mangroves located in the lee of the sand spit forming Cape Bowling Green are the ultimate site of deposition of the fine-grained terrigenous sediment (Orpin and Woolfe, 1999). The Haughton River also discharges into Bowling Green Bay and contributes to the sediment load north of Bowling Green Bay.

Much of the land in the Burdekin catchment is semi-arid pastoral land. Sugar cane is the dominant crop, currently covering an area of approximately 85,000 ha (ca. 0.8% of the total catchment area) and is largely grown on the coastal flood-plain (Figure 1.11). The area of sugarcane has expanded considerably since its introduction in the late 1870s. Some of the oldest areas are located on the Burdekin delta and land surrounding the Haughton River. Sugarcane agriculture continued to expand around these areas and from 1963, land around Clare, Millaroo and Dalbeg which had previously been used for tobacco farming was converted to sugarcane land (Johnson, 1966). Further expansion occurred in 1990 with the opening of the Burdekin River Irrigation Area (BRIA) to sugarcane. This area was developed after construction of the Burdekin Falls Dam in 1985 and was initially used for grazing and rice growing.

Sugarcane land in the Burdekin is relatively flat with slopes typically around 1:1000 to 1:24,000 (M. Hanks, BSES, pers. comm.). All of the sugarcane in the Burdekin region is irrigated. Water from the Burdekin Falls dam is used to irrigate the Burdekin River Irrigation Area. On the Burdekin Delta, irrigation water is supplied by groundwater or water from creeks draining through the sugarcane land. Sugarcane areas around Clare, Millaroo and Dalbeg are also irrigated with water from creeks draining through the sugarcane land. To supply the creeks and recharge shallow aquifers for irrigation purposes, water is pumped from the Burdekin River to the mouth of the creeks during the dry season. Water from the creeks is used to irrigate surrounding caneland with any excess water draining back into the creek or

recharging the local groundwater aquifer. Creeks above the Burdekin Delta drain back into the Burdekin River, while creeks on the Burdekin Delta drain into the coastal water surrounding the Burdekin River. Almost 100% of the crop is conventionally cultivated.

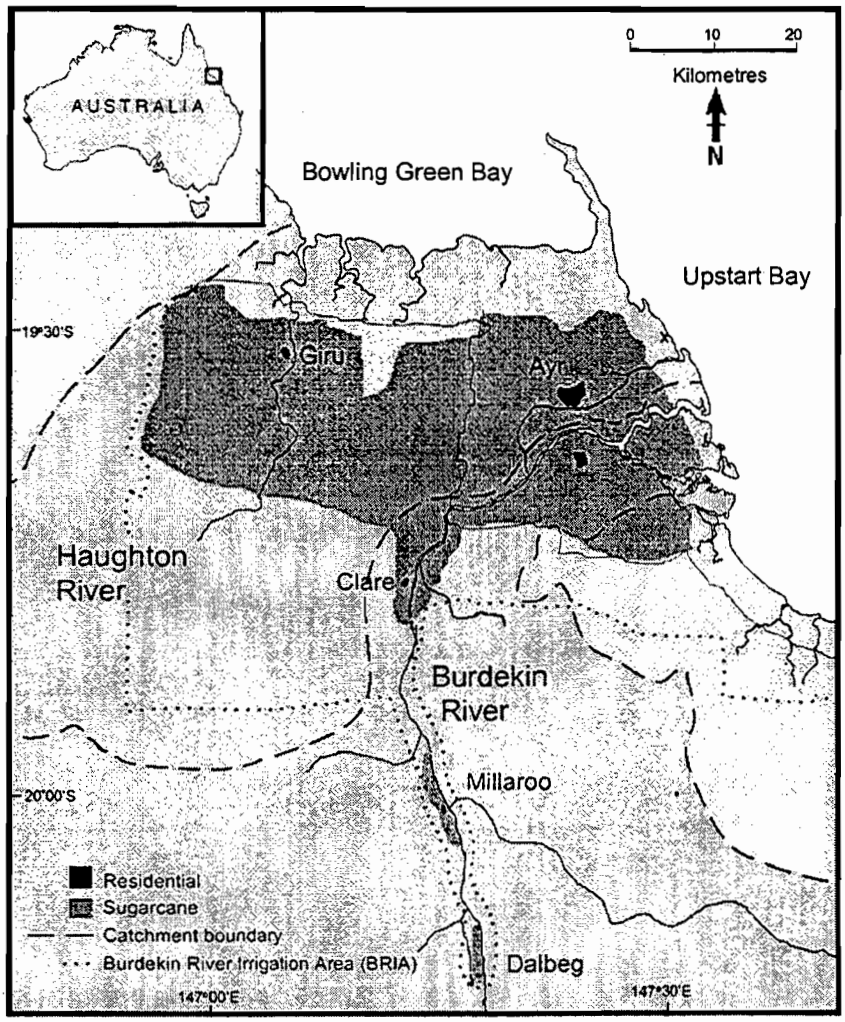


Figure 1.11. Current distribution of sugarcane in the Burdekin region.

The major insect pest in the Burdekin region is the greyback grub, which is largely confined to the delta area. HCH was predominantly used for grub control until the early 1980s when heptachlor became the dominant control (Figures 1.12 and 1.13). Aldrin, dieldrin and lindane were also occasionally used for grub control.

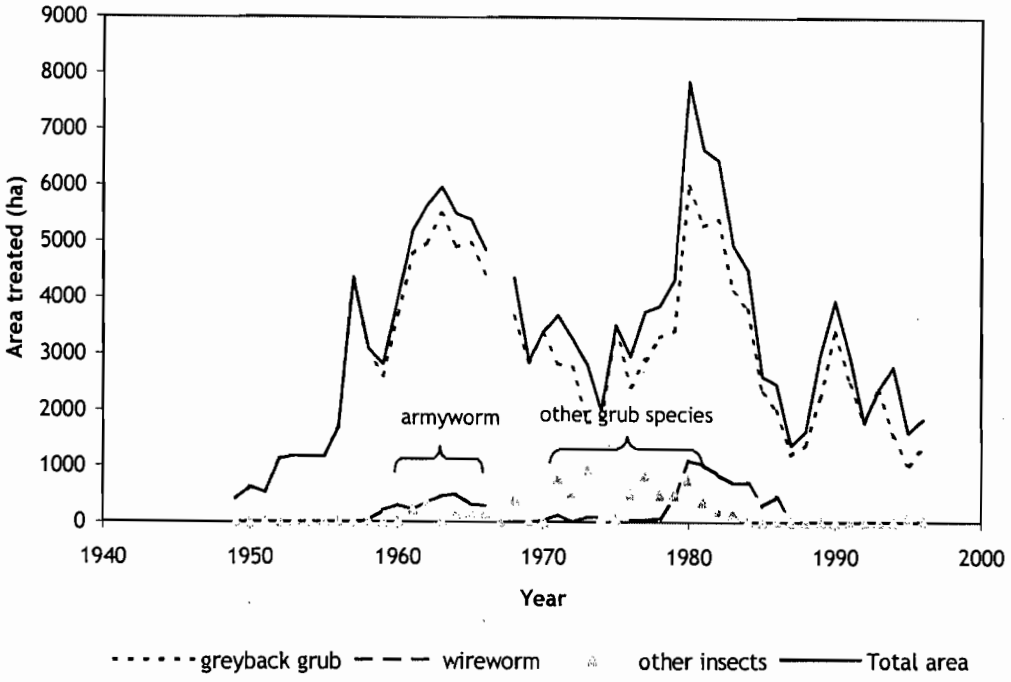


Figure 1.12. Area treated for different insect pests in the Burdekin region (Source: compiled from BSES, 1947a-1996a).

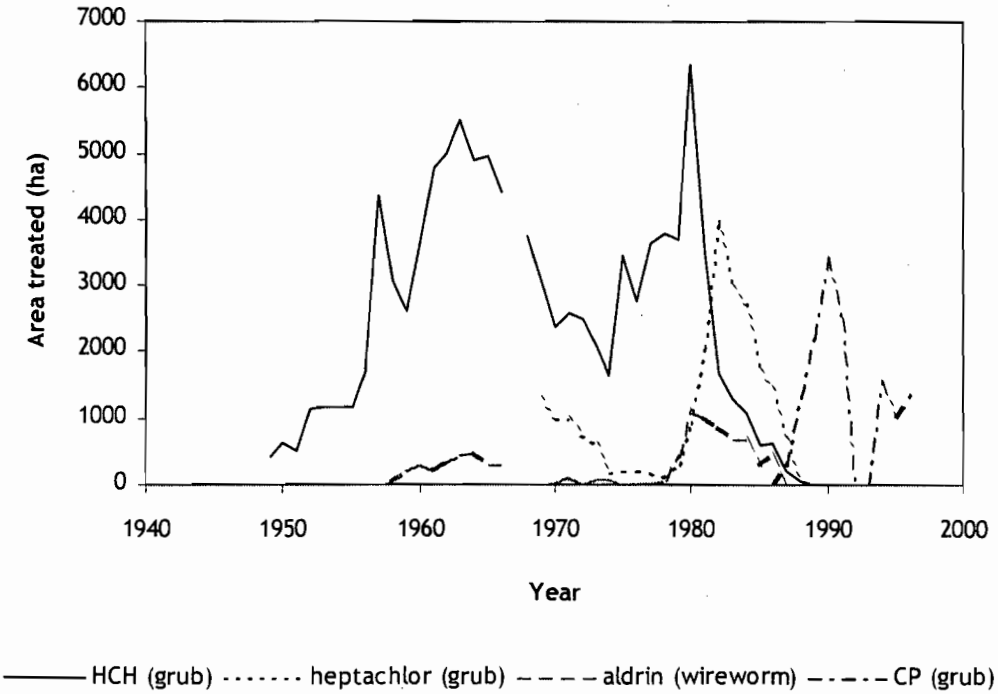


Figure 1.13. Area treated with different insecticides for different insect pests in the Burdekin region (Source: compiled from BSES, 1947a-1996a). CP - chlorpyrifos formulations.

1.5 Approach of this thesis

This thesis examines organochlorine insecticide usage in two significant sugarcane growing regions of north Queensland, the Herbert and Burdekin River regions. The first chapter has provided background information on organochlorine insecticides, the sugar industry, insecticide usage in the sugar industry, and the geographical and climatic setting of the Herbert and Burdekin regions. Chapter 2 provides an inventory of the current distribution of organochlorine residues in surface soil, soil cores, and drainage lines in sugarcane regions, together with analyses of estuarine sediment cores collected from areas of known terrigenous sediment deposition. This information is combined with estimated insecticide usage and is used to develop a mass balance for the fate of the insecticides since their introduction (Chapter 3). An initial assessment of the biological impact of organic contaminants in the Herbert and Burdekin River regions is made by examining the exposure of fish collected from agricultural and urban catchments compared with those collected from catchments that are not significantly disturbed by anthropogenic activities (Chapter 4). Chapter 5 examines the different factors (eg. economic, environmental, legislative) that have historically influenced insecticide usage in the sugar industry, to provide a broader conceptual basis for the application of risk assessment strategies to insecticide usage. The conclusions are brought together in Chapter 6 in which ideas for future work are set forth.

Chapter 2: Organochlorine insecticide residues in soils and sediments - implications for contamination of the Great Barrier Reef

2.1 Introduction

Erosion of sugarcane soils and subsequent transport of sediment-bound contaminants in river run-off to the Great Barrier Reef lagoon is a growing concern as the sugarcane industry continues to expand. Chemical tracers, such as organochlorine insecticides, can be used to identify sediment sources and provide a clearer picture of the contribution of specific land-use activities, such as sugarcane farming, to sediment and contaminant loads. The use of dated sediment core profiles of contaminants has proven to be successful in plotting the history of human impacts on many lake and marine environments (e.g. Burns and Villenveuve, 1983; Sanders *et al.*, 1992; van Zoest and van Eck, 1993; Kilby and Bately, 1993; Gerritse *et al.*, 1995; Muir *et al.*, 1995; Hendy and Peake, 1996).

The widespread application of organochlorine insecticides to sugarcane land in Queensland from the late 1940s to 1987 should provide good markers for the contribution of sediment derived from sugarcane fields and deposited during this time period. Additionally, as organochlorine insecticides are more persistent than insecticides currently in use, the extent of their distribution in the marine environment can provide a worst-case scenario for the distribution and accumulation of these insecticides, assuming they are transported by the same mechanism. Finally, concern for the environmental impact of organochlorine insecticide residue concentrations has been renewed with the discovery that some residues can act as hormone mimics and cause disruption of the endocrine system (e.g. Soto *et al.*, 1995; Silvestroni and Palleschi, 1999).

Sugarcane is the major coastal land use in the Herbert and Burdekin River regions. Limited information on the concentration of organochlorine insecticide residues in the soils and sediments of these regions exists (Brodie *et al.*, 1984; Rayment *et al.*, 1997; Hunter *et al.*, 2000). Thus, the present study has two aims: the first is to establish the environmental concentration of organochlorine insecticide residues in sugarcane soils and aquatic systems of the Herbert and Burdekin regions to assess the extent of contamination of the terrestrial and near-shore marine environment. The second aim is to investigate the application of organochlorine insecticide residues as tracers to assess the relative contribution of soil derived from the sugarcane lands to coastal sediments over the past 40 years.

2.2 Materials and Methods

2.2.1 Sample collection

2.2.1.1 Farm soil collection

Farms selected for sampling covered the geographical extent of sugarcane farming in the Herbert and Burdekin regions and were farms on which local Cane Production Board Supervisors knew organochlorine insecticides had been used for at least 20 years. Farmers were interviewed at the time of sampling to ascertain general farming practices, historical insect problems, and general attitudes toward insecticide usage. As most farms sampled were family farms, the farmers could provide a long history of farming practices and insect problems.

Surface soil samples (0-10 cm) were collected from 24 and 18 farms located in different sub-regions within the Burdekin and Herbert regions respectively (Figures 2.1, 2.2 and 2.3; *Tables A.1 and A.2*[*1]). Samples were collected from 5 random points in each field and placed in a stainless steel bowl. The combined soil samples were well mixed and a sub-sample (approximately 100 g) placed in a cleaned, solvent-rinsed glass jar. Samples were frozen as soon as possible and remained frozen until analysis. Two fields were sampled from 3 farms in the Burdekin region and 4 farms in the Herbert region to assess the variability between different fields within a farm.

2.2.1.2 Soil core and size fractions

Soil cores (1 m) were collected from fields on two farms in each of the Herbert and Burdekin regions that were known, through initial surface soil analyses, to have easily detectable concentrations of organochlorine insecticide residues (Figures 2.2 and 2.3; *Tables A.1 and A.2*). Three cores were collected from the inter-rows in fields that had standing sugarcane. One core was collected from a recently cultivated field. Soil cores were collected using a hand held "Purkhauer" auger and note taken of visual textural changes down the core length. Cores were sliced into 10 cm segments and depth segments from five individual cores were composited to provide sufficient soil for analyses. Bulk surface soil samples (0-10 cm) for soil fraction analyses were also collected at the time of core collection. Samples were collected in cleaned solvent rinsed glass jars and stored frozen until analysis.

Bulk surface soil samples were separated into size fractions using a modification of the pipette method for determination of particle size (Coventry and Fett, 1979). Briefly, samples were freeze-dried and sieved through 2 mm mesh to remove gravel and roots. Soil (50 g) and milli-Q water (250 ml) were placed in teflon screw cap bottles. Bottles were placed in an end-over-end shaker and shaken for 16 hrs. After shaking, soil suspensions were placed in 1 l

[*1] Table reference in italicised font and with a letter preceding table number are tables found in the Appendix of the relevant letter. For example, Table A.1 is Table A.1 in Appendix A.

glass measuring cylinders, made to up 1 l to give a 5 % suspension, and mixed well with a stirrer. After 4 min 20 s the top 10 cm (~300 ml) of suspension was removed yielding the <20 μm (silt and clay) fraction. The aliquots removed were placed in cleaned solvent-rinsed jars and stored frozen until analysis. Soil suspensions were remixed and allowed to stand for 5 hrs after which the top 7.5 cm (~220 ml) was removed yielding the <2 μm (clay) fraction. The aliquots removed were placed in cleaned solvent-rinsed jars and stored frozen until analysis. The remaining supernatant was drawn off to within 2 cm of the bottom and discarded. This step was repeated until the supernatant was clear. The supernatant was decanted and the remaining material (sand) frozen, freeze-dried, and sieved through 500 μm, 125 μm and 63 μm mesh using an automatic shaker. Vegetal debris in the 125-500 μm size fractions were floated off and analysed separately. Organic carbon contents were determined for the <2 μm, <20 μm, 20-63 μm, and 63-125 μm size fractions.

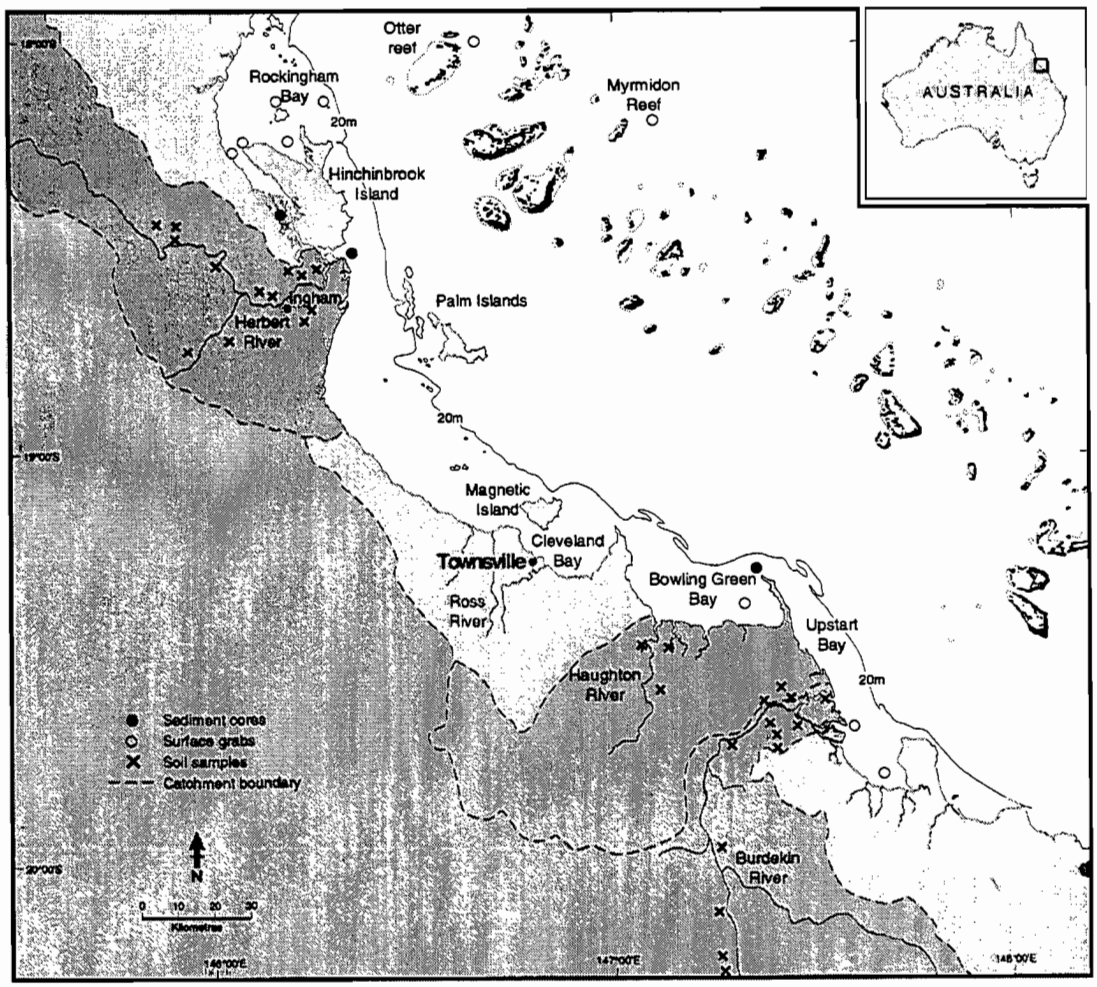


Figure 2.1. Location of soil and marine sediment samples (Note: marks indicating soil sample location indicate geographical spread only and more detail is provided in Figures 2.2 and 2.3).

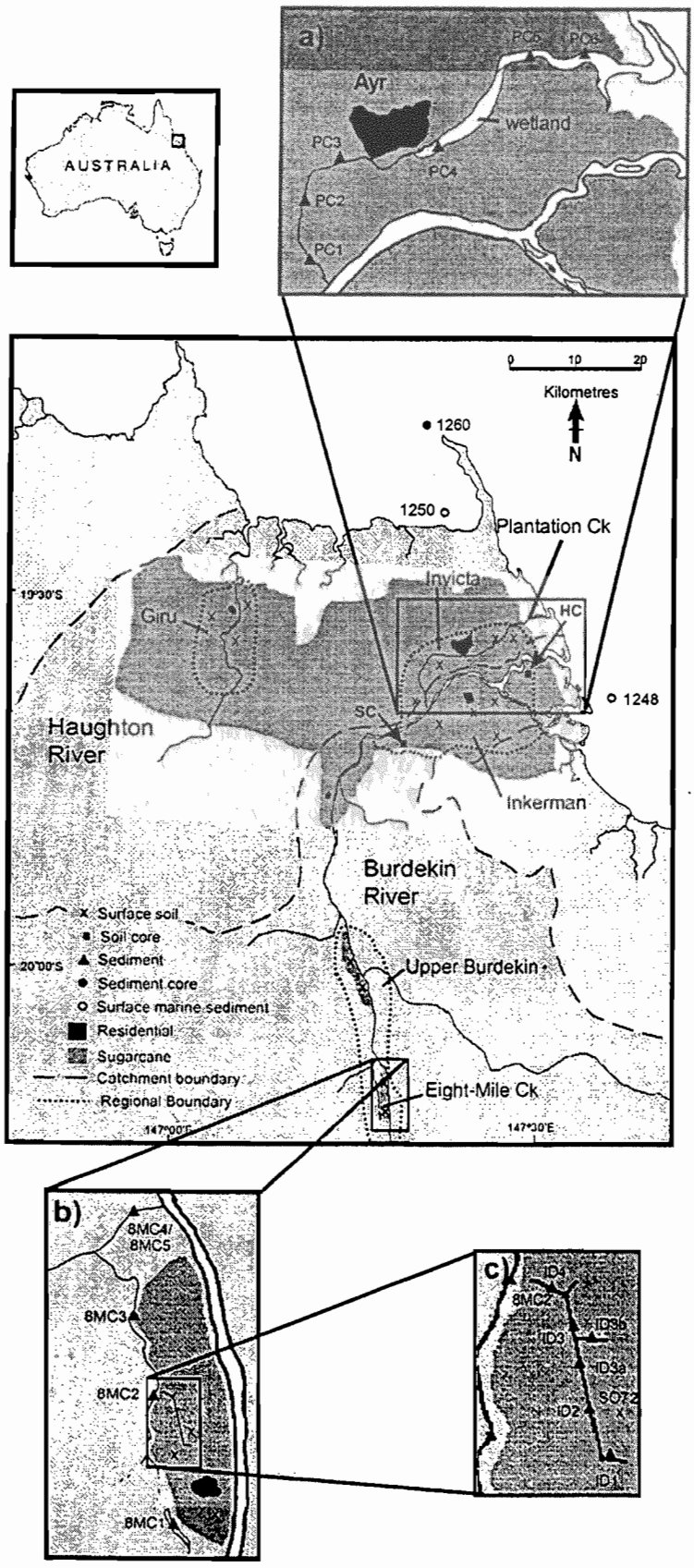


Figure 2.2. Location of surface soil, soil core, surface marine sediment and marine sediment core samples collected from the Burdekin region.

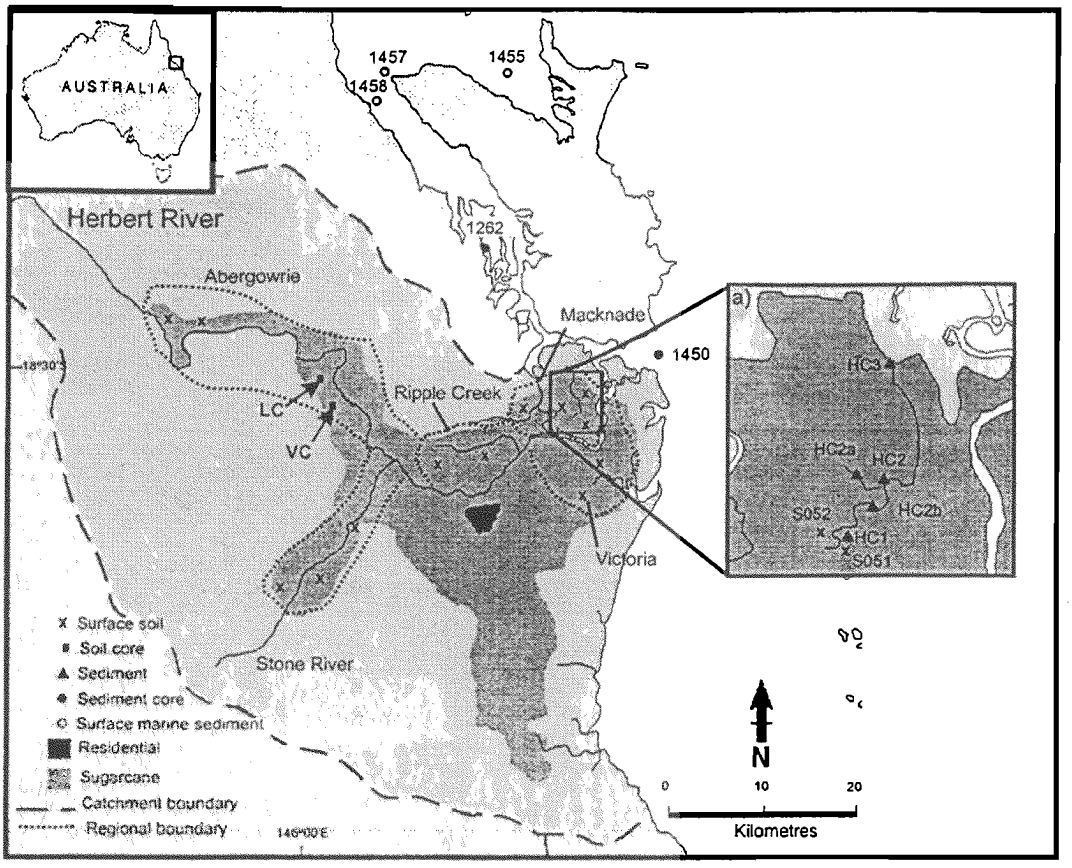


Figure 2.3. Location of surface soil, soil core, surface marine sediment and marine sediment core samples collected from the Herbert region.

2.2.1.3 On-farm and off-farm drainage

In the Burdekin region, sediment samples were collected along the length of one on-farm drainage line and surrounding sugarcane fields, Plantation Creek and Eight-Mile Creek (Figures 2.2a-c; *Table A.3*). The on-farm drainage line drained into Eight-Mile Creek, which receives run-off from approximately 130 ha of sugarcane farms prior to flowing into the Burdekin River. Water, pumped from the Burdekin River into Eight-Mile Creek during the dry season, is used to irrigate surrounding sugarcane land. Pink Lily Lagoon, located at the head of Eight-mile Creek, also receives run-off from surrounding sugarcane land. Sediment samples were collected from Pink Lily Lagoon and at three locations along Eight-Mile Creek (Figures 2.2a and b). At the time of sampling, the sediment was predominantly coarse-grained sand. However, a sample of fine sediment, presumably eroded agricultural soil, was collected from Eight-Mile Creek at 8MC4 on a second occasion after heavy rains had fallen (8MC5).

Plantation Creek is located on the Burdekin Delta. During the dry season water is pumped from the Burdekin River into Plantation Creek to recharge groundwater aquifers that supply irrigation water to surrounding farms. Sugarcane crops surrounding Plantation Creek have

been prone to cane-grub damage. A linear freshwater wetland area (approximately 9 km long and 1 km wide) is located on the creek immediately after the creek passes Ayr and prior to discharge of the creek into the mangroves (Figure 2.2a). Samples were collected from three locations upstream of the wetland area, one location in the wetland area, and two locations below the wetland (Figure 2.2a).

Sediment samples were also collected along the length of a drainage line located in the Macknade sub-region of the Herbert Region (Figure 2.3a; *Table A.3*). This drain was approximately 5 km long. A tidal flood-gate, located at the entrance of the drain to a mangrove creek, prevented the inflow of estuarine water into the drain. No creeks receiving run-off from sugarcane fields were sampled in the Herbert region.

2.2.2 Marine sediment collection

An extensive survey of the near-shore, surface marine sediments off the Herbert and Burdekin regions had previously been undertaken to identify areas of terrigenous deposition (Brunskill *et al.*, 1998). These areas were the focus for sediment sample collection during the present study. Surface samples were collected using a Van-Veen grab sampler and sediment cores were collected with a Kasten corer (Kuehl *et al.*, 1985). Open water and deep water Kasten cores were taken from the R/V Lady Basten, using a 1000 kg driving weight, with 150 mm square steel sampling tubes (2-4 m long, opening on one side for sub-sampling cores on the ship), with core top closure upon retrieval and a bottom core catcher. Upon retrieval, cores were sliced into 2 cm sections for the upper 20 cm, and then into 4 cm sections to the core bottom. Sub-samples for organochlorine analyses (approximately 80 g wet weight) were taken from each sediment slice, placed in cleaned, solvent-rinsed glass jars and stored frozen until analysis. Sub-samples for additional chemical analyses were taken from the grab samples and core slices, and were frozen in plastic vials on the ship. Sediments were handled with cleaned plastic or stainless steel tools during slicing and sub-sampling. Larger (0.5-1 kg) bulk samples were stored un-refrigerated in double Ziplock plastic bags for radiochemical measurements.

Two sediment cores (AIMS 1262, AIMS 1450) from the Herbert coastal estuary, one core from the Burdekin estuary (Bowling Green Bay, AIMS 1260) and 12 surface samples were selected for organochlorine analyses (Figures 2.1, 2.2 and 2.3; *Table A.4*). Sediment core slices covering an estimated average age of deposition from 1960-1980 and surface sediment slices were analysed. These sediment slices were considered as the most likely to contain organochlorine pesticides as maximal pesticide usage occurred over this time (section 3.2.1).

2.2.3 Radionuclide age estimates

Radiochemical measurements were conducted by John Pfitzner at the Australian Institute of Marine Science and are described in detail in Appendix B. Briefly, estimates of ^{210}Pb, ^{226}Ra,

^{137}Cs, and other isotopes present in samples were determined by gamma spectrometry. The gamma spectrometer was calibrated with known low activity spikes of suitable nuclides. Counting errors of these measurements were less than 10%. Interpretations of the radiochemical tracers of sedimentation history were made using several sub-models described by Robbins (1978, 1986), which utilises a sediment mixed layer thickness, a decadal-century scale average input of ^{210}Pb, Brisbane measurements of thermonuclear bomb fallout (^{90}Sr and ^{137}Cs) over 1950-1990, and diffusion coefficients for ^{210}Pb and ^{137}Cs in marine sediments (Li and Gregory, 1974). Estimates of atmospheric flux of ^{210}Pb and ^{137}Cs have been obtained from soil profiles in the Herbert River alluvial floodplain and near the Australian Institute of Marine Science (G. Brunskill and J. Pfitzner, AIMS, unpublished data). Confidence in sediment core ^{210}Pb chronology was enhanced by the use of ^{137}Cs data and the known history of phosphatic fertiliser application in the adjacent Herbert River valley sugarcane lands, together with the appearance of elevated concentrations of Cd (a contaminant found in the phosphatic fertilisers applied) in the sediment cores (Tesiram, 1996; Y. Tesiram and G. Brunskill, AIMS, unpublished data).

2.2.4 Chemical analysis

2.2.4.1 Organochlorine analysis

Analytical methods were adapted from Krahn *et al.* (1988) and Wade and Cantillo (1994). Just prior to extraction and analysis, frozen samples were freeze-dried and surrogate recovery standards (4,4'-dibromooctafluorobiphenyl [DBOF], octachloronapthalene [OCN] and PCB 103) added. Matrix blanks (pre-extracted soil samples) and method blanks (solvent only) were analysed with every batch of 10 samples. As a check on analytical techniques, a standard reference material (SRM, IAEA-357) was analysed in duplicate on two occasions and duplicate soil samples were analysed regularly. Sediment (40 g) or soil (80 g) were extracted with dichloromethane (CH_2Cl_2, 250 ml) for 16 hrs using Soxhlet apparatus. Extracts were concentrated to approximately 5 ml using a rotary evaporator and elemental sulfur removed by adsorption onto activated copper. The total organic material extracted during soxhlet extraction (extractable organic material, EOM) was determined gravimetrically using 10 µl aliquots.

Samples (50% aliquots) were subject to further clean-up over an alumina column (4 x 0.5 cm ID), concentrated to 50-100 µl and fractionated by high-performance liquid chromatography (HPLC). HPLC was performed using a GBC LC1150 pump with two stainless steel columns (Resolve Silica 90 Å, 5 µm film thickness, 3.9 mm ID x 150 mm) connected in series. Solvent flow-rate was set at 0.5 ml min^{-1}. A linear gradient program based on UNEP/IOC/IAEA (1992) methods was used to fractionate samples. Briefly the HPLC was programmed to run at 5% CH_2Cl_2 in hexane for 5 mins, change linearly to 20% CH_2Cl_2 over 5-9 minutes and to 100% CH_2Cl_2 over 9-23 minutes. This was maintained until 40 minutes when the system was

returned to the starting solvent composition. Three fractions were collected for analyses. Fraction 1 (5.5-9.5 min) contained DBOF, PCBs, DDE, heptachlor, OCN, and aldrin; fraction 2 (9.5-26.5 min) contained the hexachlorocyclohexanes (HCHs), chlordanes, endosulfan I, DDD, and DDT; fraction 3 (26.5-35 min) contained endosulfan II and endosulfan sulfate, dieldrin, endrin, endrin aldehyde methoxychlor. Each fraction was gently concentrated under nitrogen to 100 µl.

Samples were analysed using a Hewlett-Packard Gas Chromatograph 6890 equipped with a J & W Scientific DB-5 column (30 m x 0.32 mm ID x 0.25 µm film thickness) and electron capture detection (GC-ECD). Samples were injected at 50°C in the splitless mode with a venting time of 0.4 minutes. After 1 minute the oven temperature was programmed to increase from 50°C to 120°C at a rate of 10°C min^{-1}, then at 3°C min^{-1} to 250°C, and finally at 10°C min^{-1} to 300°C where the temperature was maintained for 15 minutes. Nitrogen was used as the carrier (1.2 ml min^{-1}) and make-up gas (60 ml min^{-1}). Peak areas were quantified using Tetrachloro-m-xylene (TCMX) as the internal standard and Chemstation software (Hewlett-Packard). Error on replicate injections was less than 5%.

Selected samples were re-analysed by GC-ECD using a pulse-pressure injection technique and 5 µl injections to decrease detection limits or by a Gas chromatography-Mass spectrometer (GC-MS) operated in selected ion monitoring mode (SIM) to confirm identification of compounds. The GC-MS was a HP 6890 GC equipped with a J & W Scientific DB5-MS column (30 m x 0.32 mm ID x 0.25 µm film thickness) and 5972A mass selective detector. The oven temperature program for both instruments was as described above. The pressure ramp program held pressure at 28 psi for 1 minute after injection and then decreased at a rate of 7 psi min^{-1} to 7 psi over the remainder of the temperature program.

Recovery of surrogate standards was typically in the range 70-110%. The limit of detection was defined as peak areas less than the areas of standards injected at a concentration of 5 pg on-column. Routine detection limits for individual compounds were 25 pg g^{-1} for marine sediments and 10 pg g^{-1} for soils. Detection limits of 5 pg g^{-1} were achieved for marine sediments using the pulsed pressure injection technique described above. Detection limits for vegetal debris collected from the soil fractions were 0.2 ng g^{-1}, due to the small amount of material available for analysis.

2.2.4.2 Total organic carbon

Organic carbon analyses were performed on all samples. Dried samples were ground to a fine powder for 3 minutes in an agate lined HUMBOLDT WEDAG grinding mill. Inorganic carbonate carbon was removed from ground samples by the addition of concentrated hydrochloric acid just prior to determination of the carbon content of dried and ground samples. Carbon content

was determined by high temperature combustion with non-dispersive Infra Red (NDIR) detection of CO_2 using a Shimadzu SSM-5000A solid sample module attached to a Shimadzu TOC-5000 total organic carbon analyser. The error associated with replicate analyses was less than 5%.

2.2.4.3 Statistical analyses

The significance of correlations between organic carbon content and organochlorine concentrations was tested using the software package "SPSS for Windows" and a two-tailed t-test of the Pearson correlation coefficient on untransformed data.

2.3 Results

2.3.1 Quality control

The results of analysis of the standard reference material (SRM, IAEA-357) are shown in Table 2.1. Concentrations of *p,p'*-DDE and HCB were within the certified values. However, *p,p'*-DDT concentrations were below the certified values while *p,p'*-DDD concentrations were slightly above the certified value. The differences between analytical results and certified values may be a result of degradation of DDT since certification of the standard reference material in 1991. The SRM was freeze-dried sediment that had been stored at <4°C since certification.

Table 2.1. Comparison of analysis of standard reference material IAEA 357.

Compound	IAEA 357 (present study) (ng g^{-1})	s.d (n=4)	Certified values (ng g^{-1})	s.d
HCB	2.1	0.4	2.4	0.7
p,p'-DDE	27	2.0	25	7
p,p'-DDD	39	5.3	30	6
p,p'-DDT	7.9	6.8	35	12
Σ*p,p'*-DDTs	75	3.1	90	25.7

s.d - standard deviation

The coefficient of variation (CV) for individual analytes of duplicate analyses of soil samples ranged from 0.5-121 %, although they were typically in the range of 5-25% (Table 2.2). The high CVs were not associated with a particular analyte and despite efforts to achieve homogeneity in the samples, may be attributed to variability in the sub-samples taken.

2.3.2 Surface soils

Easily detectable and highly variable concentrations of organochlorine insecticide residues were found in the surface soils of the sugarcane fields (Table 2.3; *Tables C.1 and C.2*). Regional differences in the residual organochlorine insecticide concentrations were evident.

HCH isomers and dieldrin were the dominant residues in soils from the Herbert region, while heptachlor epoxide and chlordanes, in addition to HCH isomers, were dominant in soils from the Burdekin region. Beta-HCH was the dominant HCH isomer present in the soils, constituting 11-78 % of the ∑HCH (Table 2.4). Soils from the Burdekin region showed an increase in the relative contribution of γ-HCH and β-HCH to ∑HCH concentration. DDE was found in high concentrations in 6 samples from the Burdekin region and 2 samples from the Herbert region (*Tables C.1 and C.2*). Highly variable concentrations of chlorpyrifos, currently the most widely used insecticide in the sugar industry, were found in addition to low concentrations of endosulfan and endosulfan sulfate (Table 2.3). The concentrations of HCH, dieldrin, and total organochlorine concentration, were generally lower in the Burdekin region compared with the Herbert region (Table 2.3).

Table 2.2. Mean concentration and coefficient of variation (standard deviation/mean x 100; CV, %) of individual analytes from duplicate soil analyses.

Compound	Mean concentration, ng g^{-1} (CV, %)				
	Dup 1	Dup 2	Dup 3	Dup 4	Dup 5
α-HCH	0.016 (15.1)	0.090 (4.4)	0.083 (9.7)	0.104 (23.0)	0.273 (11.4)
β-HCH	0.023 (13.7)	1.53 (21.2)	0.249 (50.1)	3.53 (35.2)	0.268 (5.7)
γ-HCH	0.946 (29.4)	0.234 (18.6)	0.197 (10.)	0.177 (27.2)	0.581 (0.5)
δ-HCH	<0.010	0.060 (10.4)	0.053 (70.4)	0.093 (63.5)	0.071 (4.3)
heptachlor epoxide	0.035 (23.3)	12.3 (7.9)	3.25 (12.2)	<0.010	<0.010
trans-chlordane	0.032 (23.1)	6.76 (23.0)	1.50 (5.7)	0.014 (5.5)	<0.010
cis-chlordane	<0.010	1.30 (7.0)	0.377 (4.9)	<0.010	<0.010
dieldrin	<0.010	0.182 (16.6)	0.048 (121.4)	0.243 (9.3)	1.49 (39.1)
p, p'-DDE	<0.010	<0.010	0.029 (44.5)	29.7 (8.8)	<0.010
p, p'-DDD	<0.010	<0.010	<0.010	0.238 (39.2)	<0.010
p, p'-DDT	<0.010	<0.010	<0.010	0.954 (14.5)	<0.010

Variability observed in HCH concentrations in soils collected from different fields on the same farm in the Burdekin region was generally similar to that observed in soils collected within the region (Table 2.5). In contrast, variation in heptachlor epoxide and chlordane concentrations were lower within a farm as compared to within a region. Chlorpyrifos and DDTs were variable at both scales. The variability observed in the concentration of individual compounds in soils collected from different fields on one farm in the Herbert region was generally less than that observed in soils collected from within the region (Table 2.5).

Under uniform application scenarios, the distribution of organochlorine residues in soils was anticipated to be proportional to the organic carbon content. However, organic carbon

content explained very little of the variation in individual or total organochlorine concentration in analysed samples, as demonstrated by the low r^2 values (Figures 2.4a and b).

Table 2.3. Geometric mean and range of organochlorine residue concentrations (ng g^{-1}), extractable organic matter (EOM) concentration (mg g^{-1}) and organic carbon content (%) of soils collected from sugarcane fields in the Herbert and Burdekin River regions.

Compound	Herbert (n=18)		Burdekin (n=25)	
	Mean	Range	Mean	Range
α-HCH	0.504	<0.010 - 6.00	0.041	<0.010 - 0.739
β-HCH	0.871	<0.010 - 45.6	0.198	<0.010 - 2.65
γ-HCH	0.457	<0.010 - 3.99	0.132	<0.010 - 1.65
δ-HCH	0.209	<0.010 - 2.77	0.023	<0.010 - 1.26
Σ HCH	**2.33**	**<0.010 - 57.3**	**0.615**	**<0.010 - 3.213**
aldrin	0.068	<0.010 - 0.162	<0.010	<0.010 - 0.112
dieldrin	1.25	0.029 - 27.6	0.064	<0.010 - 3.679
heptachlor	<0.010	<0.010 - 0.146	0.027	<0.010 - 0.207
heptachlor epoxide	0.065	<0.010 - 2.87	0.283	<0.010 - 18.2
trans-chlordane	0.036	<0.010 - 0.850	0.159	<0.010 - 10.09
cis-chlordane	<0.010	<0.010 - 0.290	0.064	<0.010 - 2.74
p, p'- DDE	0.121	<0.010 - 6.21	0.150	<0.010 - 27.8
p, p'- DDD	<0.010	<0.010 -0.433	<0.010	<0.010 - 0.629
p, p'- DDT	0.045	<0.010 - 0.411	0.040	<0.010 - 1.526
Σ *p, p'*-DDTs	**0.266**	**<0.010 - 6.47**	**0.222**	**<0.010 - 29.0**
chlorpyrifos	0.255	<0.010 - 37.3	0.048	<0.010 - 63.9
hexachlorobenzene	<0.010	<0.010 - 0.075	<0.010	<0.010 - 0.053
endosulfan I	<0.010	<0.010	<0.010	<0.010 - 0.040
endosulfan II	<0.010	<0.010	<0.010	<0.010 - 0.363
endosulfan sulfate	<0.010	<0.010 - 0.095	<0.010	<0.010 - 0.159
endrin	<0.010	<0.010 -0.044	<0.010	<0.010
endrin aldehyde	<0.010	<0.010 - 0.033	<0.010	<0.010
methoxychlor	<0.010	<0.010 - 0.255	<0.010	<0.010 - 0.034
Total concentration	**10.1**	**0.19 - 65.1**	**4.19**	**<0.010 - 67.7**
EOM (mg g^{-1})	0.05	0.01 - 9.3	0.02	0.01 -1.5
organic carbon (%)	1.1	0.51 - 2.3	1.7	0.31 - 0.95

Table 2.4. Percentage contribution (mean, range) of individual HCH isomers to the total concentration of HCH present in sugarcane soils from the Herbert and Burdekin regions.

HCH isomer	Herbert		Burdekin	
	mean	range	mean	range
α-HCH	24.0	8.50 - 38.3	8.40	1.00 - 52.2
β-HCH	43.7	11.3 - 79.7	37.6	1.30 - 100
γ-HCH	20.0	7.03 - 100	38.7	<0.010 - 100
δ-HCH	8.60	4.01 - 18.9	4.90	<0.010 -12.1

Table 2.5. The average coefficient of variation (%) of the concentration of selected compounds found in sugarcane soils from the same farm or within a region.

Compound	Herbert		Burdekin	
	Farm (n=4)	Region (n=5)	Farm (n=3)	Region (n= 6)
α-HCH	34.5	87.6	71.4	77.6
β-HCH	44.9	112	122	102
γ-HCH	40.0	83.7	71.2	86.4
δ-HCH	28.3	100	76.7	76.5
aldrin	42.4	91.6	n.d.	128
dieldrin	74.2	75.5	93.0	112
heptachlor	98.9	182	n.d.	72.3
heptachlor epoxide	36.3	174	79.3	117
trans-chlordane	61.2	124	57.8	116
cis-chlordane	49.3	196	21.9	112
p, p'- DDE	87.4	110	144	135
p, p'- DDD	124	157	145	100
p, p'- DDT	33.8	91.6	132	100
chlorpyrifos	124	130	103	151
HCB	50.0	54.5	31.5	43.4

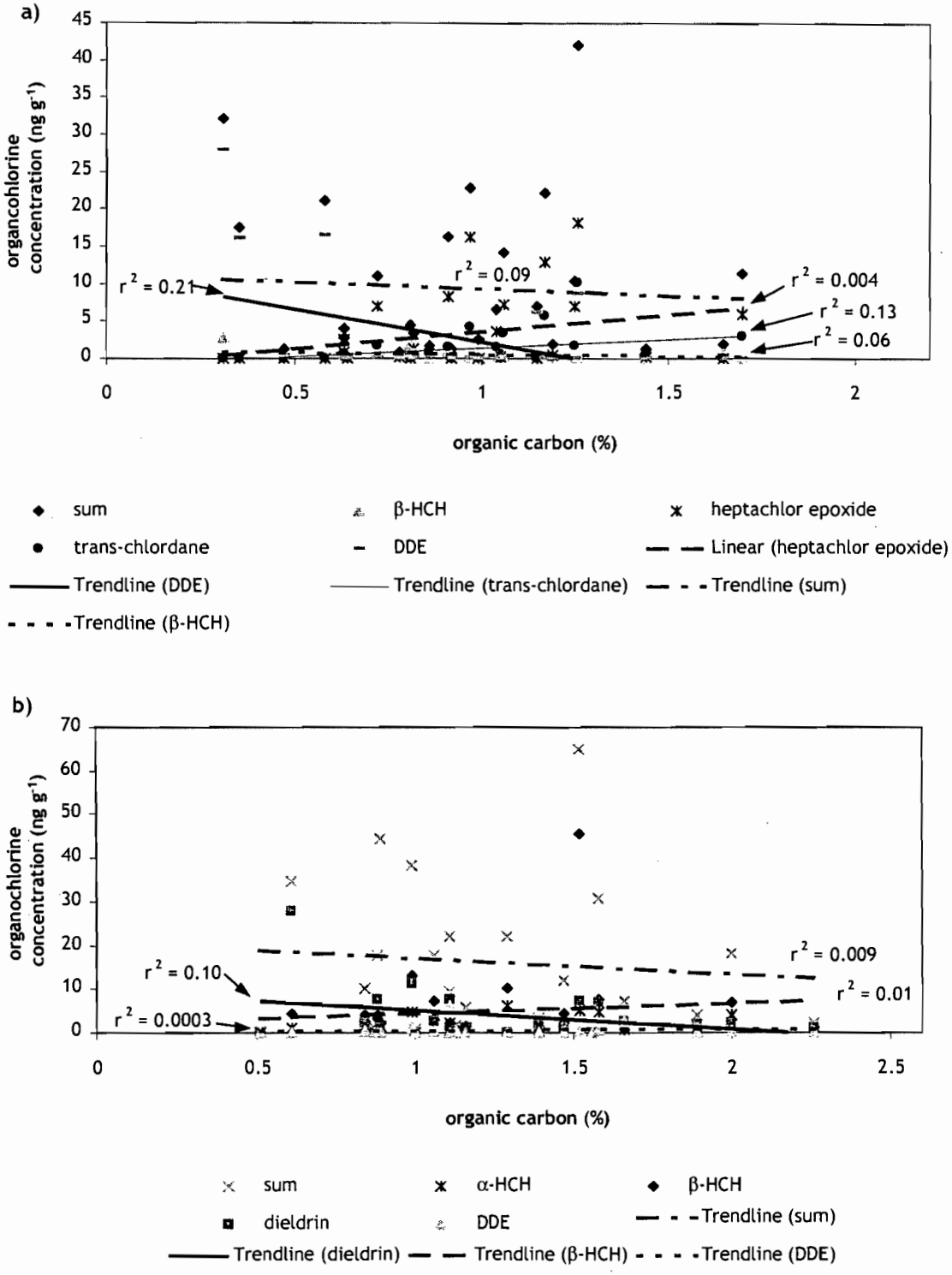


Figure 2.4. Correlations between organic carbon content (%) and concentration of selected individual organochlorine compounds or total organochlorine concentration (ng g^{-1}) in sugarcane soils of a) the Burdekin region, and b) the Herbert region.

2.3.3 Soil cores

Soil cores were analysed to a depth of 70 cm. The highest concentrations of organochlorine residues were found in the surface slice of the three cores collected from fields planted with sugarcane; concentrations declined with depth (Figures 2.5 and 2.6a; *Table C.3a and b*). Organic carbon content also declined with depth in cores SC and LC. In these cores total organochlorine concentration was correlated with organic carbon content (Figure 2.7). In core HC, organic carbon content was relatively constant down the soil core profile (Figure 2.5b). This core retained the highest relative concentrations of organochlorine residues at depth (Table 2.6a and b), and total organochlorine concentration was not correlated with organic carbon content (Figure 2.7). Soil texture in these cores changed from a relatively homogenous

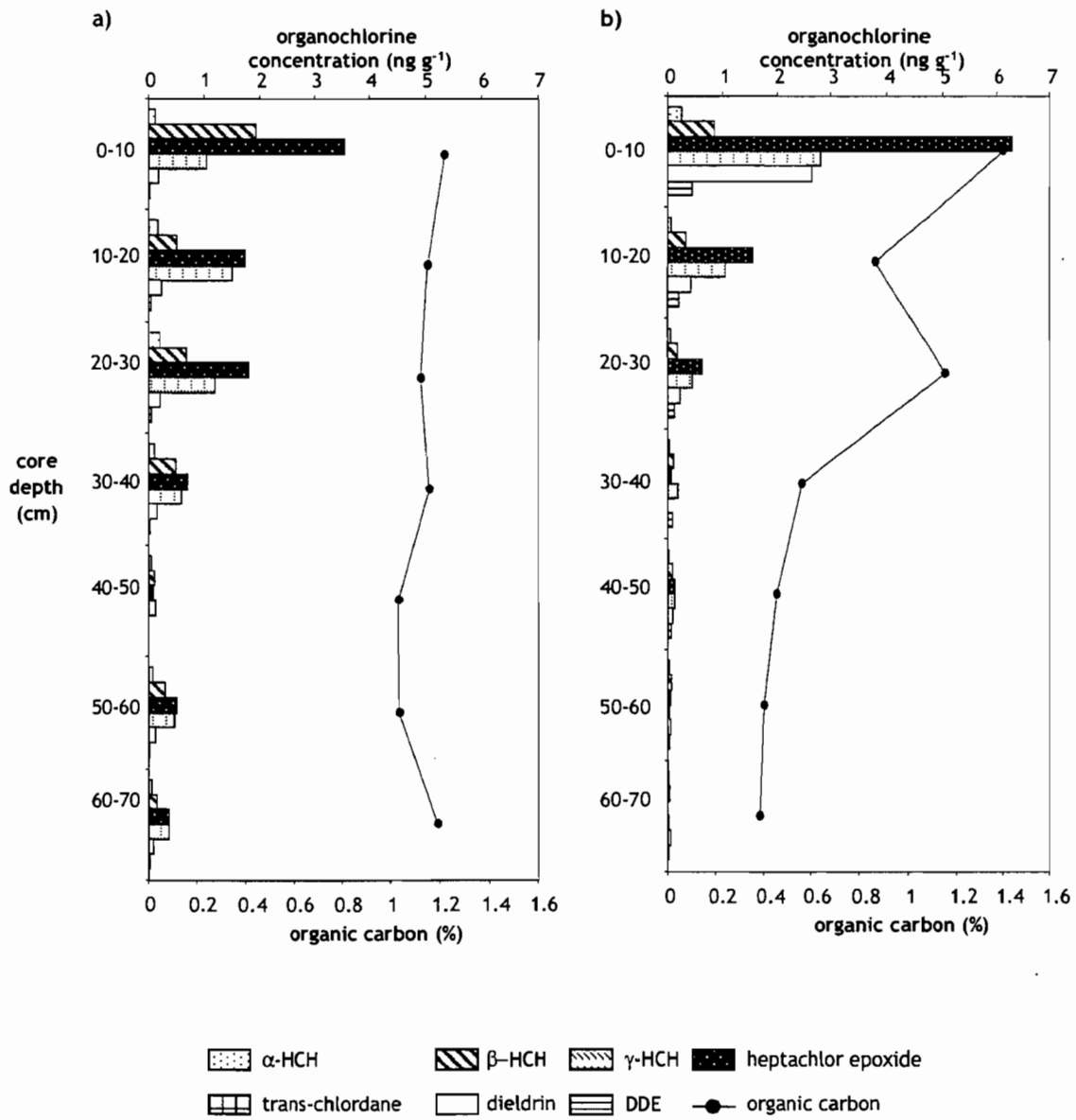


Figure 2.5. Organic carbon content (%) and concentration of selected organochlorine compounds (ng g^{-1}) in: a) core HC, and b) core SC, collected from the Burdekin region.

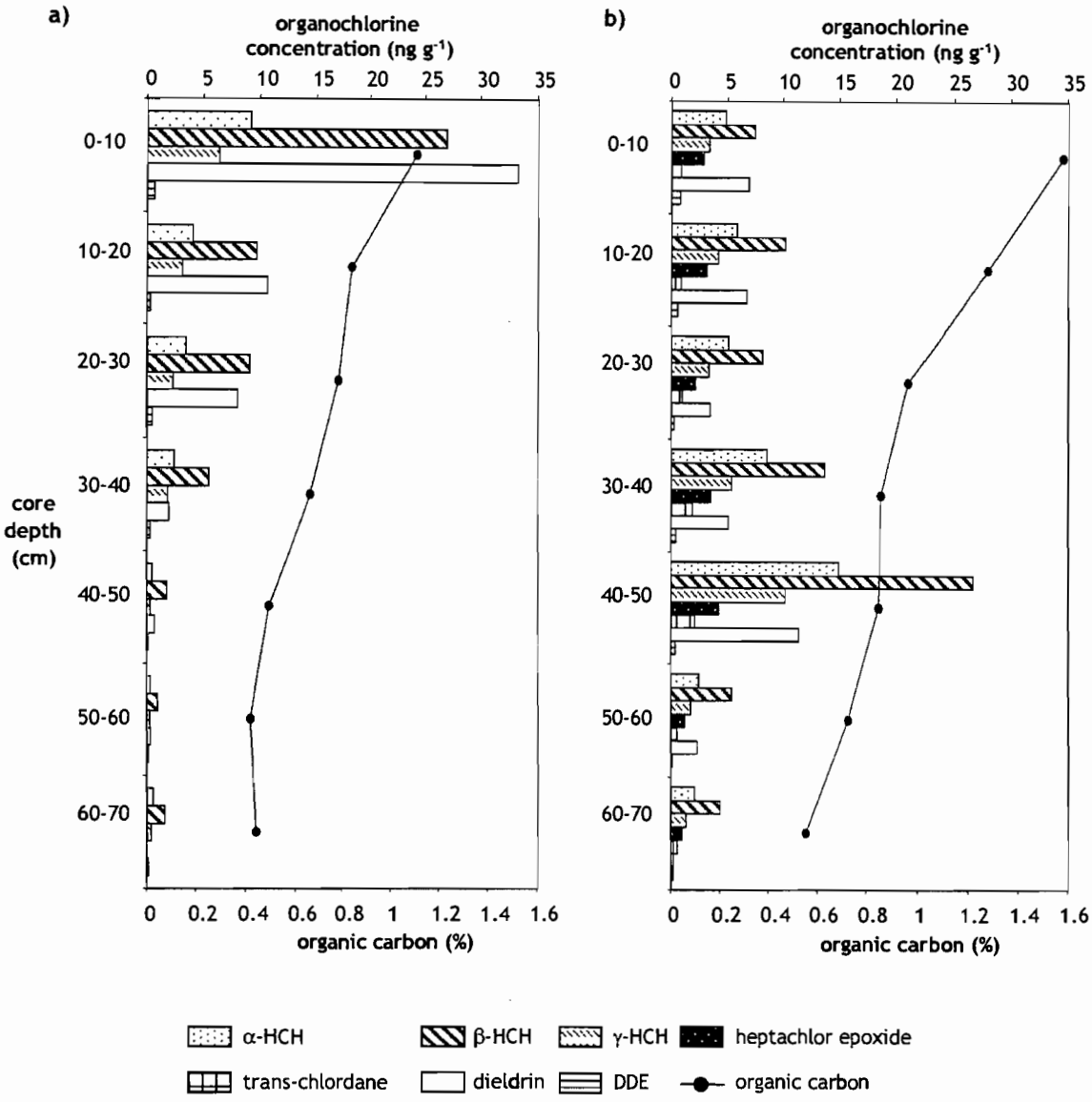


Figure 2.6. Organic carbon content (%) and concentrations of selected organochlorine compounds (ng g^{-1}) in: a) core LC, and b) core VC, collected from the Herbert region.

surface soil (sandy loam) to 30 cm (cores SC and LC) or 50 cm (core HC) to sandy clay at around 50cm (core SC), 60-75 cm (core HC) or 40-60 cm (core LC), with transition zone of mixed soil type occurring between the two soil types *(Figure C.1)*.

Core VC, collected from the recently cultivated field, showed a markedly different residue profile (Figure 2.6b). Uniform concentrations of organochlorine residues were found in the top 30 cm, a slight increase in concentration occurred at 30-40 cm with the maximum concentrations were found at 40-50 cm. Organic carbon content declined with depth and was not correlated with organochlorine concentration (Figure 2.7).

Table 2.6a. Distribution of individual organochlorine compounds in soil cores collected from the Burdekin region, expressed as a percentage of the summed concentration in the analysed depth (0-70 cm) of soil cores (Source: *Table C.3a*).

Core depth (cm)	Compound													
	α-HCH	β-HCH	γ-HCH	δ-HCH	aldrin	dieldrin	heptachlor	heptachlor epoxide	trans-chlordane	cis-chlordane	p, p'-DDE	p, p'-DDD	p, p'-DDT	chlorpyrifos
Core SC														
0-10	59	51	51	62	22	77	70	73	60	63	48	-	63	82
10-20	13	20	18	16	33	12	20	18	23	19	21	-	19	18
20-30	9.0	11	12	11	23	6.4	10	7.0	9.6	9.2	12	-	18	-
30-40	5.1	6.3	4.7	-	0.0	0.0	-	0.7	4.0	4.6	9.4	-	-	-
40-50	3.9	5.1	3.4	-	11	2.4	-	1.3	2.5	2.5	5.7	-	-	-
50-60	7.6	3.9	8.1	11	-	1.3	-	0.5	0.6	0.9	2.4	-	-	-
60-70	2.5	2.0	2.9	-	11	1.2	-	-	0.4	-	2.0	-	-	-
Total concentration (ng g^{-1})	**0.434**	**1.64**	**0.352**	**0.110**	**0.219**	**3.43**	**0.164**	**8.64**	**4.66**	**1.27**	**0.921**	**<0.010**	**0.123**	**0.091**
Core HC														
0-10	17	47	36	26	29	19	27	41	20	20	12	-	77	17
10-20	23	12	20	21	22	25	28	20	28	26	29	-	-	73
20-30	29	16	20	21	28	22	22	21	23	27	23	100.0	23	6.2
30-40	13	12	10	15	14	15	14	8.0	11	10	17	-	-	3.0
40-50	3.1	2.0	2.2	2.1	-	-	-	0.8	2.4	2.9	-	-	-	-
50-60	8.9	7.1	7.1	10	7.5	13	10	5.7	8.7	7.8	7.5	-	-	-
60-70	6.1	3.5	4.7	5.3	-	7.2	-	4.2	7.0	6.7	12	-	-	-
Total concentration (ng g^{-1})	**0.720**	**4.10**	**1.05**	**0.472**	**0.231**	**0.962**	**0.791**	**8.71**	**5.27**	**1.23**	**0.120**	**0.263**	**0.132**	**2.90**

Table 2.6b. Distribution of individual organochlorine compounds in soil cores collected from the Herbert region, expressed as a percentage of the summed concentration in the analysed depth (0-70 cm) of soil cores (Source: *Table C.3b*).

Core depth (cm)	Compound													
	α-HCH	β-HCH	γ-HCH	δ-HCH	aldrin	dieldrin	heptachlor	heptachlor epoxide	trans-chlordane	cis-chlordane	p, p'-DDE	p, p'-DDD	p, p'-DDT	chlorpyrifos
Core LC														
0-10	45	48	44	39	-	61	-	-	32	-	35	80	52	76
10-20	20	18	21	19	61	19	52	-	10	-	17	10	12	12
20-30	17	16	16	22	39	15	42	-	8.0	-	24	10	16	11
30-40	12	10	13	14	-	3.6	-	-	20	-	16	-	13	1.1
40-50	2.0	3.1	2.2	2.4	-	1.2	-	-	8.7	-	2.9	-	2.2	-
50-60	1.4	1.7	1.4	1.6	-	0.6	-	-	6.4	-	2.4	-	1.9	-
60-70	2.6	2.8	2.6	2.4	-	0.1	6.0	-	16	-	2.1	-	3.3	-
Total concentration (ng g^{-1})	**20.2**	**55.4**	**14.5**	**8.92**	**0.072**	**54.8**	**0.070**	**<0.025**	**0.11**	**<0.025**	**1.78**	**0.120**	**1.29**	**2.03**
Core VC														
0-10	11	9.8	11	9.2	42	19	27	16	11	12	31	17	31	56
10-20	13	13	14	12	20	18	14	17	11	11	22	17	14	7.5
20-30	12	11	11	12	11	9.6	12	12	13	12	10	13	10	29
30-40	19	18	18	17	14	14	20	19	25	23	15	24	15	5.1
40-50	34	35	34	40	12	32	20	23	27	26	13	23	18	2.9
50-60	5.7	7.0	6.0	5.4	-	6.5	4.4	6.5	6.2	6.9	4.1	5.8	4.5	-
60-70	4.7	5.7	4.5	4.7	-	0.6	2.4	5.4	6.9	8.6	4.2	-	7.4	-
Total concentration (ng g^{-1})	**43.5**	**75.8**	**29.6**	**14.6**	**0.384**	**36.0**	**0.540**	**18.1**	**7.62**	**2.45**	**2.55**	**2.63**	**0.331**	**2.19**

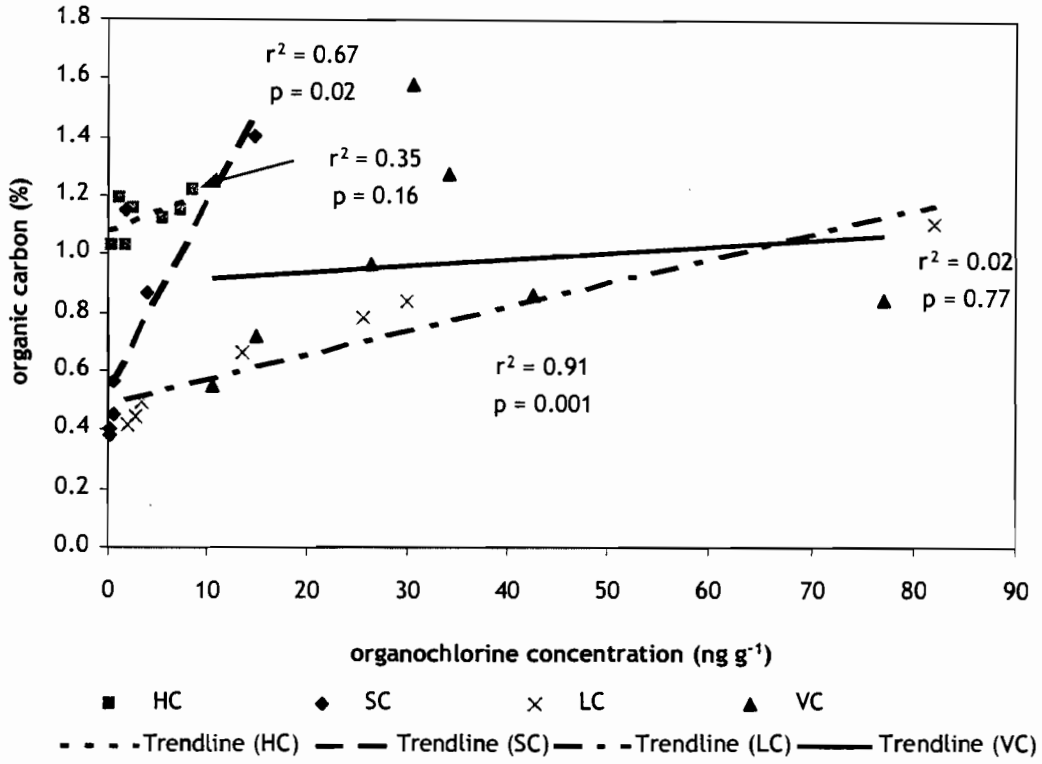


Figure 2.7. Correlations of organic carbon content (%) and total concentration of organochlorine compounds (ng g^{-1}) in soil cores HC and SC, collected from the Burdekin region, and soil cores LC and VC, collected from the Herbert region.

2.3.4 Soil fractions

The four soils used to examine the particle size distribution of the organochlorine insecticides contained similar percentages of clay and silt (Table 2.7). The major difference between the soils was the relative proportion of fine and coarse sand. Clay and silt fractions contained higher concentrations of organochlorine residues and organic carbon as compared with the sand fractions (Figures 2.8 and 2.9; *Table C.4*). Analysis of the correlation between organic carbon content and total organochlorine concentration in the different size soil fractions yielded high correlation coefficients, although there was only a significant correlation in one soil (Figure 2.10). The high r^2 values may indicate that organic carbon content is a significant factor in determining the distribution of organochlorine residues in the different size soil fractions. High concentrations of organochlorine residues were found in the vegetal debris relative to the soil fractions (Table 2.8).

Table 2.7. Particle size analysis and organic carbon content (%) in soil (0-10 cm) collected from the Burdekin region (HC and SC) and the Herbert region (LC and VC), and used to assess the particle size distribution of organochlorine residues.

Soil	Clay (<2 μm) (%)	Silt (2-20 μm) (%)	Fine Sand (20-200 μm) (%)	Coarse Sand (0.2-2 mm) (%)	Organic carbon (%)
Burdekin					
HC	22.1	25.1	50.0	2.80	1.2
SC	22.0	21.7	50.9	5.40	1.4
Herbert					
LC	17.0	20.1	32.6	30.3	1.1
VC	19.8	21.5	29.3	29.4	1.6

Table 2.8. Concentrations of organochlorine residues in vegetal debris from soil (0-10 cm) collected from the Burdekin region (HC and SC) and the Herbert region (LC and VC).

Compound	Concentration (ng g^{-1})			
	HC	SC	LC	VC
α-HCH	<0.20	<0.20	84	27
β-HCH	0.22	<0.20	201	44
γ-HCH	<0.20	<0.20	48	15
δ-HCH	<0.20	<0.20	40	8.9
aldrin	<0.20	<0.20	0.58	<0.20
dieldrin	<0.20	10	271	68
heptachlor	<0.20	2.2	0.91	<0.20
heptachlor epoxide	0.59	49	0.32	23
trans-chlordane	<0.20	ND*	1.5	ND
cis-chlordane	<0.20	ND*	0.47	ND
p, p'- DDE	<0.20	2.1	6.0	6.0
p, p'-DDD	<0.20	8.0	0.56	7.4
p, p'-DDT	<0.20	9.7	5.3	0.55
chlorpyrifos	0.07	<0.20	15	<0.20
endosulfan I	<0.20	<0.20	<0.20	<0.20
endosulfan II	<0.20	<0.20	<0.20	<0.20
endosulfan sulfate	<0.20	<0.20	1.2	<0.20

* ND - not determined due to accidental addition of standard containing 10 ng of chlordanes to samples

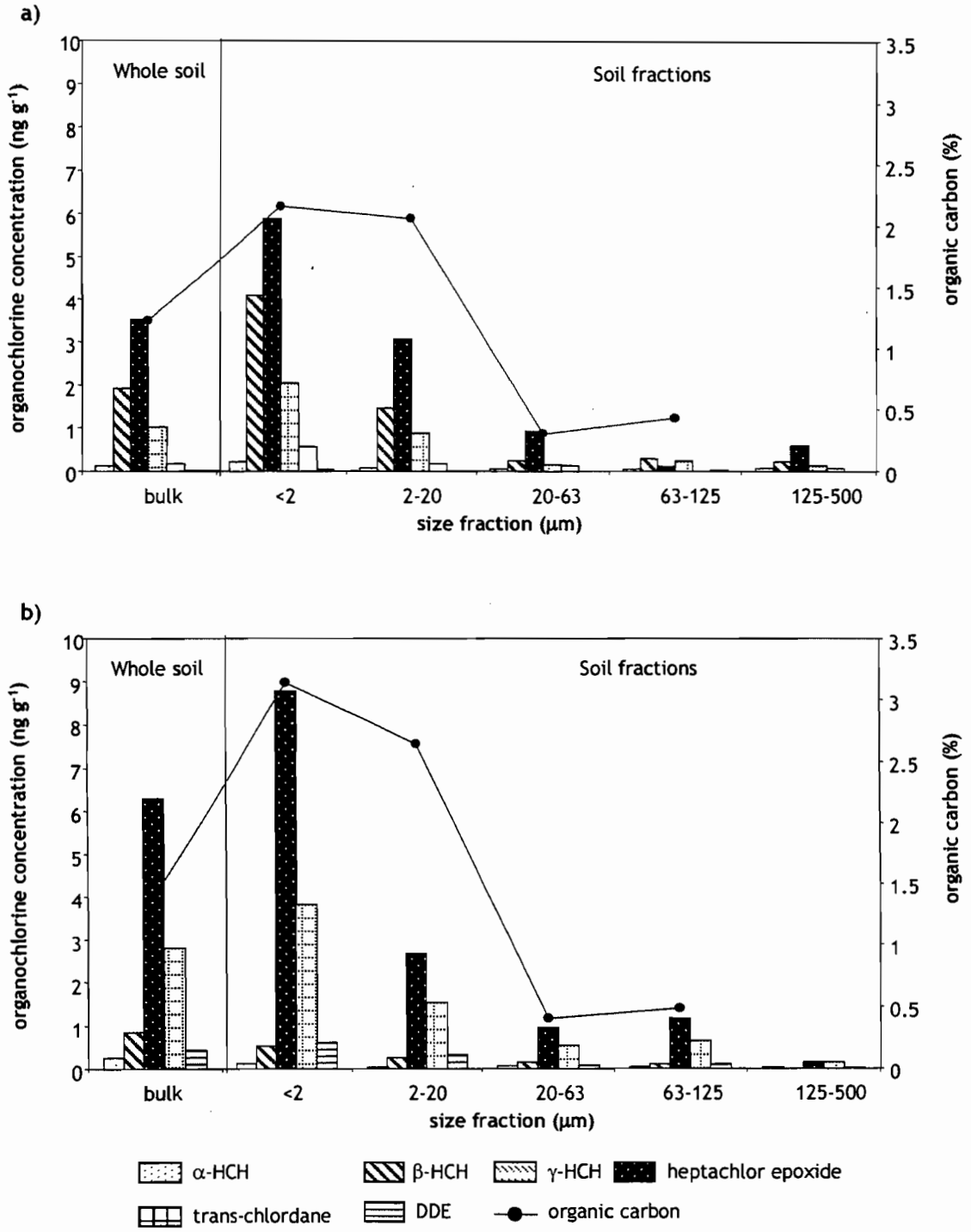


Figure 2.8. Organic carbon content (%) and concentrations of selected organochlorine compounds (ng g^{-1}) in whole soil and different size soil fractions in surface soil (0-10 cm) collected from the Burdekin region: a) soil HC, and b) soil SC.

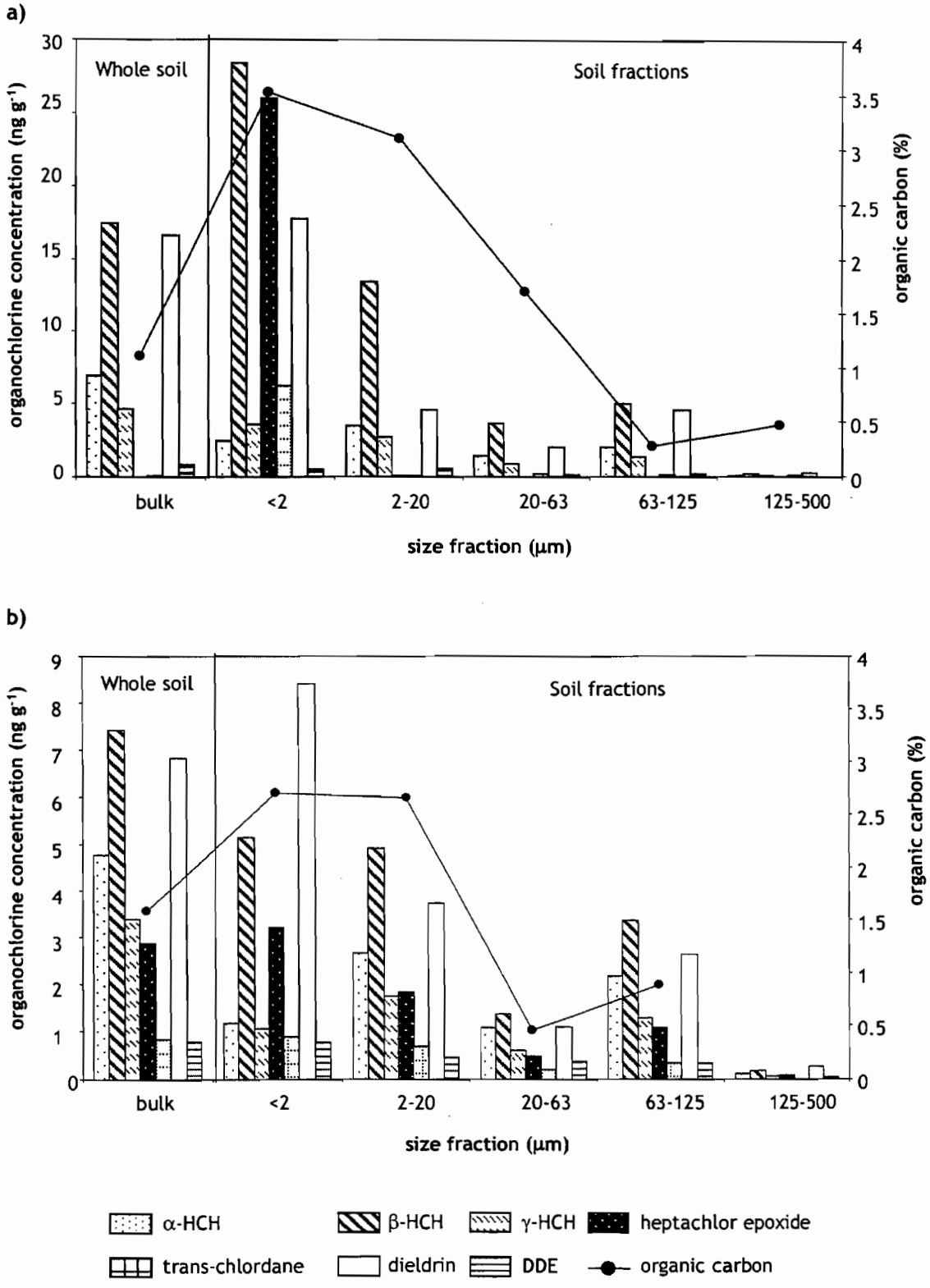


Figure 2.9. Organic carbon content (%) and concentration of selected organochlorine compounds (ng g^{-1}) in whole soil and different size soil fractions of surface soil (0-10 cm) collected from the Herbert region: a) soil LC, and b) soil VC.

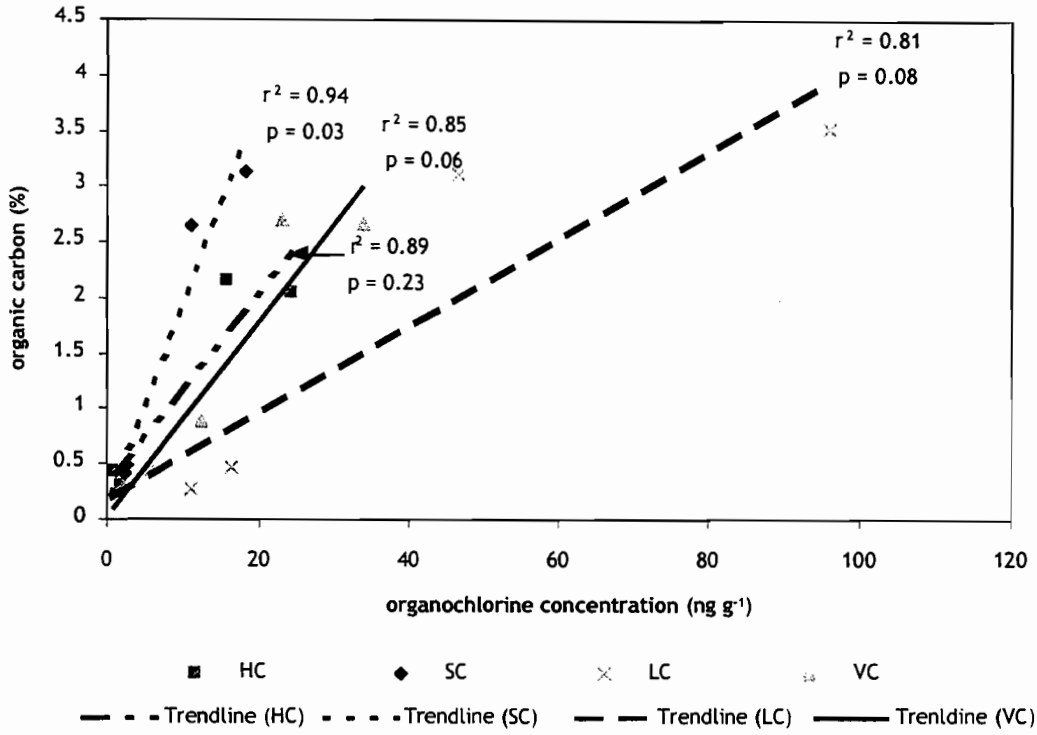


Figure 2.10. Correlations of organic carbon content (%) and total organochlorine concentration (ng g^{-1}) in soil size fractions (2 μm, 2-20 μm, 20-63 μm, and 63-125 μm) of surface soils (0-10 cm) collected from the Burdekin (HC and SC) and Herbert regions (LC and VC).

2.3.5 Drainage channels

2.3.5.1 On-farm

DDE was detected at concentrations ranging from 0.6-63 ng g^{-1} along the length of the drain from the Burdekin region (Table 2.9). HCH isomers were also present in sediment collected from the head of the drain (ID1), a side-drain (ID3a) and just prior to the drain entering Eight-Mile Creek (ID4). DDE was found in high concentrations in soil surrounding the drain (S072; Table 2.9).

Organochlorine concentrations in the on-farm drain in the Herbert region were low and dieldrin was the only residue consistently detected along the length of the drain (Table 2.10). Cane soils (S051, S052) surrounding the head of the drain contained moderate concentrations of organochlorine insecticide residues with dieldrin present at the highest concentrations (~1.9 ng g^{-1} dieldrin; Table 2.10).

No consistent trends in organochlorine concentration were observed along the length of either of these drains.

Table 2.9. Concentration of organochlorine compounds and extractable organic matter (EOM), and organic carbon content (%) in samples collected from a sugarcane field adjacent to an on-farm drainage line (ID; Figure 2.2c), and within the drainage line in the Burdekin region.

Compound	Concentration (ng g^{-1})						
	SO72	ID-1	ID-2	ID-3	ID-3a	ID-3b	ID-4
α-HCH	0.087	0.024	0.212	<0.010	<0.010	0.032	0.028
β-HCH	2.65	0.146	1.18	<0.010	0.021	0.263	0.096
γ-HCH	0.143	0.015	0.069	<0.010	<0.010	0.016	0.011
δ-HCH	0.051	0.020	0.109	<0.010	<0.010	0.024	0.013
aldrin	<0.010	0.031	0.011	<0.010	<0.010	<0.010	<0.010
dieldrin	0.227	1.07	0.208	0.022	0.041	0.069	0.023
heptachlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
heptachlor epoxide	<0.010	<0.010	0.025	<0.010	<0.010	0.039	<0.010
trans-chlordane	0.014	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
cis-chlordane	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'- DDE	27.8	6.10	63.1	1.21	0.560	0.917	4.11
p, p'-DDD	0.305	0.091	0.887	0.089	0.065	1.46	0.087
p, p'-DDT	0.856	0.108	0.264	0.030	0.076	1.55	0.024
chlorpyrifos	0.025	<0.010	0.068	<0.010	0.014	0.014	0.026
endosulfan I	<0.010	<0.010	0.301	0.017	<0.010	0.201	0.036
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	0.023	<0.010
endosulfan sulfate	<0.010	<0.010	0.216	0.069	0.375	0.640	0.137
EOM (mg g^{-1})	0.01	0.06	0.35	0.02	0.76	0.02	0.12
organic carbon (%)	0.3	0.47	1.9	0.24	1.3	0.70	0.76

Table 2.10. Concentration of organochlorine compounds and extractable organic matter (EOM), and organic carbon content (%) in samples collected from sugarcane fields adjacent to an on-farm drainage line (H; Figure 2.3a), and within the drainage line in the Herbert region.

Compound	Concentration (ng g^{-1})						
	S051	S052	H1	H2	H2a	H2b	H3
α-HCH	0.295	<0.010	0.041	0.012	<0.010	<0.010	0.142
β-HCH	0.279	0.034	0.048	0.029	0.020	<0.010	0.117
γ-HCH	0.583	<0.010	0.015	<0.010	<0.010	<0.010	0.060
δ-HCH	0.073	<0.010	<0.010	<0.010	<0.010	<0.010	0.033
aldrin	0.146	<0.010	0.004	<0.010	<0.010	0.750	<0.010
dieldrin	1.90	1.84	0.104	0.090	0.075	0.031	0.283
heptachlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
heptachlor epoxide	<0.010	0.230	0.012	0.004	<0.010	<0.010	<0.010
trans-chlordane	<0.010	0.850	0.075	0.030	0.011	<0.010	<0.010
cis-chlordane	<0.010	0.128	0.023	0.006	0.007	<0.010	<0.010
p, p'- DDE	<0.010	<0.010	0.034	0.069	0.013	<0.010	<0.010
p, p'-DDD	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'-DDT	<0.010	<0.010	<0.010	0.030	<0.010	<0.010	<0.010
chlorpyrifos	0.097	0.823	0.234	<0.010	<0.010	0.169	0.069
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	0.087	<0.010	<0.010	0.135	0.088
EOM (mg g^{-1})	0.04	0.07	0.33	0.37	0.05	6.2	0.33
organic carbon (%)	1.4	1.9	4.0	2.6	1.1	9.2	2.4

2.3.5.2 Off-farm drainage

A high concentration of DDE (27 ng) and moderate concentrations of HCH isomers, dieldrin, DDT and DDD were detected in the sample collected from Pink Lily Lagoon (8MC1) (Table 2.11). During wet seasons, excess water (and sediment) from the lagoon flows into Eight-Mile Creek and may account for some the low concentrations of organochlorine residues detected in sediments collected from Eight-Mile Creek (Table 2.11). The sediment sample collected after heavy rains (8MC5) contained low concentrations of dieldrin, DDE and chlorpyrifos residues.

Table 2.11. Concentrations of organochlorine residues and extractable organic matter (EOM), and organic carbon content (%) of samples collected from Eight-Mile Creek (Figure 2.2b).

Compound	Concentration (ng g^{-1})				
	8MC1	8MC2	8MC3	8MC4	8MC5
α-HCH	0.039	<0.010	<0.010	<0.010	<0.010
β-HCH	0.054	<0.010	0.016	0.015	<0.010
γ-HCH	0.020	<0.010	<0.010	<0.010	<0.010
δ-HCH	<0.010	<0.010	<0.010	<0.010	<0.010
aldrin	0.026	<0.010	<0.010	<0.010	<0.010
dieldrin	0.726	<0.010	0.011	<0.010	0.022
heptachlor	<0.010	<0.010	0.006	<0.010	<0.010
heptachlor epoxide	<0.010	<0.010	<0.010	0.012	<0.010
trans-chlordane	0.015	<0.010	<0.010	0.016	<0.010
cis-chlordane	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'- DDE	27.1	0.181	0.162	0.016	0.025
p, p'-DDD	0.760	<0.010	0.073	<0.010	<0.010
p, p'-DDT	0.626	0.080	<0.010	<0.010	<0.010
chlorpyrifos	<0.010	<0.010	0.088	0.120	0.110
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	0.013	<0.010	<0.010	0.106
EOM (mg g^{-1})	0.08	0.05	0.04	0.01	0.28
organic carbon (%)	1.8	0.21	0.28	0.12	1.1

Sediment collected from Plantation Creek contained variable concentrations of organochlorine residues (Table 2.12). Samples collected from the upper part of the creek (PC1, PC2) contained high concentrations of organochlorine residues, and easily detectable concentrations were present in the wetland sample (PC4). Sediment collected below the wetland area (PC5, PC6) and just above the wetland area (PC3) showed low and variable concentrations of organochlorine residues. PC3 was a sandy sample with very little fine sediment, which may account for its low organochlorine residue concentrations compared with other samples collected from this drainage system.

Table 2.12. Concentration of organochlorine residues and extractable organic matter (EOM), and organic carbon content (%) in samples collected from Plantation Creek (Figure 2.2a).

Compound	Concentration (ng g^{-1})					
	PC1	PC2	PC3	PC4	PC5	PC6
α-HCH	0.394	0.013	<0.010	0.115	<0.010	<0.010
β-HCH	2.04	<0.010	<0.010	0.236	0.011	<0.010
γ-HCH	0.509	<0.010	<0.010	0.048	0.012	<0.010
δ-HCH	0.202	<0.010	<0.010	0.024	<0.010	<0.010
aldrin	0.191	0.151	<0.010	0.275	<0.010	0.151
dieldrin	0.972	0.069	0.028	0.581	0.046	0.048
heptachlor	0.119	0.155	<0.010	0.317	0.042	0.153
heptachlor epoxide	2.60	0.084	0.003	0.319	<0.010	<0.010
trans-chlordane	0.931	0.229	0.031	0.536	<0.010	0.030
cis-chlordane	0.450	0.021	<0.010	0.140	<0.010	0.083
p, p'- DDE	0.727	0.027	<0.010	0.483	0.012	0.026
p, p'-DDD	0.572	0.025	<0.010	0.337	<0.010	0.031
p, p'-DDT	<0.010	0.019	<0.010	0.353	<0.010	0.041
chlorpyrifos	4.40	<0.010	<0.010	0.202	<0.010	0.084
endosulfan I	0.282	<0.010	<0.010	0.061	<0.010	0.015
endosulfan II	0.411	0.013	<0.010	0.025	<0.010	<0.010
endosulfan sulfate	2.07	<0.010	0.024	0.151	<0.010	0.039
EOM (mg g^{-1})	0.42	0.16	0.04	1.3	0.07	0.11
organic carbon (%)	3.4	0.51	0.11	2.4	0.82	2.1

2.3.6 Marine sediments

No organochlorine insecticide residues or PCBs were detected (<0.005 ng g^{-1}) in any sediment core slices or surface sediments collected from the near-shore environment of the Herbert and Burdekin River regions. All cores showed ^{210}Pb in excess of atmospheric supply rate (50 Bq m^{-2} yr^{-1}) indicating significant focussing of fine sediments into a small area of high sedimentation rate (Table 2.13). The chronology determined for the core AIMS 1260 was supported by the presence of enhanced mercury concentration at a ^{210}Pb estimated date of 1870-1900. This correlates with use of mercury in gold extraction in the Burdekin catchment during this period (Walker and Brunskill, 1996). Figure 2.11 shows the chronology, organic carbon content, and extractable organic material (EOM) of the analysed slices from the marine sediment cores. Table 2.14 shows organic carbon and extractable organic material (EOM) for the surface marine sediments.

Table 2.13. Estimated sediment accumulation parameters, based upon excess ^{210}Pb and ^{137}Cs and particle tracer models. Atmospheric flux of unsupported ^{210}Pb in this region is approximately 50 Bq m^{-2} yr^{-1}, and the integrated burden of ^{137}Cs from atmospheric fallout is approximately 300 Bq m^{-2} for 1950-1980.

Core	Mass accumulation rate (kg m^{-2} yr^{-1})	Mixed layer (cm)	Time equivalent mixed layer (yr)	^{210}Pb Flux Bq m^{-2} yr^{-1}
1450	8.8	3.8	3.5	191 ± 47
1262	2.6	15	35	130 ± 44
1260	17	61	23	695 ± 166

Table 2.14. Organic carbon and extractable organic matter (EOM) analyses of surface marine sediments of the Herbert and Burdekin regions.

Sample	Organic carbon (%)	EOM (mg g^{-1})
1241	0.87	0.04
1248	0.99	0.02
1250	1.0	1.0
1451	3.7	0.07
1453	0.32	0.04
1455	2.5	0.13
1457	0.72	0.04
1458	0.78	0.04
1468	0.45	1.1
1470	0.53	0.01
1473	ND	0.01
1477	0.14	0.01

ND-not determined

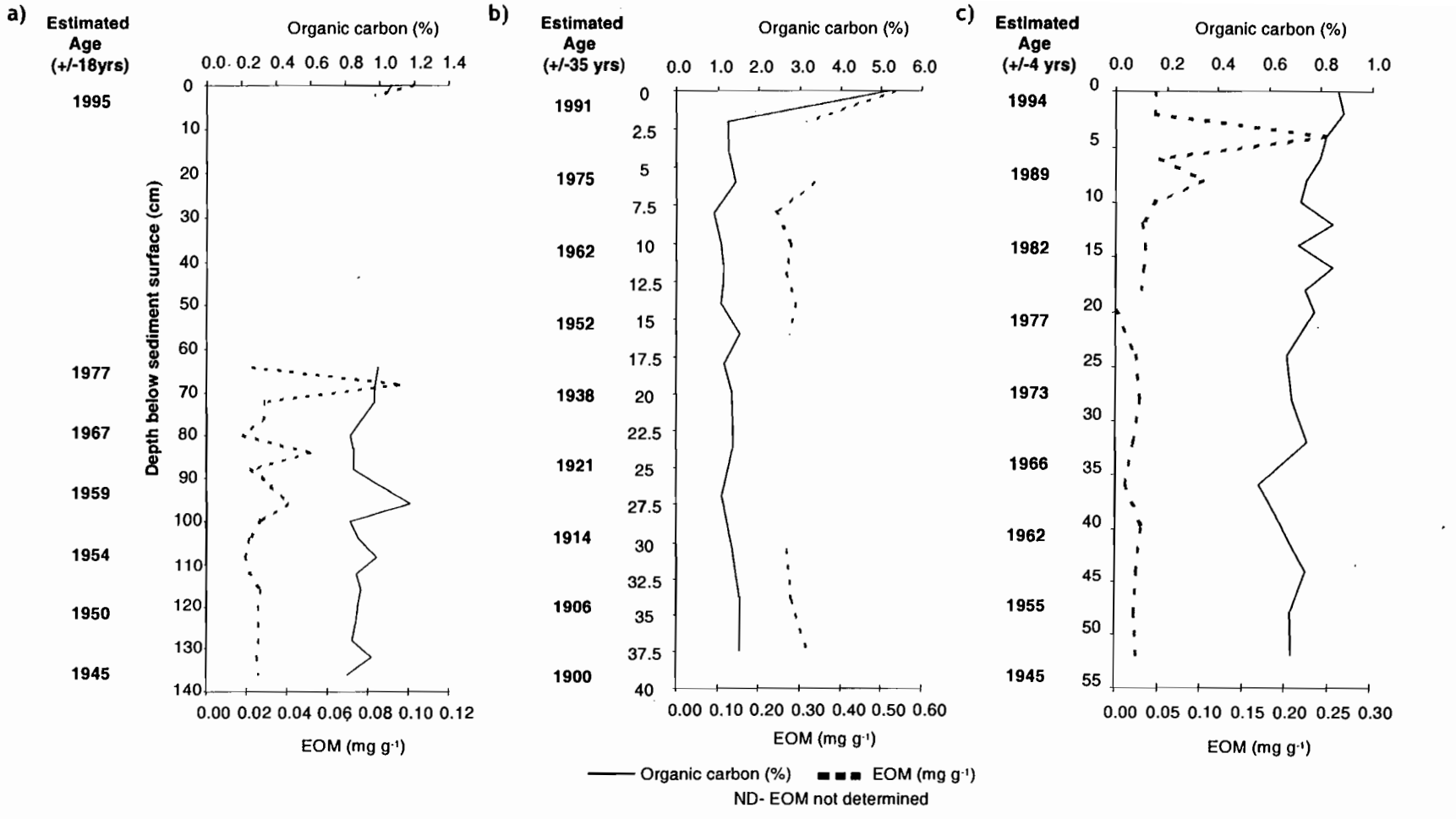


Figure 2.11. Estimated age, organic carbon content (%) and extractable organic matter (EOM, mg g^{-1}) in marine sediment cores: a) AIMS 1260 from the Burdekin region, and b) AIMS 1262, and c) AIMS 1450 from the Herbert region.

2.4 Discussion

2.4.1 Vertical distribution of residues

Farming practices such as insecticide placement and cultivation, or processes such as volatilisation or movement of resides down a soil profile by dissolution in water or attached to colloidal material, may influence the vertical distribution of organochlorine insecticide residues in the soil (Capel and Eisenreich, 1990; Spencer *et al.*, 1996). Insecticides used on sugarcane were generally placed at a depth of 20-30 cm relative to the surface of the "hilled-up" row, or 10-20 cm relative to the surface of a flat field as a result of burial after application (either during planting or "hilling-up" operations, Figure 2.12). Cultivation techniques such as discing, rotary-hoeing and ploughing may mix the soil up to a depth of 30 cm, resulting in redistribution, and homogenisation of insecticides in the depth of soil disturbed by cultivation (BSES, 1970c; Spencer *et al.*, 1996). These cultivation techniques are commonly practised in the Herbert and Burdekin regions. Deep-ripping is another cultivation practice that occurs in the Herbert and Burdekin regions. This process can disturb the soil down to depth of 40-60 cm to break up dense clay pans. Deep-ripping does not mix the soil effectively and, in certain soil types, it may enhance the migration of organochlorine residues down the soil profile by creating channels through which water and colloidal material can move more readily.

Given the application of insecticides at a depth of 10-20 cm, the occurrence of the highest organochlorine residue concentrations in soil cores collected from fields in which sugarcane was growing, in the surface 0-10 cm is initially surprising. These cores were collected from the inter-rows of sugarcane fields in which the soil surface was approximately 10-20 cm lower than the soil surface of the adjacent sugarcane rows and roughly equivalent to a depth of 10-20 cm in a flat field (Figure 2.12), which then matches the depth of application. This suggests that the highest concentrations of organochlorine residues in these soil cores are present at the depth of insecticide application.

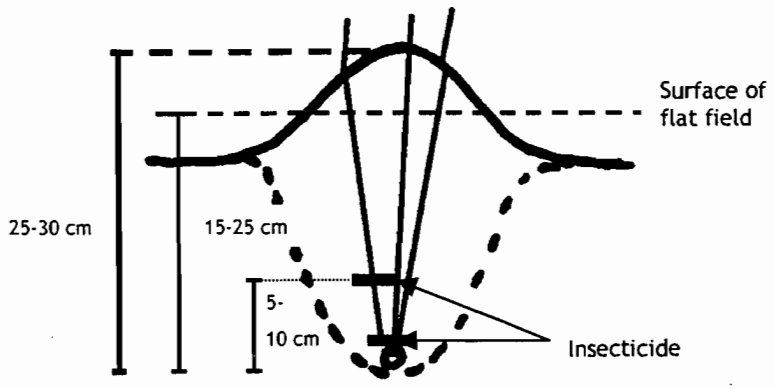


Figure 2.12. Cross-section of a hilled up furrow showing approximate relationship of insecticide placement to surface of hilled-up and flat field.

Detectable organochlorine residue concentrations found below a soil depth of 10 cm indicates that residues have moved down the soil profile through soil cultivation, dissolution in water and subsequent movement of the water down the soil profile (leaching), or by adsorption on colloidal material and subsequent transport of the colloidal material down the soil profile (translocation). The latter is generally considered to be the major mechanism for movement of organochlorine residues (Capel and Eisenreich, 1990). The high concentrations of organochlorine residues in the surface 10 cm and low concentrations declining with depth below 10 cm in soil cores collected from fields that had not been recently cultivated suggests soil cultivation has had little influence on the distribution of organochlorine residues and that little migration or leaching of organochlorine has occurred in these soil cores. In soil cores that showed a decline in organic carbon content with depth (cores SC and LC), total organochlorine residue concentration was correlated with soil organic carbon content (Figures 2.5b, 2.6b and 2.7). In contrast, total organochlorine content was not correlated with soil organic carbon in core HC, which showed no decline in organic carbon content with depth (Figures 2.5a and 2.7).

The contrasting profile of the soil core collected from the recently cultivated field (core VC) may reflect the importance of cultivation in determining the distribution of insecticide residues in the soil profile. The uniform organochlorine residue concentrations observed in the top 30 cm may suggest that cultivation has redistributed residues in this depth. The occurrence of the highest residue concentrations at 40-50 cm may reflect enhanced migration of organochlorine residues down the soil profile by deep-ripping (Figure 2.6b). However, changes in soil properties in this core may also account for the observed organochlorine residue distribution. Soil texture in this core changed from a sandy loam to fine clay with a transition zone occurring over 50-70 cm (*Figure C.1b*). The change in soil texture at 50 cm may have restricted the downward movement of water and resulted in an accumulation of leached or adsorbed residues above this depth. Total organochlorine concentration was not correlated with soil organic carbon content in this core.

Volatilisation is generally considered to be the major mechanism of loss of insecticide residues from the soil profile, including soil-incorporated insecticides, and may account for 80-90% of the loss of all organochlorine residues from the soil profile (Spencer *et al.*, 1973; Taylor and Spencer, 1990; Wauchope, 1978). Soil moisture is generally considered to be the most significant factor influencing volatilisation with negligible volatilisation occurring from dry soils (Spencer *et al.*, 1973; Taylor and Spencer, 1990). Volatilisation of organochlorine residues present in the surface soil layer is primarily dependent upon soil moisture and vapour pressure of the compound. Volatilisation of soil-incorporated residues is controlled by the rate of diffusion or convection of the residues to the surface soil after the surface soil is depleted (Spencer *et al.*, 1973; Taylor and Spencer, 1990). Diffusion is the movement of compounds from areas of high concentration (e.g. sub-surface soil) to areas of low

concentration (e.g. surface soil). Convection is the upward movement of water as a result of evaporation of water from the soil surface that also transports organochlorine residues towards the soil surface. Spencer and Cliath (1973) showed that, for lindane and dieldrin under laboratory conditions, volatilisation supported by convective flow was up to 5 times faster than that controlled by diffusion alone. Diffusive and convective processes are negligible when the surface soil is dry (Spencer *et al.*, 1973; Taylor and Spencer, 1990). Additionally, atmospheric humidity is also an important factor in determining the rate of convection. Under conditions of high humidity, reduced evaporation and replenishment of water to the surface soil results in negligible convection of soil incorporated residues (Spencer *et al.*, 1973).

In order for volatilisation to be the dominant mechanism of removal of organochlorine residues from sugarcane soils, a significant net upward movement of insecticide residues by diffusive or convective processes must occur, given the sub-surface placement of insecticides. If it is assumed that cultivation homogenously distributes organochlorine residues in the top 30 cm (effective depth) of a soil profile, the occurrence of the highest concentrations of organochlorine residues in the surface 10 cm (effective depth 10-20 cm) in soil cores not recently disturbed by cultivation may reflect upward movement of residues from the deeper soil. Alternatively, these high concentrations may indicate that cultivation of these fields has not disturbed the soil to a depth greater than 20 cm.

2.4.2 Regional distribution of organochlorine residues

Variations in soil organic carbon content are often anticipated to account for variability observed in organochlorine residue concentrations as a consequence of the preferential absorption of these residues onto organic matter (Karickhoff, 1984; Capel and Eisenreich, 1990), and observations that soil organic matter may increase the persistence of organochlorine residue (Edwards, 1973). While some authors have observed correlation of organochlorine concentration with soil organic carbon content (Szeto and Price, 1991), others have not (Harner *et al.*, 1999). In the present study, the low r^2-values (0.0003-0.13) demonstrated the weak correlation between concentrations of individual organochlorine compounds and total organochlorine concentration with soil organic carbon content in sugarcane soils collected from different locations in the Herbert and Burdekin regions. In contrast, and with the exception of core VC, trends in organic carbon content generally reflected trends in total organochlorine concentration in individual soil cores (r^2 = 0.35-0.91) and was significantly correlated in two cores. Similarly, trends in organic carbon content reflected trends in total organochlorine concentration in different size soil fractions of individual soils (r^2 = 0.81-0.93). In one soil organic carbon content and total organochlorine concentration was significantly correlated and in two other soils correlation of organic carbon content and organochlorine concentration approached significance. The absence of any correlation between organic carbon content and organochlorine residue concentration in the

surface soils suggests other factors were more important in determining current distributions of organochlorine residues in these soils.

It is proposed that application history is the most likely factor influencing the distribution of organochlorine insecticide residues both within and between regions. The distribution of organochlorine residues in the surface sugarcane soils of the Herbert and Burdekin regions reflects the known historical application of insecticides in each region.

In the Herbert region, formulations of technical HCH in rock dust, were predominantly used as insecticides for cane grub control (Figure 1.10). Beta-HCH has the lowest volatility of the different HCH isomers and is most resistant to microbial degradation (Willett *et al.*, 1998). Despite comprising only 5-7% of technical HCH, β-HCH is generally the dominant isomer detected in soils treated with technical HCH. The presence of β-HCH as the dominant HCH isomer in the sugarcane soils from this region reflects the historical usage of technical HCH. The ubiquitous distribution of dieldrin reflects the widespread usage of aldrin for wireworm control (Figure 1.10). Lindane (γ-HCH) and DDT were occasionally used for control of insect pests in the Herbert region, which may account for the observed increase in the contribution of γ-HCH to ΣHCH in some soils, and the variable concentration of DDTs.

Technical HCH formulations were predominantly used to control cane grubs in the Burdekin region until the early 1980's when an increasing area was treated with heptachlor formulations (Figure 1.13). Technical heptachlor also contained trans-chlordane at approximately 20% by weight (Stickley, 1971). The high concentrations of heptachlor epoxide and chlordanes detected in the majority of sugarcane soils from the Burdekin region reflect the application of heptachlor for greyback grub control. The variable concentrations of lindane and dieldrin in the soils from the Burdekin region probably reflects the occasional use of lindane, aldrin, and dieldrin to control cane grub or other insects in the Burdekin region. Additionally the greater contribution of γ-HCH to ΣHCH in some soils probably reflects the historical use of lindane in these fields.

A number of soils collected from the Burdekin region also showed high concentrations of *p,p'*-DDE. These soils were mainly collected from the upper Burdekin region where tobacco was widely grown until the mid-1960s (Johnson, 1966). DDT was widely used in the tobacco industry (Connell, 1993). Soils collected from the upper Burdekin region that were known to have not been previously used for tobacco, showed only low concentrations of *p,p'*-DDE (*Tables A.1* and *C.1*). The detection of *p,p'*-DDE in soils that were not known to have been previously used for tobacco farming may also reflect the occasional use of DDT on sugarcane.

Application history may also account for the lower total organochlorine load in sugarcane soils of the Burdekin region compared with that in the Herbert region, and the high variability of

organochlorine residue concentrations in sugarcane soils collected within a region. In the Burdekin region, heptachlor was applied at approximately 2.2 kg ha^{-1} (and trans-chlordane at approximately 1 kg ha^{-1}) while in the Herbert region technical HCH was applied at approximately 17.3 kg ha^{-1}, α-HCH at 10.5 kg ha^{-1}, β-HCH at 0.9 kg ha^{-1}, γ–HCH at 2.1 kg ha^{-1} and δ-HCH 1.0 kg ha^{-1} and aldrin at 0.2 kg ha^{-1} (Table 3.1).

Volatilisation may also account for the lower organochlorine residue concentration in soils collected from the Burdekin region. Irrigation is attributed to increasing loss of organochlorine residues by increasing volatilisation or enhancing microbial degradation (Willis *et al.*, 1972; Boule *et al.*, 1994). In the Burdekin region, irrigation of sugarcane fields during the dry season is widespread. This keeps the surface soil moist for extended periods during dry times of the year and is likely to increase volatilisation losses. In contrast, little irrigation occurs in the Herbert region. While a greater amount of rain falls in the Herbert region compared with the Burdekin region (section 1.4), higher air humidity generally occurs during periods of significant rainfall (wet season), which may then reduce volatilisation of soil-incorporated residues (Spencer and Cliath, 1990). Additionally, the presence of crop residues on the soil surface of sugarcane fields in the Herbert region may form a physical barrier and reduce volatilisation.

Insecticides were typically applied at the time of planting and buried immediately after application. The same plant crop remains in the ground for the life of the crop, which is harvested annually for 3-7 years (ratoon crops) and then the land left to lie fallow for a growing season. The number of ratoon crops a farmer chooses to grow will determine how frequently cane is planted on a given field, and thus the frequency of insecticide application. As insecticides were not applied annually, the year of last application will also influence the concentrations of organochlorine residues currently remaining in the soil. As insecticides for cane grub and wireworm control were generally applied as preventative measures, a farmers' perception of the risk of insect damage to the sugarcane crop for a given year will influence the application history of particular fields or farms, and hence the residual insecticide concentrations. During interviews, some farmers indicated that they did not apply insecticides when the risk of insect damage was perceived to be low, while other farmers preferred to apply insecticides "just in case". This attitudinal difference may account for the reduced variability of organochlorine residue concentrations in sugarcane soils collected from the same farm as compared to the variability observed in soils collected within a given region of the Herbert and Burdekin region. However, as only a limited number of farms were sampled at two locations, and the year of last application was not known for any field, further investigation is required to fully assess this.

Chlorpyrifos is currently the most widely used insecticide in the sugar industry (Hamilton and Haydon, 1996). The primary application of insecticides to plant cane also probably accounts

for the high variability observed in chlorpyrifos concentrations in the present study, which ranged from undetectable to 64 ng g^{-1} (Table 2.3). The absence or low concentrations of chlorpyrifos in some soils, despite current usage, is likely to reflect the lower environmental persistence of chlorpyrifos (30-60 days) as compared to the organochlorine insecticides (400 to greater than 1000 days; Mackay *et al.*, 1997). The low concentrations of endosulfan sulfate in the sugarcane soils of both regions may reflect usage on vegetable crops grown opportunistically between cycles of sugarcane.

Soil type may indirectly influence insecticide applications within a region, through its influence on insect pest distribution. For example, in the Herbert and Burdekin regions organochlorine insecticides were primarily applied for control of the greyback grub. The distribution of greyback grubs, and hence the area treated with insecticides for cane grub control, is generally restricted to certain, mainly sandy, soils (Ward, 1997; 1998) although, during years of increased grub populations, greyback grubs may also occur in other soil types (Ward, 1998). As such, insecticide applications (HCH and heptachlor) for control of the greyback grub were likely to be restricted in certain soil types, creating a "patchy" distribution dependent upon the location of grub-prone soils within a region. In contrast, insecticide application (primarily aldrin) for wireworm in the Herbert region was generally not restricted to particular soil types. As such, a greater area was treated and more regular insecticide applications occurred for wireworm control compared to cane grub control. The more regular and widespread application may account for the reduced variability in dieldrin concentrations as compared to HCH concentrations.

Two other factors may also influence the regional distribution of insecticide residues, in-field deposition of sediment during major flood events, and distribution of "mill mud" on cane fields located close to sugar mills. In both the Herbert and Burdekin regions the majority of sugarcane land is located in the flood plains of the two rivers. During large flood events farmers more commonly have observed deposition of sediment on their fields. Work by Wasson et al. (Dr. A. Johnson, CSIRO, pers. com.) have demonstrated that cane fields in the Herbert region act as a net sediment sink and that much of the sediment is mobilised from adjacent fallow paddocks. A large amount of surface soil is transported to the mill during green cane harvesting. Much of this is redistributed as "mill mud" on cane fields located close to the sugar mills. These factors provide a "homogenising" effect on the distribution of organochlorine residues in the surface soils, however, the extent to which these factors influence the regional distribution of insecticide residues will be difficult to determine.

2.4.3 Distribution of organochlorine residues in aquatic systems associated with sugarcane fields

Organochlorine residues are primarily transported from agricultural land to aquatic systems by adsorption on, and erosion of, soil particles (Karrickhoff, 1984; Young *et al.*, 1985). The

riparian and coastal sediments of north Queensland are considered to be the first stopping point for terrigenous sediment. Northward advection by waves and currents generated by South-east Trade Winds (Woolfe and Larcombe, 1998) confines sediment to the inner shelf region of the Great Barrier Reef lagoon (< 20 m deep) and within 10-15 km of the coast (Belperio, 1983; Johnson, 1996). Mangroves lining the estuaries of most of the small floodplain creeks play an important role in the movement of terrigenous sediment. North Australian creeks and rivers receive little freshwater input during the dry season (March-November). Thus, for a large part of the year (9-10 months), movement of sediment is largely controlled by tidal dynamics. This can result in a net landward movement of sediment (Larcombe and Ridd, 1996; Bryce *et al.*, 1998) in addition to a slow flushing of nutrients and contaminants from smaller mangrove-lined creeks (Wolanski and Ridd 1986, 1990; Wolanski *et al.*, 1990). Mixing of outwelled water from mangrove creeks with that of surrounding coastal water can be delayed (for at least two weeks) due to formation of a coastal boundary layer along mangrove fringed coastline (Wolanski and Ridd, 1986; Wolanski and Ridd, 1990). These small-scale sediment dynamics can act to trap sediment, and hence sediment-bound contaminants, in estuaries.

The absence of detectable concentrations of organochlorines in the coastal sediments of the Herbert and Burdekin regions was unexpected, especially given the presence of easily detectable concentrations in soils of the adjacent catchments. Low and variable concentrations of organochlorine residues found in farm drains in the Herbert and Burdekin regions, Eight-Mile Creek, and Plantation Creek indicates that some movement of organochlorine residues from the sugarcane fields to the aquatic systems is currently occurring. Additionally, the presence of enhanced levels of cadmium and mercury in recently deposited marine sediments strongly suggests that some amount of agricultural soil is reaching the near-shore environment (Tesiram 1996; Walker and Brunskill 1996).

A number of factors may contribute to the observed absence of detectable concentrations of organochlorine pesticides in the near-shore marine environment, including sub-surface application of insecticides (section 1.3.1.1), retention of organochlorine residues in the soil, land management techniques, sediment dilution, and degradation of organochlorine residues. Additionally, factors influencing soil erosion and sediment transport will influence the detection of organochlorine residues in aquatic systems surrounding sugarcane farms. Land management techniques, topography, and soil type play a significant role in soil erosion at a catchment scale. In catchments of similar topography and soil type, land management techniques may play a significant role in loss of soil from sugarcane fields. For example, the traditional practice of burning sugarcane prior to harvest and removal of crop residues after harvest exposes bare soil, which is highly susceptible to erosion in the event of high rainfall. In contrast, "green-cane" harvesting, in which no pre-harvest burning occurs, the excess foliage (trash) remains on the ground after harvesting, forming a thick, organic mulch layer

on the soil surface, which significantly reduces soil erosion and increases soil organic content. Conventional burnt cane cultivation was widely practised from World War II to the late 1970 s when green cane harvesting and trash blanketing techniques were introduced as soil erosion controls (Anon., 1984; Prove *et al.*, 1986). Estimated reductions in soil loss are from 150 t ha^{-1} $year^{-1}$ under burnt cane harvesting to 5 t ha^{-1} $year^{-1}$ under green cane harvest (Prove and Hicks, 1991). Despite marked differences in land management techniques in the Burdekin (almost 100% burnt cane harvesting) and Herbert regions (almost 100% green cane harvesting), no organochlorine residues were detected in the near-shore sediments of either catchment.

Catchment topography is also an important factor in determining erosion of soil at a catchment scale. The sugarcane lands of the Burdekin and Herbert regions are relatively flat compared to sugarcane lands of other catchments in north Queensland. Thus, movement of soil and associated contaminants off the sugarcane land in these regions would be markedly lower than that expected from sugarcane grown on moderately sloping fields. Previous studies of the concentrations of organochlorines in fish, invertebrates and sediments in a number of north Queensland catchments also failed to find detectable concentrations of organochlorines in the coastal region of the Burdekin region (Rayment *et al.*, 1997), with the exception of Dyall and Johns (1984) who found 5.2 ng g^{-1} of lindane in one sediment sample collected from the Burdekin River. However, low concentrations of organochlorine residues were detected in farm drains and creeks from this region (Hunter *et al.*, 2000; G. Ham, BSES, pers. comm.). No studies were conducted in the Herbert region. In contrast, detectable concentrations of organochlorine residues have been found in fish, mud crabs and sediments of other rivers such as the North Johnstone River (approximately 100 km north of the Herbert River) in which sugarcane is grown on elevated moderately sloping land (Russell and Hales, 1993; Russell *et al.*, 1996; Kannan *et al.*, 1995; Rayment *et al.*, 1997).

Trapping of eroded soil in farm drains or wetland areas may also reduce the amount of soil reaching the coastal environment. For example, up to 80% of the soil eroded from a paddock may remain in drainage lines on the farm (Prove and Hicks, 1991), although during periods of high rainfall this soil will be washed through to the riverine or estuarine systems. Freshwater or estuarine wetlands may play an integral role in reducing soil movement to riverine and marine environments by trapping eroded soil. Although only a limited number of samples were collected from wetland areas (Pink Lily Lagoon, PC4), these samples showed elevated organochlorine residue concentrations, relative to surrounding creek systems, and may reflect trapping of sediment and sediment-bound residues. In recent years considerable areas of wetlands in the Herbert and Burdekin regions have been converted to agricultural land (Johnson *et al.*, 1997 and 1999; J. Tait, Australian Centre for Tropical Freshwater Research, pers. comm.), which could alter hydrological regimes and result in increased sediment and

contaminant loads reaching the marine environment (Arakel *et al.*, 1989; Johnson *et al.*, 1997 and 1999).

Sediment dilution and chemical partitioning will further reduce the concentration of organochlorine residues reaching the estuarine environment. Eroded sugarcane soil that reaches the riverine environment is diluted with sediment, which is largely uncontaminated with organochlorine residues and derived from upstream regions of the catchment (largely grazing land for cattle), prior to deposition in the marine environment. Additionally, the diffusion of chemicals from areas of high concentration (contaminated soil particles) to areas of low concentration (surrounding uncontaminated environment). Finally, degradation of organochlorine residues by biotic or abiotic processes in the coastal sediments will also contribute to their observed absence.

2.4.4 Significance of current organochlorine concentrations

The concentrations of organochlorine residues present in the sugarcane soils of the Herbert and Burdekin regions suggest that these soils would be considered to be relatively unpolluted in comparison with soils and sediments in Europe and the US (UNEP/IAEA/IOC/FAO, 1992). The sugarcane soils from the Herbert and Burdekin regions contain lower HCH concentrations than soils collected from India and Vietnam, although higher concentrations than soils collected from Taiwan and Thailand (Table 2.15). DDT residues were generally lower than those found in soils from US (Table 2.15).

Comparison of organochlorine concentrations determined in the present study with sediment quality guidelines (Australia and New Zealand Environment Conservation Council (ANZECC), 1999), soil quality guidelines for beef cattle (Department of Primary Industries (DPI), 1997) and contaminated sites guidelines (Department of the Environment (DoE), 1998) provides an indication of the environmental and human health hazard posed by residual organochlorine concentrations.

The ANZECC sediment quality guidelines are based on those developed by Long and Morgan (1990) and Long *et al.* (1995, cited in ANZECC 1999) from a database of biological effects and the concentrations at which these effects were observed are shown in Table 2.16. The concentration at which less than 10% of the studies detected an effect was designated the "low concentration". The guideline "high concentration" corresponds to the sediment concentration at which effects were observed in 50% of studies. The DPI guideline values are "rule of thumb" soil concentrations which, if cattle were confined to grazing on these soils, organochlorine residues accumulated in beef fat are not likely to be above established residue limits (DPI, 1997). Contaminated site guidelines exist for a range of land-uses and include an environmental investigation threshold. The guideline values for the environmental investigation levels and a "standard" residential setting are shown in Table 2.16.

Table 2.15. Range and mean[¥] of organochlorine compounds in agricultural soil from various countries.

Country	Year sampled	Location	Concentrations (ng g^{-1})				Source
			ΣDDTs	ΣHCH	Heptachlor epoxide	Dieldrin	
Vietnam	1990	Paddy field	5.5 - 1,300	0.15 - 55	ND	ND	Thao *et al.* 1993
	1990	Paddy field	0.009 -1.2	0.43 - 5.2			Iwata et al. 1994
Thailand	1988	Paddy field	0.71 - 98	0.07 - 0.71	ND	ND	Thao *et al.* 1993
India	1987-1989	Paddy field	0.25 - 6 2.5	1.1 - 1,100[®] 230	ND	ND	Ramesh *et al.* 1991
	1988-1992	Farm soil	0.85 - 4,400 480	5.6 - 8,600 2,800	ND	ND	Kannan *et al.* 1995
	-	Paddy field	0.85 - 2200 99	0.42 - 280 34	ND	ND	Kawano *et al.* 1992
Indonesia	-	Paddy field	nd - 20 1.2	ND	ND	ND	Kuwutsuka *et al.* 1986
Malaysia	-	Paddy field	4.7 - 5.8 5.3	ND	ND	ND	Meier *et al.* 1983
Taiwan	1990	Paddy Field	5.6-78	1.3-1.9	ND	ND	Thao *et al.* 1993
Japan	1996	Farm soil				50	Nagami 1997
USA	1995/1996	Cornfields	nd - 118,000 9.63**	nd -1.23 0.09**	nd -15.2 0.58**	nd - 4,250 1.05**	Aigner *et al.* 1998
	1999	Farm soils	<0.2-112[#] 17.5**	<0.02-2.36* 0.128**	<0.02-0.179 0.046**	<0.02-2.07 0.219**	Harner *et al.* 1999
British Columbia	1989	Farm soil	nd - 4,685	nd - 455	nd - 308	nd - 692	Szeto and Price 1991
Australia	1990-1992	Agricultural soil	0.48 - 8,000 490	0.05-38 5			Kannan *et al.* 1995
	-	Rural area	0.77 - 1.2	0.045 - 0.057			Iwata *et al.* 1994
	1997	Sugarcane soil, Burdekin	<0.01- 29 0.2**	<0.010-3.2 0.62**	<0.01-18.2 0.28**	<0.010-3.7 0.06**	This study
	1997	Sugarcane soil, Herbert	<0.01-6.5 0.27**	<0.01-57.9 2.3**	<0.01-2.8 0.065**	0.03-27.6 1.25**	This study

[¥] arithmetic mean, unless otherwise mentioned.

[®]wet season, dry season values: ΣHCH range 1.1-190 ng g^{-1}, mean 35 ng g^{-1}, ΣDDT range 0.25-4.3 ng g^{-1} mean 1.5 ng g^{-1};

nd- not detected; ND-not determined; ** geometric mean; *α-HCH only; [#]DDE only;.

Table 2.16. Draft Australia and New Zealand Environment Conservation Council (ANZECC) sediment quality guidelines, Department of Primary Industries (DPI) guidelines and Department of Environment and Heritage (DoE) contaminated sites guidelines. (Source: DPI, 1997; DoE, 1998; ANZECC, 1999).

Compound	ANZECC (ng g^{-1} dry wt)		DPI (µg g^{-1}dry wt)	DoE (µg g^{-1} dry wt)	
	Low	High		Environment investigation levels	Residential*
dieldrin	0.02	8.00	0.01	-	-
aldrin + dieldrin	-	-	-	0.2	10
γ-HCH	0.32	1.00	-	-	-
ΣHCH	-	-	0.01	-	-
chlordane	0.5	6.00	-	-	50
p, p'-DDE	2.20	27.00	-	-	-
ΣDDTs	1.60	36.00	0.1	0.2	200

* "standard" residential exposure setting; includes children's day-care centres, pre-schools and primary schools

Of the organochlorine residues detected by the present study in soils of the Herbert region, dieldrin and lindane most frequently exceeded the ANZECC (1999) guideline "low concentration". Two locations exceeding the ANZECC guideline "high concentration" for dieldrin and nine for γ-HCH (Table 2.17). Additionally, 9 locations exceeded the DPI guidelines for total HCH isomers (Table 2.17). In the Burdekin region, dieldrin, γ-HCH and chlordane most frequently exceeded the ANZECC guideline "low concentrations". Two locations exceeded the ANZECC guideline "high concentration" for γ-HCH and one location exceeded the guidelines for chlordane (Table 2.17). No organochlorine insecticide residues exceeded DPI guidelines in Burdekin region. No concentrations of soils exceeded the contaminated sites guidelines for the environmental investigation levels or standard residential settings.

In samples from the two on-farm drains (Herbert and Burdekin regions) and the two creeks (Burdekin region), dieldrin most frequently exceeded the ANZECC guideline "low concentration" (Table 2.18). Additionally, there was a low incidence of γ-HCH and chlordane concentrations in sediments collected from an on-farm drain in the Burdekin region,and Plantation Creek exceeding ANZECC sediment quality guidelines (Table 2.18).

The incidence of sugarcane soils exceeding the DPI and Contaminated Sites guideline values suggest that residual amounts of organochlorine residues, in particular dieldrin, in the soils may cause problems if alternate land uses, such as propagation of root crops or cattle grazing, were considered. Furthermore, other horticultural activities such as peanuts and

Table 2.17. Incidence of organochlorine concentrations in sugarcane soils of the Herbert and Burdekin regions exceeding ANZECC, DPI and DoE guidelines (Source: Tables 2.16, *C.1* and *C.2*)*.

Compound	Incidence / number of samples							
	Burdekin				Herbert			
	ANZECC Low	ANZECC High	DPI	DoE	ANZECC Low	ANZECC High	DPI	DoE
dieldrin	19/25	0/25	0/25	NA	18/18	2/18	2/18	NA
aldrin + dieldrin	NA	NA	NA	0/25	NA	NA	NA	0/18
γ-HCH	10/25	2/25	NA	NA	11/18	9/18	NA	NA
ΣHCH	NA	NA	0/25	NA	NA	NA	9/18	NA
chlordane	10/25	1/25	NA	0/25	1/18	0/18	NA	0/18
p, p'-DDE	3/25	1/25	NA	NA	2/18	0/18	NA	NA
ΣDDTs	3/25	1/25	0	0/25	2/18	0/18	0/18	0/18

*Values indicate the number of observations that exceed the threshold value as a ratio of all observations; NA-not applicable

Table 2.18. Incidence of organochlorine compounds present in sediment samples collected from on-farm drains and creeks draining sugarcane land exceeding ANZECC sediment quality guidelines (Source: Tables 2.8-2.11 and 2.16)*.

Compound	Incidence / number of samples							
	On-farm drain				Creeks			
	Herbert		Burdekin		Plantation Ck		Eight-Mile Ck	
	ANZECC Low	ANZECC High	ANZECC Low	ANZECC High	ANZECC Low	ANZECC High	ANZECC Low	ANZECC High
dieldrin	5/5	0/5	6/6	0/6	6/6	0/6	2/5	0/5
γ-HCH	1/5	0/5	1/6	0/6	2/6	0/6	0/5	0/5
chlordane	0/5	0/5	2/6	1/6	2/6	0/6	0/5	0/5
p, p'-DDE	0/5	0/5	0/6	1/6	0/6	0/6	0/5	1/5
ΣDDTs	0/5	0/5	0/6	0/6	0/6	0/6	1/5	0/5

*Values indicate the number of observations that exceed the threshold value as a ratio of all observations

potato farming have industry-based guidelines, which may be more stringent than the guidelines given above. Peanuts are considered as an alternative crop for sugarcane farming in the Burdekin region. Some farmers in this region indicated their soil had failed industry soil quality guidelines.

The incidence of organochlorine concentrations in sugarcane soils exceeding the ANZECC sediment quality guidelines, in particular dieldrin, suggests that significant erosion of these soils could constitute an environmental threat to aquatic systems. Additionally, the ANZECC sediment quality guidelines for dieldrin were also most frequently exceeded in sediments collected from on-farm drains and creeks receiving sugarcane run-off, suggesting dieldrin is most likely to cause ecological impacts in aquatic systems close to sugarcane land.

There was an absence of detectable organochlorine residues in the coastal sediments, which has important implications for contamination of the outer Great Barrier Reef environment. The coastal sediments of north Queensland are considered to be the first stopping point for terrigenous sediment. However, there is little cross-shelf movement of sediment in the Great Barrier Reef lagoon and the mid-shelf region is generally considered to be starved of terrigenous sediment (Orpin *et al.*, 1999). The most visibly obvious cross-shelf movement is during flood events in which fine clays have been observed to extend into the outer shelf regions of the Great Barrier Reef lagoon (Johnson, 1996; Steven *et al.*, 1996). While the clay and silt size fractions have a considerably higher concentrations of organochlorine residues as compared with the larger sand fractions, the overall contaminant, and sediment, load of these flood plumes is considered to be negligible (Johnson, 1996). The absence of detectable organochlorine insecticide residues in coastal sediments, in combination with known sediment transport processes, suggests that little contamination of the Great Barrier Reef lagoon from historical applications of organochlorine insecticides in the Herbert and Burdekin River regions is occurring.

Global environmental concerns of organochlorine usage arise due to the atmospheric transport of organochlorine compounds from the regions of use to remote regions such as Arctic and Antarctic environments (eg. Muir *et al.*, 1988; Risebrough *et al.*, 1990; Muir *et al.*, 1995). Tropical regions are considered to be the current primary source of organochlorine residues, particularly as organochlorine insecticides are still in use in many developing tropical countries. Additionally, warmer temperatures to enhance volatilisation in these regions (Racke *et al.*, 1997). One study, conducted in India, examined the flux of technical HCH applied to rice paddies indicated that 99.9% of the annual application was lost to the atmosphere (Takeoka *et al.*, 1991). However, incorporation of the insecticide into the soil can significantly reduce the rate of volatilisation. For example, Taylor and Spencer (1990) observed losses of 4% and 7% of surface applied dieldrin and heptachlor, incorporated to a depth of 7.5 cm, over a period of 170 days. In contrast, losses of greater than 90% of surface applied heptachlor over 60 days and 20% of surface applied dieldrin in 50 days were observed in other studies (Willis *et al.*, 1972; Glotfelty, 1981). The immediate burial of insecticides applied in sugarcane farming is likely to have reduced volatilisation losses in comparison with other studies. However, there may still be a small contribution of organochlorine residues

resulting from historical usage in the sugar industry to the global atmospheric loading occurring.

2.5 Conclusions

The present study provides baseline information on the distribution of residues of organochlorine insecticides, which were historically widely used in the sugar industry, in soils and aquatic sediments of the Herbert and Burdekin River regions. Concentrations of organochlorine residues in sugarcane soils reflect historical usage patterns, and application history is suggested to account for the observed variability in surface soil concentrations between and within regions. Insecticide placement, cultivation, volatilisation, leaching, and migration processes are all thought to influence the vertical distribution of organochlorine insecticide residues in the soil profile. Detection of organochlorine residues in on-farm drains and creeks adjacent to sugarcane fields indicates that some movement of organochlorine residues from the sugarcane fields is occurring. However, no detectable organochlorine residue concentrations were found in coastal marine sediments of the Herbert and Burdekin River catchments, implying that the amount lost is not sufficient to counteract degradation and dilution effects. This absence suggests that no detectable organochlorine insecticide contamination of the Great Barrier Reef lagoon would be expected from agricultural activities in these catchments.

Publications

A subset of the surface soil data, and all data relating to the marine sediments formed the basis of the paper by Cavanagh *et al.* (1999; Appendix I.1)

Chapter 3: Where did all the organochlorine insecticides go? A mass balance for the Herbert and Burdekin regions.

3.1 Introduction

The scale and proximity of the sugar industry to the Great Barrier Reef lagoon in both the Herbert and Burdekin regions has given rise to concern regarding the present and past contribution of the industry to contaminant loading of the lagoon and surrounding environment. Organochlorine insecticides are one group of contaminants that are of concern due to their widespread usage in the sugar industry for 40 years until 1987. Regional environmental concerns relate to the amount of contaminants present in run-off from the sugarcane fields and leached into groundwater. Global environmental concerns relate to the amount of organochlorine contaminants volatilised to the atmosphere and transported to cooler temperate and polar regions of the world. The magnitude of transport of organochlorine residues, and the relative contributions of different transport and degradation mechanisms of organochlorine insecticide residues, are foci for assessing environmental impact. The magnitude of organochlorine residue transport is ultimately dependent upon the amount of insecticides applied, while the contribution of different transport or degradation mechanisms to total loss rates is ultimately dependent upon the physico-chemical properties of the different insecticides. Climatic conditions and the mode of application (e.g. surface spray, soil incorporation) will substantially influence the relative contribution of a particular mechanism to the total transport and degradation of organochlorine insecticides.

Despite 40 years of widespread usage of organochlorine insecticides in the Australian sugar industry, surprisingly little information exists on past and present distributions of residues in Queensland in general, and almost no information is available for the Herbert and Burdekin regions. Two relevant studies are those of Brodie *et al.* (1984) and Stickley (1972). Brodie *et al.* (1984) examined the distribution of nutrients and pesticides, including lindane and heptachlor, in groundwaters of the Burdekin Delta region in 1975 and 1976; the study provides the only attempt to relate observed concentrations to known usage. Stickley (1972) examined the persistence of various organochlorine insecticides in field trials in sugarcane soils of the Bundaberg region (~800 km south of the present study area) and provides the only estimates for the persistence of organochlorine insecticides in Queensland soils. Previous studies conducted have generally focussed on the concentration and distribution of organochlorine insecticide residues in the coastal environment (e.g. Russell *et al.*, 1996; Rayment *et al.*, 1997; Hunter *et al.*, 2000), and have not attempted to address relationships

between residue concentration, usage, and effects on biota, nor have they estimated the magnitude of transport from agricultural areas to coastal environments.

A mass balance can provide a useful means to assess the magnitude of organochlorine insecticide losses from contaminated soils by different mechanisms and therefore, provide an assessment of the relative importance of these mechanisms to environmental contamination. In this chapter, Microsoft Excel® spreadsheet models were used to provide a mass balance for the fate of organochlorine insecticides applied in the study areas. These models assessed the relative importance of transport and degradation mechanisms to past and present environmental contamination. Additionally, estimates of the amount of organochlorine insecticide residues remaining in the Herbert and Burdekin regions were calculated from measurements of organochlorine insecticide residue concentrations in soils and aquatic sediments determined in the present study (Chapter 2), and estimates of historical organochlorine insecticide usage in each region.

3.2 Methods

3.2.1 Historical usage

Historical records maintained by the Herbert, Inkerman, Invicta, and Ayr Cane Production Boards provided annual estimates of the area treated for different insect pests with different insecticides. Insecticide usage estimates were determined by multiplying the area treated for different insect pests by the areal application rates used for different insecticides and insect pests. Summing the amount of each insecticide used for different insect pests each year provided estimates of the total annual usage for each insecticide. Information on the application rates was obtained through discussions with staff of the Cane Production Boards and information contained in King *et al.* (1953, 1965) and is shown in Table 3.1. Estimates were made for technical hexachlorocyclohexane (HCH), aldrin, and heptachlor as these insecticides were widely used in the Herbert and Burdekin regions from 1947 until their general banning in 1987. Limited use of technical HCH occurred in the Burdekin region in 1988. The composition of technical HCH used in the Queensland sugar industry was approximately 72% α-HCH, 6% β-HCH, 15% γ-HCH and 7% δ-HCH (Stickley, 1972). These percentages were used to estimate the application of individual HCH isomers. Trans-chlordane was determined to be present in commercial formulation of heptachlor used in the sugar industry at 21% (Stickley, 1971) and was used to estimate the application of trans-chlordane. DDT was occasionally used in the Herbert and Burdekin regions for the control of armyworms. However, the recommendation of the application a "broad band of 2 % DDT a foot or so wide before the marching worms" (Mungomery, 1965) did not enable an appropriate areal application rate to be determined and hence estimates of DDT usage were not made.

Table 3.1. Recommended application rates of organochlorine insecticides used in the Herbert and Burdekin regions for different insect pests (Source: Mungomery, 1965).

Insecticide	Insect	Application rate (kg/ha) active ingredient
Technical HCH	Cane grub*	17.3
α-HCH**		10.5
β-HCH		0.87
γ-HCH		2.19
δ-HCH		1.02
Heptachlor	Cane grub	2.25
Aldrin	Wireworm	0.28
Dieldrin	Cane grub	2.21

*application rates for cane grub control given are those recommended to provide protection for a three year crop cycle.

** application rate of individual HCH isomers is based on a technical HCH composition determined by Stickley (1972).

3.2.2 Estimation of environmental half-lives and loss by different mechanisms

Environmental half-lives and removal of organochlorine insecticides from sugarcane soils by volatilisation, degradation, or run-off were estimated as described below (sections 3.2.2.1, 3.2.2.2). Estimates were made only for organochlorine compounds for which estimates of usage could be made (HCH, aldrin, heptachlor) or derived (dieldrin, heptachlor epoxide, trans-chlordane; sections 3.2.1, 3.2.2.2) and are dependent upon insecticide application frequency and the last year of insecticide application. Estimates of volatilisation losses, degradation and environmental half-lives were made by adjusting these parameters so that predicted soil concentrations matched concentrations determined during soil analyses (Table 3.2; sections 2.3.2 and 2.3.3). Application frequencies of one application every 3 years (Burdekin) or 5 years (Herbert) were used and were based on discussions with farmers and sugar industry personnel regarding cultivation practices conducted in the two regions. Organochlorine insecticides were generally banned from usage in the sugar industry in 1987. This was considered to be the most recent year of last application. The median year of last application and the earliest year of last application were based upon Cane Production Board data (section 3.2.1) and are shown in Table 3.3. Initial estimates were based upon a 1 ha field and assuming regular application since 1948. These estimates were extrapolated to provide estimates of loss on a catchment basis.

Table 3.2. Concentrations (geometric mean, 95% confidence interval) of organochlorine compounds detected in surface (0-10 cm) sugarcane soil in the Burdekin and Herbert regions, and used in model estimates (Source: Table 2.3).

Compound	Concentration (ng g^{-1}) Mean (95% CI)	
	Burdekin region	Herbert region
α-HCH	0.041 (0.023, 0.072)	0.503 (0.065, 3.91)
β-HCH	0.197 (0.036, 1.083)	0.871 (0.069, 11.0)
γ-HCH	0.132 (0.044, 0.394)	0.457 (0.096, 2.17)
δ-HCH	0.023 (0.014, 0.038)	0.209 (0.039, 1.11)
Dieldrin	0.063 (0.021, 0.190)	1.25 (0.269, 5.78)
Heptachlor epoxide	0.283 (0.019, 4.13)	
Trans-chlordane	0.159 (0.023, 1.10)	

Table 3.3. Median and earliest year of last insecticide application in the Herbert and Burdekin regions used in environmental half-life and mechanism model.

Compound	Year of last application			
	Burdekin		*Herbert*	
	Median	*Earliest*	*Median*	*Earliest*
Technical HCH	1984	1980	1985	1983
Aldrin			1985	1983
Heptachlor	1986	1985		

3.2.2.1 Estimates of environmental half-lives

Dissipation of organochlorine compounds from soils occurs by a number of different mechanisms including volatilisation, degradation, migration to sub-surface soil, and run-off. The soil environmental half-life is the time it takes for half of the amount of a compound present in the soil to dissipate. As a first approximation, dissipation of organochlorine insecticide residues from the soil may be considered to follow exponential decay (Ghadiri *et al.*, 1995; Hornsby *et al.*, 1996; Equation 1, below), which can also be expressed in terms of the number of half-lives (Equation 2, below). The half-lives of HCH isomers, aldrin, dieldrin, heptachlor, heptachlor epoxide and trans-chlordane were calculated by substituting values for the half-life into Equation 4 and summing the amount remaining from each year of application (using the application frequencies discussed in section 3.2.2 and application rates from Table 3.2, Equation 3). The amount remaining was expressed as the concentration present in the surface (0-10 cm) soil using a bulk soil density of 1.5 g cm^{-3}. The value of the

half-life was varied until the predicted concentration matched a given organochlorine soil concentration for each compound in the surface soil of each region. Half-lives for heptachlor epoxide and dieldrin were calculated assuming 5 % and 100 % conversion of heptachlor to heptachlor epoxide, and 30 % and 100 % conversion of aldrin to dieldrin based upon work conducted by Stickley (1972).

$$C_t = C_0 e^{-kt} \quad (1)$$

where:

C_t and C_0 are concentrations at time t and t_0, and k is the decay constant.

The half-life, $t_{½}$, is given by $t_{½} = \ln 2/k$. Rearrangement of (1) gives

$$C_t = C_0 \times 0.5^{n½} \quad (2)$$

where:

$n½$ is the number of half-lives, given by $n½ = t\text{-}t_0$ (days)/half-life (days)

$$\sum_{i=1949}^{1997} REM_i = \sum_{i=1949}^{1997} APP_i \times 0.5^{n_i} \quad (3)$$

where:

REM_i = mass of residues remaining in the 0-10 cm soil layer at year *i* (kg)

APP_i = the mass of insecticide applied in year *i* (kg)

n_i = the number of half-lives from year *i* to 1997, the year of surface soil collection; given by:

$$n_i = (1997 - \text{year } i) \times 365/\text{half-life} \quad (4)$$

Estimates of the maximum half-life for an individual compound were calculated using the maximum measured concentration of that compound in the surface soil of each region (Table 3.2) and the earliest year of last application (Table 3.3) in Equation 3. Minimum half-life estimates were made using the lower 95% confidence estimate of the mean surface soil concentration of a particular compound (Table 3.2) and 1987 as the last year of application. Geometric mean organochlorine surface soil concentrations (Table 3.2) and median year of last application (Table 3.3) were used to estimate catchment environmental half-lives. The

upper and lower 95% confidence limits of the geometric mean soil concentration and the median year of last application in each region were used to provide upper and lower bounds of catchment estimates. As application history, including the year of last application for an individual field was not known, application frequency and the year of last application were also varied to examine the influence of these parameters on environmental half-life estimates.

The relative contributions of organochlorine insecticides applied over different time periods (1960, 1960-1969, 1970-1979, and 1980-1988) to current soil concentrations, were calculated by summing the amounts remaining from each time period of application using Equation 3 and the frequencies and rates (Table 3.1; section 3.2.2). Regular application since 1949 was assumed, and the contribution expressed as a percentage of the expected organochlorine concentration present in 1997. The final expected concentration was the geometric mean concentration of individual organochlorine compounds in the surface soil of each region (Table 3.2). This information was used to determine the contribution of organochlorine insecticides applied over different time periods to the total concentration of individual organochlorine compounds remaining in 1997.

Estimates of the time for current concentrations of individual compounds in the soil to fall below detection limits (<0.010 ng g^{-1}) were made using Equation 5.

$$T = -0.6913 \times t_{1/2} (\ln C_0 - \ln C_t) \quad (5)$$

where:

T = time for individual organochlorine concentrations in the soil to fall below detection limits (days)

C_o = detection limit (0.01 ng g^{-1})

C_t = maximum concentration, mean concentration (ng g^{-1}; from Table 2.3)

$t_{1/2}$ = half-life calculated using Equations 3 and 4 (days).

3.2.2.2 Dissipation mechanism model

The conceptual model (Figure 3.1) is indirectly process driven, as the distribution of organochlorine residues in the soil profile is assumed to be a function of the long-term influence of factors affecting dissipation such as volatilisation, soil mixing, degradation, run-off, translocation, and therefore, the physico-chemical properties of individual organochlorine compounds. Microsoft Excel® was used to develop a spread-sheet model and a

diskette containing the model is included in a pocket at the back of this thesis with example calculations for individual field and catchment based calculations shown in Appendix *D*.

The model considers the soil profile as having a mixed layer and an undisturbed layer. In the mixed layer applied insecticides are mechanically mixed by cultivation practices. A mixed layer of 30 cm was used in model calculations, based on discussion with sugar industry personnel. The undisturbed layer of the soil profile has not been disturbed by cultivation processes, but may contain significant amounts of organochlorine residues due to the combined processes of leaching (dissolution in soil water and movement down the profile) and translocation (transport down the soil profile by adsorption on colloidal materials). An undisturbed layer 30-70 cm thick was used in model calculations, based on soil core analyses which showed that generally less than 5 % of the total amount of organochlorine compounds present in the top 70 cm of the soil profile were found at 60-70 cm (Table 2.6).

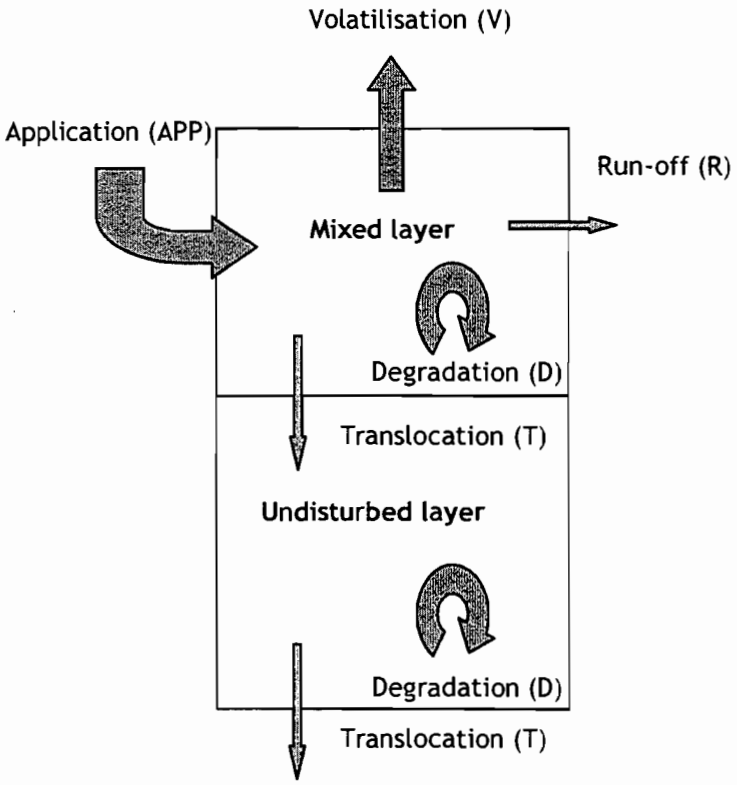


Figure 3.1. Conceptual structure of the dissipation mechanism model.

Dissipation by different mechanisms were calculated on an annual basis and assumed to represent the long-term average transport rates or losses by all degradation processes. In the dissipation mechanism model, degradation includes microbial decomposition, photochemical decomposition and chemical transformation (e.g. hydrolysis) of the organochlorine insecticides and is assumed to be constant throughout the soil profile. Degradation losses were assumed to follow exponential decay with the number of half-lives calculated as the

number in one year (Equation 7). Volatilisation is the loss of organochlorine residues to the atmosphere. Run-off loss is the off-field movement of organochlorine residues dissolved in water, or adsorbed on soil particles that are ultimately deposited in coastal sediments. Translocation loss is the movement of organochlorine residues from the mixed layer to the undisturbed layer, and also from the undisturbed layer, by adsorption on colloidal material or dissolution in soil water. The annual volatilisation, translocation and run-off losses were expressed as a percentage of the cumulative amount remaining in the mixed layer to reflect concentration dependent loss.

Volatilisation, degradation, run-off and translocation all reduce the amount of individual organochlorine compounds in the mixed layer (Equation 6). Degradation and continued translocation to ground-water reduce the amount remaining in the undisturbed layer (Equation 8).

$$\sum_{i=1949}^{1997} REM_i = \sum_{i=1949}^{1997} (CUM_i - CUM_i V - CUM_i T - CUM_i R - D_i) \quad (6)$$

where:

REM_i = residual mass of insecticide remaining in the mixed soil layer at year i (kg)

APP_i = mass of insecticides applied in year i (kg)

CUM_i = cumulative mass of insecticide given by, $CUM_i = APP_i + REM_{i-1}$ (kg)

V = percentage annual volatilisation loss (% $year^{-1}$)

T = percentage annual translocation loss (% $year^{-1}$)

R = percentage annual run-off loss (% $year^{-1}$)

D_i = degradation loss, given by:

$$D_i = CUM_i - CUM_i \times 0.5^{n_i} \quad (7)$$

and n_i = 365/half-life (days)

$$\sum_{i=1949}^{1997} REMTr_i = \sum_{i=1949}^{1997} (CUM_i M \times 0.5^{n_i}) - (CUM_i M \times 0.5^{n_i}) M \quad (8)$$

where:

$REMTr_i$ = amount remaining in the undisturbed layer at year i (kg)

Concentrations of organochlorine compounds in the mixed and undisturbed layers were calculated assuming homogenous distribution of compounds in each layer and a soil bulk density of 1.5 g cm^{-3}. These predicted concentrations were used to adjust degradation half-lives or volatilisation losses such that predicted concentrations matched the average concentration in the mixed and undisturbed layers in "typical" soil profiles.

"Typical" soil profiles were generated by interpolation of the distribution of organochlorine compounds in soil cores collected from the Burdekin (cores SC and HC) and Herbert (cores VC and LC) regions (sections 2.2.1.2, 2.3.3) expressed as a percentage of the surface soil concentrations (*Table E.1*), with the geometric mean surface soil concentrations (Table 3.2). The upper 95% confidence limit of the estimate of the geometric mean surface soil concentration and soil cores which gave the highest total amount of organochlorine residues (core VC in Herbert region and core HC in the Burdekin region), were used to provide estimates of the maximum amount remaining in the soil profile in each region. Estimates of the minimum amount of organochlorine residues remaining in the soil profile of each region were generated using the lower 95% confidence limit of the estimate of the geometric mean surface soil concentration and soil cores that gave the lowest total amount of organochlorine residues (core LC in the Herbert region and core SC in the Burdekin region. Values for the mixed and undisturbed layers were calculated by averaging the soil concentration in the mixed layer (0-30 cm) and undisturbed layer (30-70 cm depth) (Tables 3.4a and b).

Table 3.4a. Mean, upper, and lower estimates of organochlorine residue concentrations present in the mixed layer and the undisturbed layer generated by interpolation of soil core profiles (HC and SC) in the Burdekin region.

Compound	Layer	Concentration (ng g^{-1})		
		Mean HC	Mean SC	Range
α-HCH	Mixed	0.055	0.018	0.011-0.097
	Undisturbed	0.018	0.003	0.002-0.033
β-HCH	Mixed	0.107	0.107	0.019-0.580
	Undisturbed	0.026	0.017	0.003-0.141
γ-HCH	Mixed	0.093	0.070	0.023-0.279
	Undisturbed	0.022	0.010	0.004-0.067
δ-HCH	Mixed	0.020	0.011	0.023-0.342
	Undisturbed	0.007	0.001	0.004-0.123
Heptachlor epoxide	Mixed	0.189	0.126	0.011-2.75
	Undisturbed	0.032	0.002	0.001-0.476
Trans-chlordane	Mixed	0.193	0.081	0.009-1.32
	Undisturbed	0.060	0.005	0.001-0.411

Table 3.4b. Mean, upper and lower estimates of organochlorine residue concentrations present in the mixed layer and the undisturbed layer generated by interpolation of soil core profiles (VC and LC) in the Herbert region.

Compound	Depth	Concentration (ng g^{-1})		
		Mean VC	Mean LC	Min, Max
α-HCH	Mixed	0.548	0.306	0.039-4.26
	Undisturbed	0.736	0.049	0.006-5.72
β-HCH	Mixed	1.01	0.493	0.039-12.7
	Undisturbed	1.47	0.079	0.006-18.6
γ-HCH	Mixed	0.490	0.281	0.059-2.33
	Undisturbed	0.630	0.048	0.010-2.99
δ-HCH	Mixed	0.252	0.141	0.026-1.34
	Undisturbed	0.38	0.027	0.005-2.03
dieldrin	Mixed	1.03	0.651	0.140-4.78
	Undisturbed	0.87	0.027	0.006-4.04

Volatilisation and/or microbial degradation are generally considered to be the major mechanisms of dissipation of insecticides from soils (e.g. Taylor and Spencer, 1990; Racke *et al.*, 1997). As no information was collected during the present study to enable apportionment of volatilisation or degradation, estimates of volatilisation rates were calculated assuming that negligible degradation occurred. Similarly, degradation rates were calculated assuming negligible volatilisation occurred. Under these conditions the rate of volatilisation and degradation (expressed as a percent of the cumulative amount of residues remaining per year) are maximum values and are the same. To provide a more useful illustration of the differences in degradation rates of different compounds, degradation rates are expressed in terms of the estimated half-life for individual compounds.

Transport of organochlorine insecticides in run-off from agricultural fields is generally considered to constitute no more than 5% of the annual application and generally between 0.1%-1% (Wauchope, 1978). A run-off loss of 0.5% was selected as an average value and used in most model calculations. Run-off losses were also varied in the calculations to examine the effect of run-off on estimates of degradation and volatilisation rates.

Regional degradation half-lives and volatilisation rates were determined using soil core profiles generated by interpolation of the geometric mean surface soil concentration with the distribution of organochlorine residues in soil cores expressed as a percentage of the surface soil concentration (Table 3.4a and b) and the median year of last application (Table 3.3). The maximum degradation half-life and minimum volatilisation losses for each organochlorine compound were calculated using the earliest last year of application and the interpolated soil

profile that gave the maximum amount of organochlorine residues remaining in the profile. The minimum degradation half-lives and maximum volatilisation losses were calculated using 1987 as the year of last application and the interpolated soil profile that gave the minimum amount of organochlorine residues. The effect of assuming a different year of last application on estimates of degradation half-lives and volatilisation losses was also assessed.

The mean, maximum, and minimum estimates of degradation half-lives and volatilisation losses were used to determine annual and total losses of applied insecticides by degradation or volatilisation from each region. Additionally, as the majority of sediment in the coastal area of each region is derived from soil eroded from the respective catchments, the influence of riverine sediment loads, run-off rates, and degradation rates on the concentration of organochlorine residues in the coastal sediment were examined. Estimates of organochlorine insecticide residue concentrations in coastal sediments were calculated using different run-off rates and assuming different degradation rates and river sediment loads. Estimates of the average annual sediment load for the Herbert River range from 0.55×10^9 kg to 1.43×10^9 kg (Moss *et al.*, 1992; Belperio, 1983, respectively) and 2.8×10^9 kg to 8.6×10^9 kg for the Burdekin River (Moss *et al.*, 1992; Neil and Yu, 1996, respectively).

3.2.3 Estimates of the amount of organochlorine residues remaining in the sugarcane soils

Estimates of the amount of individual organochlorine compounds remaining in the sugarcane soils of the Herbert and Burdekin regions were calculated by the environmental half-life and dissipation mechanism models, measured soil core and surface soil concentrations, and the area treated with individual organochlorine insecticides. The estimates were compared to assess the agreement between the different models.

The environmental half-life model provided estimates of the amount of organochlorine residues remaining in the sugarcane soils of each region by using the estimated catchment half-life of each compound (section 3.2.2.1), and the estimated annual application of each compound in each region (section 3.2.1).

The loss mechanism model provided estimates of the amount of individual organochlorine residues remaining in the sugarcane soils of each region by using the maximum, minimum, and mean estimates of degradation half-lives and volatilisation losses calculated for an individual field (section 3.2.2.2) and the estimated application of each organochlorine compound in each region (section 3.2.1).

A soil bulk density of 1.5 g cm^3 and interpolated soil core profiles (section 3.2.2.2) were used to provide the depth-integrated concentration of individual organochlorine compounds (Equation 9). Regional values were calculated using the geometric mean concentrations of

organochlorine compounds in soil cores collected from each region. The upper and lower limits of the amount remaining in a region were calculated using the upper and lower 95% confidence limits of the geometric mean surface soil concentration of organochlorine residues and interpolation of the soil core profile that gave the highest and lowest estimate of total organochlorine concentration ($\mu g\ kg^{-1}$) per m^2 in each region (Tables 3.4 a and b; Equation 9).

$$OC_a = \sum_{0}^{0.7} (OC \times DEP \times SOILD) \qquad (9)$$

where:

OC_a = mass of individual organochlorine compounds ($kg\ m^{-2}$)

OC = concentration of individual organochlorine compounds in each core slice ($\mu g\ kg^{-1}$)

DEP = thickness of core slice (0.1 m)

SOILD = bulk soil density ($1500\ kg\ m^{-3}$)

Regional estimates of masses of organochlorine compounds remaining in the soil were calculated using Equation 10. The area treated with insecticides was generally a small proportion of the total area of sugarcane in a region and was confined to selected areas within a region. Despite the increasing area of sugarcane, the area treated annually with insecticides has fluctuated around a constant value (Figures 1.9 and 1.11). Constant areas of application of 10,000 ha for technical HCH, heptachlor, heptachlor epoxide and the chlordanes in the Burdekin region and 12,000 ha for technical HCH and 15,000 ha for aldrin and dieldrin in the Herbert region were used in Equation 10. These areas were based upon the areas treated with insecticides from Cane Production Board data and discussions with Cane Production Board staff.

$$TOT = OC_a \times A_a \qquad (10)$$

where:

TOT= total amount of individual organochlorine compounds remaining in a region

A_a= area of application of organochlorine insecticides (ha)

Estimates of the amount of soil that would need to be eroded from each region in order for detectable concentrations of organochlorine residues to be found in coastal sediments were made using Equation 11. These estimates were expressed on an areal basis using the estimated area of application discussed above.

$$ES = (DL \times S) / (OC \times A_a) \quad (11)$$

where:

ES = amount of soil eroded from sugarcane land (tonne yr^{-1} ha^{-1})

DL = instrument detection limit (0.01 ng g^{-1})

S = annual sediment load (tonne)

OC = geometric mean concentration of individual organochlorine compounds in surface soils of each region (ng g^{-1})

A_a = area of application of organochlorine insecticides (ha)

3.3 Results and Discussion

3.3.1 Historical usage

Estimates of annual and cumulative usage of technical HCH, heptachlor and aldrin in the Burdekin and Herbert regions are shown in Figures 3.2 and 3.3, with the total amounts applied over the period 1949-1987 shown in Table 3.5. Estimates for technical HCH and aldrin usage in the Herbert region agreed with those compiled by Johnson and Ebert (2000) who had also collected chemical sales data for the region. This provided confidence in the estimation techniques for the Burdekin region, for which no cross-check was available. Technical HCH usage in the Burdekin region is likely to be slightly overestimated as, prior to 1969, no distinction of the area treated with different insecticides to control cane grubs was made. Aldrin and lindane were used for cane grub control prior to this time in the Burdekin region. For example, 1,830 ha were treated with lindane in 1961 and 2,830 ha were treated with aldrin in 1962 (Wilson *et al.*, 1962). Additionally, lindane was also used after 1969. However, the area treated with lindane was included with the area treated with technical HCH.

For the reasons described in section 3.2.1, no estimates were made of DDT usage. DDT was used for army-worm control in the Herbert region with up to 3,200 ha being treated annually between 1961 and 1969 (Figure 1.9). Up to 300 ha were treated annually in the Burdekin region over this same time period (Figure 1.12).

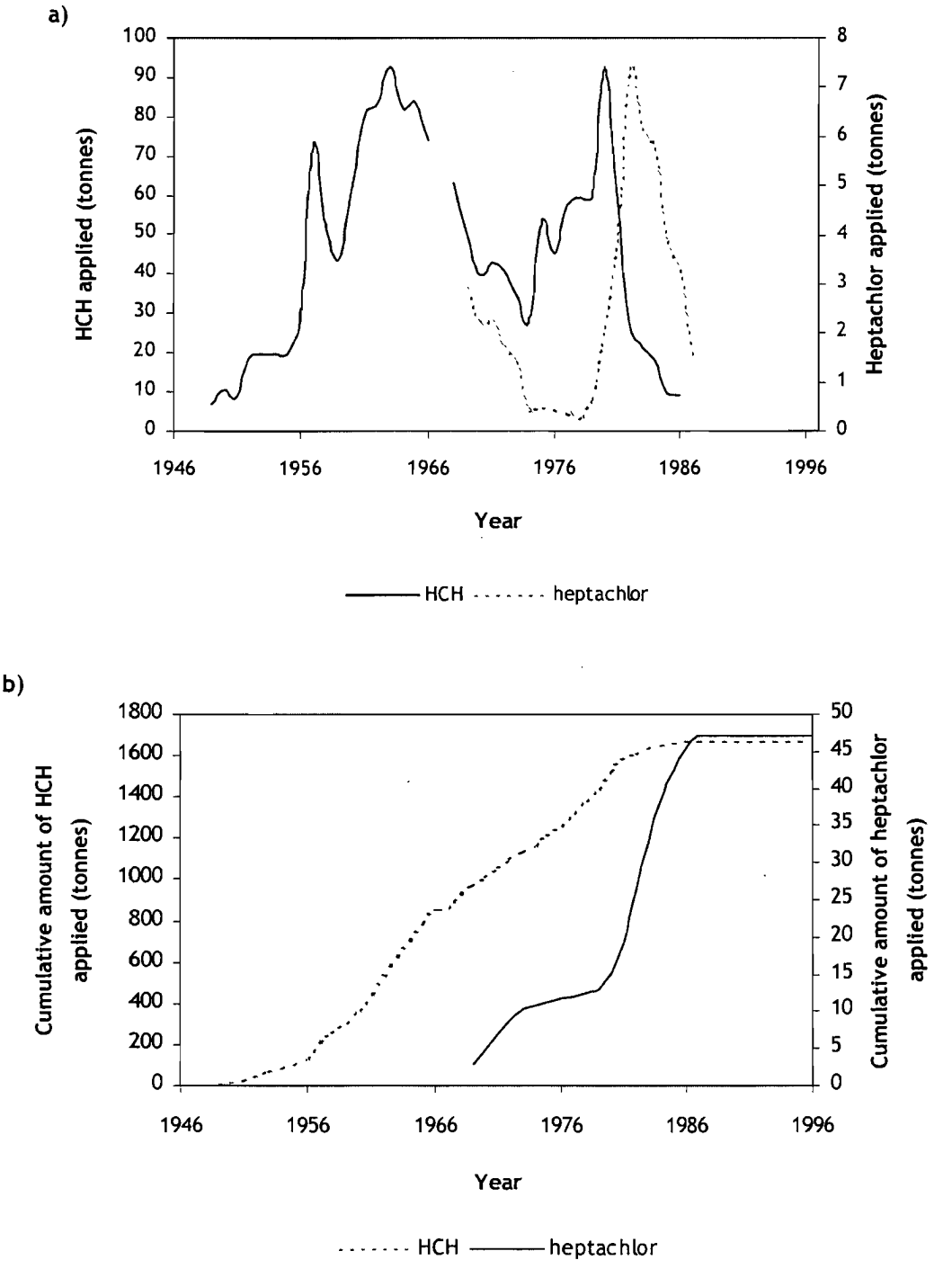


Figure 3.2. Application of technical HCH and heptachlor in the Burdekin region over the period of 1949-1997: a) annual amount, and b) cumulative amount. Note: usage was banned in 1987.

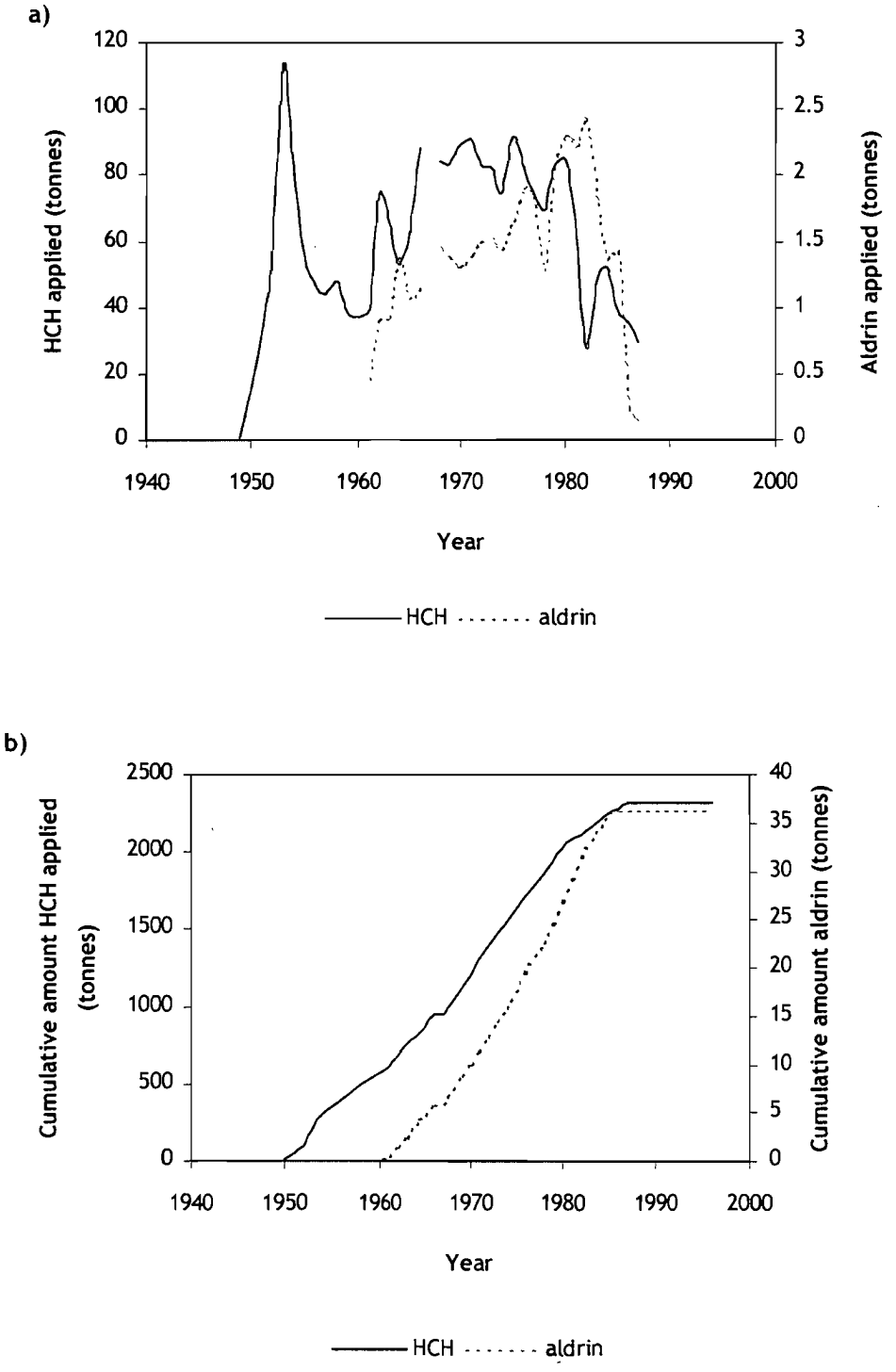


Figure 3.3. Application of technical HCH and aldrin in the Herbert region over 1949-1996: a) annual application, and b) cumulative application. Note: usage was banned in 1987.

Table 3.5. Estimates of the total amount of organochlorine insecticides applied in the Herbert and Burdekin Regions over the period 1949-1988.

Compound	Amount applied (tonnes)			Estimated global production/use (tonnes)
	Herbert	*Burdekin*	*Total*	
HCH	2264	1671	3975	$10 \times 10^{6*}$
α-HCH	1630	1203	2833	$7 \times 10^{6**}$
β-HCH	136	100	236	$0.7 \times 10^{6**}$
γ-HCH	340	250	590	$1.3 \times 10^{6**}$
δ-HCH	158	116	274	$1 \times 10^{6**}$
aldrin	37.7	2.4	40.1	$0.24 \times 10^{6\#}$
dieldrin	-	0.32	0.32	$0.24 \times 10^{6\#}$
heptachlor	0.39	45.5	45.9	No data$^{\#}$
DDT				$2.8\text{-}3 \times 10^{6\#}$

*Estimated use (Li, 1999)

** derived from Li (1999) assuming the composition of technical HCH as 70% a-HCH, 7% b-HCH, 13% g-HCH, 10% d-HCH

#Estimated production (Cooney, 1999)

On a global scale, sugarcane farming in the Herbert and Burdekin regions together have used approximately 0.04% of the estimated 10 million tonnes of technical HCH used worldwide from 1940-1990 (Li, 1999) and 0.02% of the estimated 0.24 million tonnes of aldrin produced since 1950 (Cooney, 1999). Estimates of global production of heptachlor are not available. Although estimates of DDT use in the Herbert and Burdekin regions were not made, given the infrequent use of DDT in sugarcane farming and the considerable global usage, it is unlikely that sugarcane farming in the Herbert and Burdekin regions would have contributed significantly to the global usage of DDT.

Sugarcane farming in the Herbert and Burdekin regions comprised approximately 25% of the total area of sugarcane farming in Queensland over the period of organochlorine insecticide usage. If it is assumed that insecticide usage in the Herbert and Burdekin regions is typical of other sugarcane growing regions in Queensland, insecticide usage by the entire Queensland sugar industry can be made. Using this extrapolation, approximately 16,000 tonnes, or 0.2 % of the global usage of technical HCH, and approximately 160 tonnes, or 0.08 % of the global production of aldrin, was used by the Queensland sugar industry since 1949. However, given regional differences in the distribution and importance of different insect pests, it is unlikely that the assumption that insecticide usage in the Herbert and Burdekin regions is typical of other sugarcane growing regions is correct (Agnew, 1997). Nonetheless, these estimates

indicate the order of magnitude of technical HCH and aldrin usage in the Queensland sugar industry compared with the scale of global usage.

3.3.2 Environmental half-lives

3.3.2.1 Effect of application frequency and year of application

Varying the frequency of insecticide application did not significantly alter environmental half-life estimates for α-HCH and β-HCH applied in the Herbert region (Figure 3.4). However, changing the year of last insecticide application from 1987 to 1983 resulted in increasing the estimated half-life of α-HCH from 226 to 316 days and the half-life of β-HCH from 325 to 451 days (Figure 3.4), indicating the importance of the year of last application to model estimates. These trends were typical of half-life estimates of other compounds.

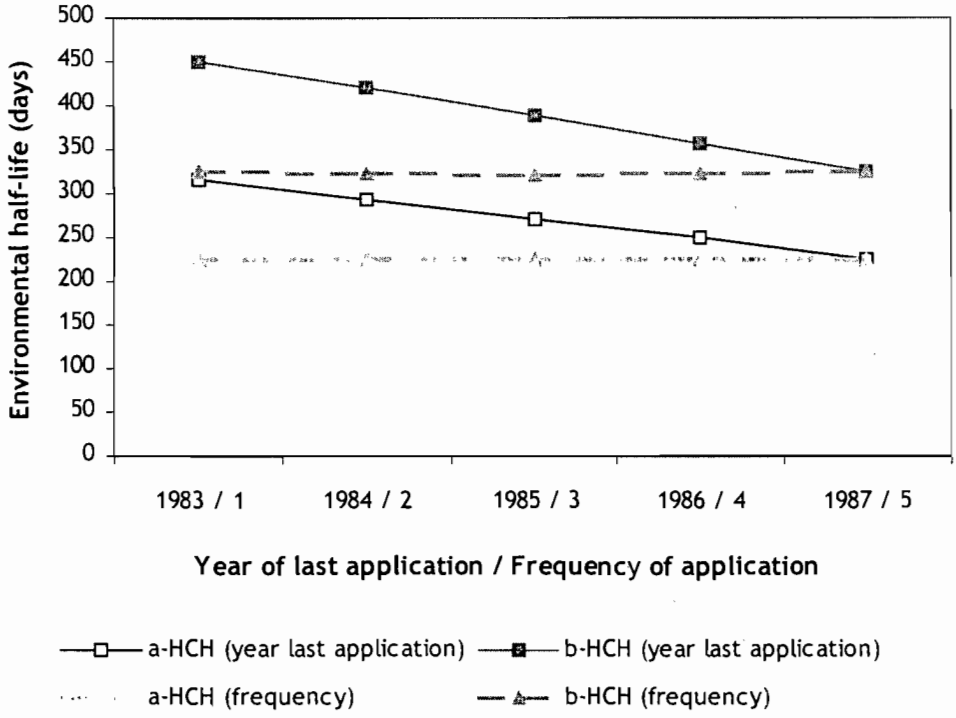


Figure 3.4. Effect of varying the year of last application and frequency of application on environmental half-life estimates (Equation 3). Note: "Frequency of application" refers to the number of years between applications e.g. a frequency of 3 refers to one application every three years.

3.3.2.2 Environmental half-life estimates

Maximum, minimum, and regional environmental half-life estimates for individual organochlorine compounds calculated using Equation 3 are shown in Table 3.6. These half-lives generally lie within the estimates obtained from the literature for γ-HCH, dieldrin,

heptachlor and trans-chlordane (Table 1.2). No information is available on half-life estimates of α–HCH, β–HCH, δ -HCH, and heptachlor epoxide. However, environmental half-lives are highly dependent upon climatic and local conditions (as reflected by the broad range of literature estimates). The only comparable information available for persistence of organochlorine insecticides in the Queensland environment is that of Stickley (1972) who investigated the persistence of the HCH isomers, aldrin, dieldrin, heptachlor and, heptachlor epoxide in soils from the Bundaberg region (Table 3.7).

Table 3.6. Estimated mean, minimum, and maximum catchment half-lives and maximum environmental half-lives of organochlorine insecticides applied to individual fields in the Herbert and Burdekin regions (Section 3.2.2.2).

Compound	Environmental half-lives (days)			
	Burdekin		*Herbert*	
	Catchment half-life (95% CI)	*Max*	*Catchment half-life (95% CI)*	*Max*
α-HCH	229 (220, 239)	372	256 (217, 310)	378
β-HCH	318 (271, 376)	574	344 (287, 479)	729
γ-HCH	282 (258, 310)	463	292 (245, 344)	429
δ-HCH	260 (251, 271)	486	278 (243, 325)	413
dieldrin (100% conversion)			398 (330, 501)	797
dieldrin (30% conversion)			474 (378, 620)	1050
heptachlor epoxide (100%)	255 (205, 335)	439		
heptachlor epoxide (5%)	348 (262, 510)	730		
trans-chlordane	257 (217, 312)	446		

Table 3.7. Half-lives of organochlorine insecticides in soils of the Bundaberg region from Stickley (1972).

Compound	Half-life (days)	
	Mean	Min, Max
dieldrin	1260	840,1800
γ-HCH, in BHC	270	210, 360
aldrin + dieldrin	240	240
γ-HCH, as lindane	180	60, 210
heptachlor + heptachlor epoxide	180	60, 270
heptachlor only	90	60, 150
aldrin only	60	30, 120

The half-lives calculated in the present study are generally longer than those estimated by Stickley (1972), with the exception of that calculated for dieldrin. The shorter half-life of dieldrin calculated in the present study may be attributed to a lower actual application rate due to a smaller proportion of applied aldrin being converted to dieldrin, or to soil-specific differences (section 1.2.2). The increased calculated half-lives are possibly explained by previous observations that compounds exhibit increasing persistence as more readily dissipated fractions are lost (e.g. residues on soil surfaces; Hornsby *et al.*, 1996). The processes that lead to increased persistence include stronger binding to soil organic matter over time (Ghadiri *et al.*, 1995; Cornelisson *et al.*, 2000), entrapment within soil organic matter, diffusion into spatially remote areas such as soil micro and macro-pores (Gevao *et al.*, 2000). As organochlorine insecticides have not been applied in the Herbert and Burdekin regions for more than 10 years, the estimates of environmental half-lives provided here are likely to reflect long-term half-lives of these compounds.

Using the environmental half-lives shown in Table 3.6, the time for the highest concentrations of organochlorine residues measured in 1997 to reach undetectable concentrations in soil can be estimated (Table 3.8). Generally, this was in the order of 5-11 years for organochlorine compounds present in the Herbert region and 4-8 years in the Burdekin region.

Table 3.8. Estimated time for maximum concentrations of individual organochlorine compounds measured in 1997 to fall below detection limits using mean and maximum half-lives (Source: Equation 5; Tables 3.2 and 3.6).

Compound	Time (year)			
	Burdekin		*Herbert*	
	mean	max	mean	max
α-HCH	1.9	3.0	3.1	4.6
β-HCH	5.3	9.7	5.5	11.6
γ-HCH	2.7	4.5	3.3	4.9
δ-HCH	2.4	4.5	3.1	4.9
dieldrin (100% conversion)			6.0	12.0
dieldrin (30% conversion)			7.1	15.8
heptachlor epoxide (100%)	3.0	6.2		
heptachlor epoxide (5%)	4.8	10.4		
trans-chlordane	3.4	5.8		

The model calculations indicated that organochlorine residues derived from insecticide application during the 1980's contributed more than 98% of the observed insecticide concentration in the soil. The relative contribution of α-HCH and β-HCH applied over different time periods to current concentrations of α-HCH and β-HCH present in the surface soils of the Herbert region in 1997 are shown as an example (Table 3.9).

Table 3.9. The contribution of α-HCH and β-HCH, applied over different time periods, to 1997 surface soil concentrations in the Herbert Region assuming a year of last application of 1987 and 1983, expressed as a percentage of the 1997 surface soil concentrations (Source: Equation 3, section 3.2.2.1).

Application period	Contribution to surface soil concentrations in 1997			
	α-HCH		*β-HCH*	
	1987	1983	1987	1983
pre-1960	<0.001	<0.001	<0.001	<0.001
1960-1969	0.001	<0.001	<0.001	0.01
1970-1979	0.04	0.40	0.40	1.9
1980-1987	99.96	99.6	99.6	98.1

3.3.3 Estimates of degradation and transport by different mechanisms

3.3.3.1 Effects of run-off rate and last year of application

Increasing the run-off rate up to 1% of the amount of α-HCH remaining in sugarcane soils did not change maximum degradation half-life and volatilisation estimates significantly (Table 3.10). However, above a 1% annual loss, a greater increase in degradation half-life estimates and a decrease in volatilisation estimates was calculated. The estimated degradation half-life increased, while the volatilisation rate decreased as the year of last application became earlier (Table 3.10).

Table 3.10. Influence of varying the last year of application and run-off rate on estimates of degradation half-lives and maximum volatilisation rates of α-HCH applied in the Herbert region.

Run-off rate (%)/Year of last application	Degradation half-life	Volatilisation loss (%)
Run-off rate		
0.25	352	56
0.5	353	56
1	357	55
5	396	51
10	454	46
Year of last application		
1987	353	56
1986	384	53
1985	415	50
1984	445	47
1983	476	44

3.3.3.2 Estimates of degradation half-lives and volatilisation losses

The mean estimated degradation half-lives and volatilisation losses are shown in Table 3.11. The order of the calculated volatilisation rates from the Herbert region followed the order of the vapour pressure of the individual compounds and may suggest that loss of organochlorine residues from the Herbert sugarcane soils was primarily dependent upon volatilisation. The order of vapour pressures was α-HCH > γ-HCH > δ-HCH > chlordane > β-HCH> dieldrin (Table 1.2; Mackay *et al.*, 1997) although, the vapour pressure of γ-HCH, δ-HCH and chlordane are close.

Table 3.11. Estimates of degradation half-lives and translocation losses under conditions of negligible volatilization losses, and estimates of maximum volatilisation losses assuming negligible degradation losses (Source: Dissipation model and Table 3.4).

Compound	Degradation half-life (days)		Translocation*	Volatilisation (% yr^{-1})	
	Mean	Min, max		Mean	Min, max
Burdekin region					
α-HCH	264, 293	201, 390	1.3, 2.2	60, 63	49.6, 73
β-HCH	375, 382	255, 581	1.2, 1.9	50.3, 50.5	36.8, 64.5
γ-HCH	332, 344	240, 485	1.3, 1.8	53.8, 54.7	42.1, 66.6
δ-HCH	299, 328	236, 549	0.7, 2.4	56, 57.9	39, 66.7
Heptachlor epoxide	290, 313	220, 452	0.2, 1.6	57, 58.3	44.1, 69.5
5% conversion	400, 440	284, 721	0.2, 1.5	45.2, 47	30.9, 59.3
Chlordane	327, 336	232, 468	0.6, 1.5	54.5, 55.9	44.3, 67.6
Herbert region					
α-HCH	307, 383	221, 567	1.3, 7.2	55.5, 57.4	43.4-69.6
β-HCH	418, 590	272, 1140	1.4, 9.0	43.4, 46.8	29-62.1
γ-HCH	355, 451	261, 647	1.4, 7.4	50.2, 52.3	39.9-61.2
δ-HCH	359, 473	261, 700	1.5, 8.5	50, 52.1	39-63.9
dieldrin	488, 640	340, 985	0.4, 6.0	38.7, 40.8	28.2-52.9
30% conversion	588, 812	396, 1340	0.4, 6.0	33.1, 35.3	22.3 , 47.6

*Translocation estimates shown are those for mean degradation half-lives. Under conditions of maximum volatilization and negligible degradation losses, translocation losses were <0.02%.

In the Burdekin region, loss of the HCH isomers (Table 3.11) generally followed that of the literature values for their vapour pressures (Table 1.1). The limited vapour pressure estimates for heptachlor epoxide available in the literature range from 2.6×10^{-4} to 4.5×10^{-2} Pa (from four measurements; Mackay *et al.*, 1997). If the lower value is accepted, then the vapour pressure of heptachlor epoxide is less than chlordane and greater than β-HCH (Table 1.2). However, the calculated rates of volatilisation loss of heptachlor epoxide and trans-chlordane are generally less than that of β-HCH, which is the opposite to that expected from the vapour pressures. This may indicate that degradation processes are more important in the loss of heptachlor epoxide and trans-chlordane from the Burdekin soils.

The estimated annual volatilisation losses suggest comparable losses to the atmosphere of 0.2-5.9 kg ha^{-1} yr^{-1} for α-HCH, 0.1-1.1 kg ha^{-1} yr^{-1} for γ-HCH and 0.01-0.14 kg ha^{-1} yr^{-1} for dieldrin (assuming 100% conversion of aldrin to dieldrin) applied in the Herbert region (Table 3.12). Losses in the Burdekin region were slightly higher for individual HCH isomers (0.08-6.5

kg ha^{-1} yr^{-1}) while losses of heptachlor epoxide and trans-chlordane were estimated to be in the order of 0.2 -1.5 kg ha^{-1} yr^{-1} and 0.01-0.06 kg ha^{-1} yr^{-1} respectively. Spencer and Cliath (1973) observed volatilisation rates equivalent to 9.5 - 26 kg ha^{-1} yr^{-1} for lindane, and 0.4-2.6 kg ha^{-1} yr^{-1} for dieldrin, 30 days after their incorporation in the soil during laboratory trials. Caro and Taylor (1971) observed volatilisation losses equivalent to 0.45 kg ha^{-1} yr^{-1} and 0.62 kg ha^{-1} yr^{-1} of dieldrin and heptachlor applied at a rate of 5.6 kg ha^{-1} and incorporated into the soil to a depth of 7.6 cm in corn fields in Ohio. With the exception of α-HCH, lindane and dieldrin span the vapour pressure range of the organochlorine compounds applied in the Herbert and Burdekin regions. As the maximum volatilisation losses calculated in the present study were lower than the values observed by Spencer and Cliath (1973), the calculated volatilisation estimates are thought to be realistic, which may indicate that volatilisation is the dominant mechanism of dissipation of organochlorine insecticide residues from the sugarcane soils.

Table 3.12. Estimates of annual amounts of individual organochlorine compounds volatilised from a 1 ha field in the Herbert and Burdekin regions since 1948 to present day (Source: Dissipation Model).

Compound	Volatilisation losses	
	Burdekin (*kg yr^{-1}*)	*Herbert* (*kg yr^{-1}*)
α-HCH	0.96-6.5	0.1-5.9
β-HCH	0.08-0.54	0.03-0.40
γ-HCH	0.18-0.68	0.06-1.1
δ-HCH	0.08-0.68	0.03-0.52
dieldrin		0.007-0.14
heptachlor epoxide	0.18-1.5	
trans-chlordane	0.01-0.06	

3.3.4 Regional Perspective

3.3.4.1 Organochlorine insecticide residue masses

Estimates of the amount of individual organochlorine insecticide residues remaining in the sugarcane soils of the Herbert and Burdekin regions calculated by the different models generally agreed within an order of magnitude (Table 3.13). Estimates calculated by the environmental half-life model and dissipation mechanism model were lower than those calculated using soil concentration and area of application data (Equation 9). The latter were dependent upon the soil profile used and varied widely (as demonstrated by the estimates derived for the Herbert region; Table 3.13). Thus, estimates of the amount of organochlorine compounds remaining in each region may be refined by the analysis of additional soil cores.

The sugarcane soils of the Herbert region were estimated to contain higher amounts of organochlorine residues than those of the Burdekin region, which probably reflects the greater quantity of insecticides applied in the Herbert region (Tables 3.5). Generally less than 0.1% of the amount of the different organochlorine compounds applied is estimated to remain in each region in 1997 (Table 3.13).

Table 3.13. Estimates of the amount of selected organochlorine residues present in the sugarcane soils of the Burdekin and Herbert regions in 1997, as calculated using the environmental half life model, dissipation model and soil concentration data (Source: Dissipation model, Table 3.2, section 3.2.3).

Compound	Amount remaining (kg)				
	Environmental half-life model		*Dissipation model*	*Soil concentration data*	
	Mean	Min, Max	Mean*	Mean*	Min, Max
Burdekin region					
α-HCH	0.10	0.06, 0.20	0.11, 0.28	1.0, 3.6	0.60, 6.4
β-HCH	0.29	0.06, 1.3	0.40, 0.41	5.8, 6.3	5.8, 34
γ-HCH	0.22	0.08, 0.60	0.30, 0.38	3.9, 5.5	1.3, 17
δ-HCH	0.04	0.03, 0.07	0.05, 0.09	0.60, 1.4	0.20, 2.3
heptachlor epoxide	0.18	0.01, 2.7	0.24, 0.37	5.8, 11	0.40, 40.6
trans-chlordane	0.10	0.01, 0.7	0.36, 0.37	3.9, 12	0.30, 84.4
Herbert Region					
α-HCH	1.9	0.30, 12.5	3.0, 5.2	20, 100	2.5, 800
β-HCH	2.5	0.50, 27.5	3.9, 5.1	32, 200	2.5, 2500
γ-HCH	1.5	0.40, 6.4	2.4, 4.2	18, 89	3.9, 46
δ-HCH	0.70	0.20, 3.2	1.2, 2.1	9.0, 51	1.8, 270
dieldrin	2.1	0.40, 11.3	4.6, 7.7	37, 640	8.0, 690

*two values are given as these estimates are based on data of each soil core from each region.

3.3.4.2 Volatilisation losses

Under conditions of maximum volatilisation losses, the estimated annual losses in the Herbert and Burdekin regions are of the order 0.4-63 tonnes for α-HCH, 0.02-13 tonnes for the other HCH isomers, and 0.2-5.6 tonnes for heptachlor epoxide and trans-chlordane (Table 3.13). Estimates of Wania and Mackay (1995) for the area and atmospheric height of the Southern Hemisphere tropical climatic zone, allows calculation of a volume of 1.73×10^{18} m^3 for the atmosphere in this zone. If the calculated maximum annual volatilisation of α-HCH (63 tonnes) were released into this environment, a concentration of 40 pg m^{-3} would be observed. This is considerably greater than what has been observed in two previous studies of atmospheric concentrations of HCH isomers in air over the Western Pacific Ocean, within

latitudes 0^0-20^0S. One study found the total concentration of HCH isomers to be less than 5 pg m^{-3} in 1980-1981 (Tatsukawa *et al.*, 1990), while the other study detected concentrations of α-HCH and γ-HCH of approximately 10 pg m^{-3} and 5 pg m^{-3} in 1987 (Kurtz and Atlas, 1990).

The maximum regional annual volatilisation of technical HCH, assuming no loss by degradation, is estimated, by the present study, to be 52 % of the cumulative amount remaining in the soil (or 60-70 % of the annual application). This estimate is less than that calculated by Takeoka *et al.* (1991), in the only other study that provides an estimate of the regional volatilisation loss of technical HCH from a tropical environment. Takeoka *et al.* (1991) estimated that 99.9% of the annual application of technical HCH to rice paddies in India volatilised to the atmosphere. The lower volatilisation estimates in the present study are likely to be a consequence of soil incorporation of the insecticides and the absence of recent organochlorine insecticide application.

Table 3.14. Estimates of annual and total amounts of individual organochlorine compounds volatilised from the Herbert and Burdekin regions (Source: Dissipation model, Table 3.2).

Compound	Volatilisation losses			
	Burdekin		*Herbert*	
	tonnes yr^{-1}	Total (tonnes)	tonnes yr^{-1}	Total (tonnes)
α-HCH	1.8-62	1190	0.40-63	1670
β-HCH	0.20-5.1	99	0.02-5.2	140
γ-HCH	0.50-12.1	250	0.06-13	350
δ-HCH	0.02-6.0	115	0.03-6.0	160
dieldrin			0.20-2.1	37
heptachlor epoxide	0.40-5.6		0.40-5.6	
trans-chlordane	0.20-3.0		0.20-3.0	

3.3.4.3 Run-off losses

The influence of run-off rate on the concentration of organochlorine compounds in coastal sediments may be examined by assuming that no degradation occurs in the coastal environment. In this case, annual transport of 0.5% of the residual α-HCH concentration remaining in the soils of the Herbert region would give rise to detectable concentrations in Herbert River sediment deposited over 1971-1984 (using an estimated annual sediment load of the Herbert River of 1.43×10^9 kg; Belperio, 1983; Figure 3.5). Assuming an equivalent degradation half-life to that in the soils of the region (307 days) and an estimated run-off loss of 0.5%, detectable concentrations may still be expected in sediment eroded from the Herbert catchment between 1980 and the present day (Figure 3.5). Similar calculations were

made from predicted concentrations of the remaining HCH isomers and dieldrin. However, no detectable concentrations of organochlorine insecticide residues were found in sediment deposited over the period of 1960-1997 in marine sediment cores collected from the Herbert region (section 2.3.6). This may suggest that run-off losses were less than that used in model estimates, degradation rates in the marine environment are faster than those in the terrestrial system, or, given the relatively small time period over which detectable concentrations of organochlorine concentrations are estimated to be detected, mixing of the sediment containing detectable residues with other sediment.

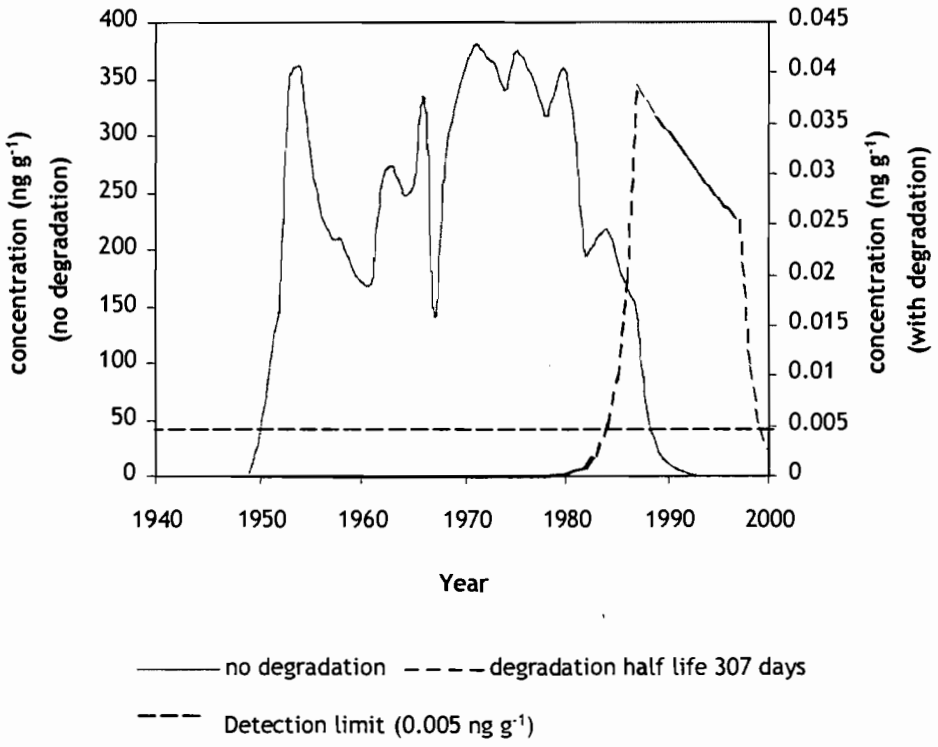


Figure 3.5. Predicted α-HCH concentration in 1997 in coastal sediment deposited over 1940-1997 in the Herbert region assuming a 0.5% run-off and with either no degradation occurring in the coastal sediments, or a degradation rate of 307 days.

In the Burdekin region, under conditions of 0.5% annual run-off loss, no degradation in the marine environment and an estimated annual sediment load of 8.6×10^9 kg (Neil and Yu, 1996) detectable concentrations of α-HCH are expected in marine sediment (Figure 3.6). However, assuming a degradation rate of 380 days, which is slower than that estimated for the soils, sediment concentrations become undetectable (Figure 3.6). A general trend of marine degradation rates being slower than those observed in soils resulted in undetectable concentrations in the marine sediment of the Burdekin region for the remaining HCH isomers, heptachlor epoxide and trans-chlordane.

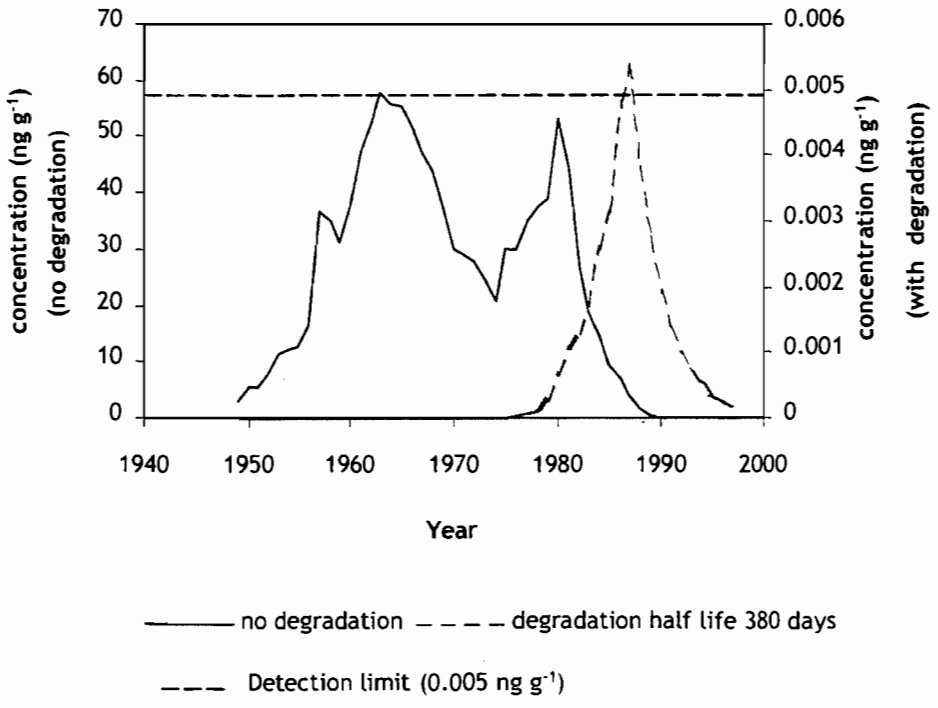


Figure 3.6. Predicted α-HCH concentration in 1997 in coastal sediment deposited over 1940-1997 in the Burdekin region assuming a 0.5% run-off and with either no degradation occurring in the coastal sediments, or a degradation rate of 380 days.

Considering erosion losses in another context, at current organochlorine insecticide residue concentrations in the soil, a soil loss of 1.1 MT (or 110 tonnes $ha^{-1} yr^{-1}$ over the area of application of HCH) in the Burdekin region would be required for detectable concentrations of α-HCH to be found in sediment deposited from the Burdekin River (Table 3.15). Surface soil erosion of around 22 tonnes ha^{-1} yr^{-1} could result in detectable concentrations of β-HCH, while soil losses of around 15 tonnes ha^{-1} yr^{-1} would be required to detect heptachlor epoxide. In contrast, soil losses in the order of 1-6 tonne ha^{-1} over the area of application could result in detectable concentrations of the HCH isomers being found in the coastal estuarine sediment of the Herbert region. The lower soil loss calculated for the Herbert region is due to the higher concentration of HCH isomers in the Herbert region soils, and the lower sediment load of the river.

Table 3.15. Estimates of the amount of soil required to be eroded from the sugarcane soils of the Herbert and Burdekin regions to enable organochlorine residues to be detected in coastal sediments in 1997 (Source: Equation 11).

Compound	Soil loss (tonnes ha^{-1})			
	Burdekin		Herbert	
River sediment load (tonnes yr^{-1})	2.8	8.6	0.55	1.4
α-HCH	136	419	1.8	4.7
β-HCH	28	86	1.1	2.7
γ-HCH	43	130	2.0	5.2
δ-HCH	241	740	4.4	11
heptachlor epoxide	20	61	17	44
trans-chlordane	35	108	31	79
cis-chlordane	86	267	ND	ND
dieldrin	88	270	0.59	1.5
p,p'-DDE	37	114	9.1	24

ND-not determined

Annual soil loss from sugarcane fields is dependent upon topography, climate and soil types (e.g. Matthews and Makepeace, 1981; Prove and Hicks, 1991). While soil erosion losses of up to 380 tonnes ha^{-1} from moderately sloping land under high rainfall conditions have been observed (Matthews and Makepeace, 1981), losses of this magnitude are unlikely to occur in either the Herbert or the Burdekin catchments. This is primarily due to the location of sugarcane on the coastal flood-plains with low relief in these catchments. Additionally, the location of sugarcane land on the coastal flood-plains, which accumulate sediment in times of flood, will result in minimal soil losses occurring from these regions even during flood events. Erosion rates of 15-22 tonnes ha^{-1} yr^{-1} are also unlikely to be achieved in the Burdekin region, due to the combined effects of low relief and low rainfall of the sugarcane growing region. Soil erosion from sugarcane fields in the Ripple Creek area of the Herbert region during March 1998, when high rainfall occurred, were estimated to be in the order of 1 tonne ha^{-1} (F.Visser, CSIRO, pers. comm.). Thus, soil losses of <1-6 tonne ha^{-1} could be expected to occur in the Herbert region and therefore, detectable concentrations of the organochlorine residues in the coastal sediments might also be expected to be found. There was an absence of detectable concentrations of organochlorine insecticide residues in marine sediment cores collected from coastal areas off each region (section 2.3.6). This absence was initially surprising, given the easily detectable concentrations present in the surface soils of the two regions. However, model estimates indicate that the combined effects of degradation and dilution of eroded agricultural soil in riverine sediment loads will result in undetectable concentrations of organochlorine residues in the coastal sediments of the Herbert and Burdekin regions. The absence of detectable concentrations of organochlorine residues may also indicate that soil

erosion is occurring at rates less than those calculated, or that trapping of eroded soil, such as by coastal wetlands, may be occurring.

3.4 Conclusions

Since 1949, in the order of 3,900 tonnes of technical HCH, 40 tonnes of aldrin, and 46 tonnes of heptachlor have been used on sugarcane in the Herbert and Burdekin regions (Table 3.5). The usage of technical HCHs represents approximately 0.04 % of the total global usage over the period 1940-1990 (Li, 1999). Currently less than 0.01% of the applied amount is estimated to remain in the sugarcane soils of the studied regions and it could take up to 15 years for the residues present in the Herbert region soils, and 10 years for residues present in the Burdekin region soils, to fall below detectable concentrations.

If volatilization is assumed to be the major mechanism of removal of organochlorine compounds from the soil, annual losses of 0.4-64 tonnes of α-HCH and 0.02-13 tonnes of other HCH isomers could have occurred annually (Table 3.14). The total mass of organochlorine compounds released to the atmosphere since 1949 is of the order of 3,600 tonnes. If degradation processes were assumed to be the major mechanism of removal of organochlorine compounds from the soil, half lives of 264-440 days and 307-812 days are required for individual organochlorine compounds in the Burdekin and Herbert regions respectively.

At a run-off loss rate of 0.5% of the cumulative amount of residues remaining in the soil each year, degradation rates of individual compounds in the marine environment that are slower than those estimated for degradation in the soil, will result in organochlorine residues being undetectable in coastal sediment of the Burdekin region (assuming a river sediment load of 8.6×10^9 kg). In contrast, marine degradation rates as fast as predicted soil degradation rates, will result in detectable residues in coastal sediments of the Herbert region, although only in sediment derived from soil eroded since mid-1980s. The absence of detectable residues in this region suggests that either degradation rates are faster than those used, or that other processes are important in reducing organochlorine concentrations. At current soil concentrations, soil losses in the order of <1-6 tonne ha^{-1} in the Herbert region and 15-110 tonne ha^{-1} in the Burdekin region would be required to produce detectable concentrations of insecticide residues in coastal sediments. These rates of soil loss would not be achieved in the Burdekin region, thus it is unlikely that detectable concentrations of organochlorine residues will be found in the adjacent coastal marine sediments. Soil loss rates of <1-6 tonnes ha^{-1} in the Herbert region are, however, realistic. Thus, the absence of detectable concentrations in the coastal sediments demonstrates the relative importance of other mechanisms (e.g. degradation, trapping of eroded soil) in determining the amount of organochlorine residues present in the adjacent coastal marine sediments.

Chapter 4: Investigation of the application of an enzyme assay as a screening tool for the exposure of *Acanthopagrus berda* (Pikey Bream) to organochlorine insecticide residues

4.1 Introduction

A variety of sources of organic contaminants to the Great Barrier Reef lagoon exist including urbanisation (combustion of fossil fuels, stormwater, sewage treatment plant effluent), boating (recreational and commercial), and agriculture. Off-site movement of soil and associated contaminants from urban and agricultural activities is generally considered to be the major source of contaminants to the north Queensland coastal environment (e.g. Bramley and Johnson, 1996; Furnas and Brodie, 1996; Hunter *et al.*, 1996; Mitchell *et al.*, 1996), although these studies have mainly focussed on nutrients and pesticides. Particular emphasis has been placed on the contribution of the sugar industry as it is the dominant land-use on the coastal plain of Queensland and has under-gone rapid expansion in recent years. Easily detectable residues of organochlorine pesticides from historical usage are present in older cane soils (section 2.3.2). Additionally, polycyclic aromatic hydrocarbons are present in cane soil due to a regime of burning prior to harvest (Mueller *et al.*, 1996) although this practice has ceased in some areas.

The detection of organochlorine residues in on-farm drainage lines and small creeks of the sugarcane lands in the Herbert and Burdekin regions indicates that some movement of organochlorine residues from paddocks into adjacent waterways has occurred. The residence time of sediments, hence that of sediment-bound contaminants, in these creeks is variable and dependent upon climatic (rainfall) and tidal conditions. As such, sediment analyses may not necessarily provide an appropriate measure of biological exposure to sediment bound contaminants.

The cytochrome P-450 1A system in fish has been widely used as an indicator of biological exposure to sediment bound organic contaminants in aquatic systems (e.g. Burns, 1976; Stegeman, *et al.*, 1986; Galgani *et al.*, 1991; Livingston *et al.*, 1993; Vrolijk *et al.*, 1994), and has been incorporated into environmental monitoring programs (e.g. Collier *et al.*, 1998). This system is especially sensitive to induction by a range of organic contaminants, including PCDDs/PCDFs, PCBs, and PAHs (Payne *et al.*, 1987; Goksøyr and Förlin, 1992; Holdway *et al.*,

1995; Denison and Heath-Pagliuso, 1998). P-450 1A induction can be measured using catalytic enzyme assays such as ethoxyresorufin *O*-dethylase (EROD) activity or ethoxycoumarin-*O*-dethylase (ECOD), immunoassays, and DNA sequencing (Goksøyr and Förlin, 1992; Holdway *et al.*, 1995). Catalytic assays, such as EROD or ECOD, provide a rapid and relatively inexpensive means for assessment of fish exposure to organic contaminants.

Limited studies of induction of cytochrome P-450 1A in fish have been conducted in Australia (e.g. Ahokas *et al.*, 1994; Holdway *et al.*, 1994; Brumley *et al.*, 1995), and no studies have previously been conducted in tropical Australia. Similarly, few studies have assessed the response of the P-450 system in fish to organochlorine insecticide exposure. Those that have, indicated a variable response to different insecticides. For example, aldrin is rapidly metabolised to dieldrin via aldrin epoxidase; dieldrin caused an increase in aniline hydroxylase and a decrease in aminopyrine demethylase (Vink, 1975); the DDT group has been shown not to cause induction in fish, although induction occurs in mammalian P450 systems (Buhler and Rasmussen, 1968; Addison *et al.*, 1977; Smith 1991).

Laboratory trials were undertaken in the present study to establish the response of the P-450 1A system in *Acanthopagrus berda*, pikey bream, which is a common tropical estuarine fish species, to exposure to β-napthoflavone (BNF), and a mixture of hexachlorocyclohexane (HCH) isomers. BNF is a known inducer of the P-450 1A system, and has been widely used in laboratory trials as a model compound to characterise the response of individual species (Zhang *et al.*, 1990). The response of the P-450 1A system to a mixture of HCH isomers was also examined, as HCH isomers were the most ubiquitous organochlorine compounds detected in sugarcane soils surrounding some of the study sites (section 2.3.2). No information is available on the response of the P-450 1A system in fish to HCH exposure.

Cytochrome P-450 activity was also examined in fish collected from creeks draining agricultural (sugarcane) and urban areas, and from catchments not significantly disturbed by anthropogenic activities in the Herbert and Burdekin region. The present study assumes that contaminants present in the creek systems were predominantly derived from land-use in the local catchment, and that the types of inducing compounds were similar between catchments under similar land-use. In addition to cytochrome P-450 activity, general parameters of fish health, nutritional and reproductive status, and age were also measured and their relationship to cytochrome P-450 activity examined.

4.2 Materials and Methods

4.2.1 Fish species

Acanthopagus berda (pikey bream) was selected as the target species to assess the application of P-450 1A induction for organic contaminant exposure assessment in tropical

Australian fish. *A. berda* is ubiquitously distributed in the estuarine mangrove creeks of northern Australia (Sheaves, 1992). It resides close to the sediment surface around fallen trees or mangrove roots and it is omnivorous, feeding on detrital matter, sedentary molluscs (e.g. oysters) and crustaceans (e.g. prawns) (Beumer, 1978). *A. berda* is an hermaphroditic species, with a male to female sex change occurring when the fish reach 170-200 mm long (Tobin *et al.*, 1997). No exchange of *A. berda* between creek systems has been observed (Sheaves *et al.*, 1999) and, with the exception of migration toward creek mouths during spawning season (June-September), movement within a creek system is generally less than 500 m (Sheaves *et al.*, 1999). The ability to target male fish on the basis of size distribution, and general knowledge of the ecology of *A. berda*, is a means of reducing the influence of biological variables (such as sex, age, spawning status) on the environmental induction of P-450 1A. Additionally, the limited movement of *A. berda* enables the localised effects within a given catchment to be examined.

4.2.2 Study locations

Fish used in laboratory trials were captured from Baldy Creek located in Bowling Green Bay National Park on Cape Cleveland (Figure 4.1). Fish collected for the field study were collected from:

a) two creeks with no significant agricultural or urban activity (Baldy Creek, Cape Cleveland and Fisher Creek, Hinchinbrook Channel;
b) two creeks in each of the Herbert River (Victoria Creek and Seymour River) and Burdekin/Haughton River catchments (Plantation Creek and Cromarty Creek), all of which had significant areas under sugarcane; and
c) one creek with significant urban land-use (Ross Creek).

Locations of the creeks are shown in Figures 4.1-4.3, and more detailed descriptions of the individual creeks are given below and summarised in Table 4.1.

4.2.2.1 Undisturbed catchments

Baldy Creek

Baldy Creek, a small tidal creek approximately 2 km long is located on Cape Cleveland, 35 km southeast of Townsville (Figure 4.2). Undisturbed eucalypt forest within the Bowling Green Bay National Park dominates the catchment. Boating activity in Baldy Creek and the surrounding area is limited. Fish were captured about 1 km upstream of the mouth of the creek.

Fisher Creek

Fisher Creek catchment is located approximately 50 km north of the Herbert River catchment and includes some of the coastal hills of the Cardwell Range, which are designated State Forest and National Park (Figure 4.3). Fisher Creek drains into the extensive interconnected

mangrove swamps of Hinchinbrook Channel, which is a popular recreational boating area. Despite the absence of significant disturbance in the Fisher Creek catchment, fish captured in the creek may receive some exposure to sediment and contaminants originating from the Herbert River and surrounding creeks. This is due to the location of the creek within the protected waters of Hinchinbrook Channel in which sediment is trapped due to an unusual hydrological regime (Wolanski *et al.*, 1990). Fish were captured at two locations in the creek.

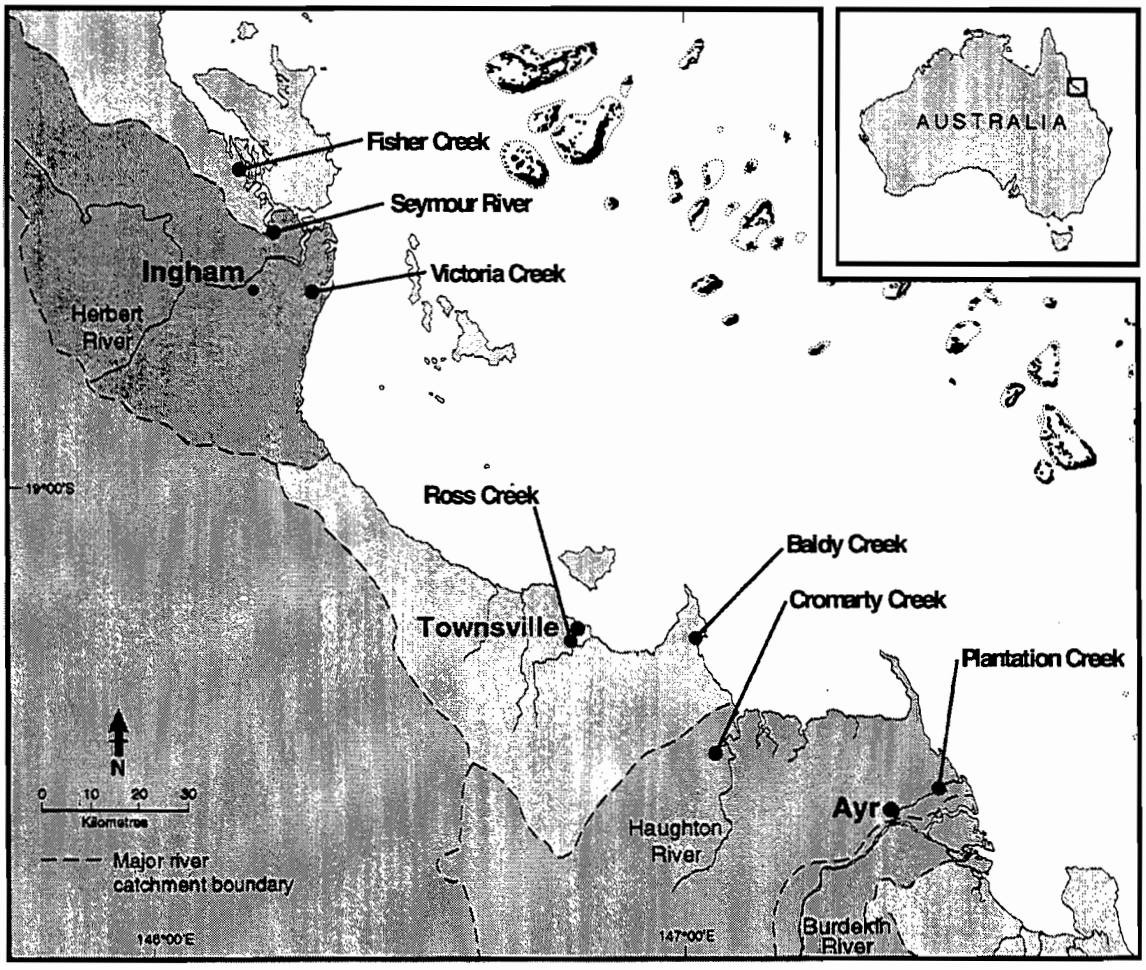


Figure 4.1. Map showing locations of fish collection for laboratory trials and field studies.

4.2.2.2 Sugarcane catchments

Victoria Creek

Victoria Creek is a distributary of the Herbert River. During flood events, river water is diverted through Victoria Creek and inundation of the catchment occurs. The upper reaches of the creek drain sugarcane land (which have been farmed for longer than 60 yrs) and receive an unknown contribution from urban run-off from the town of Ingham and wastewater discharge from a local sugarcane mill (Figure 4.3). The lower reaches of Victoria Creek drain freshwater and estuarine wetlands, and enter into mangrove swamps that extend along most

of the lower 13 km of the creek. Commercial fishing activities (barramundi) in addition to recreational boating activity occur within the creek. Fish were captured in the upper reaches of the estuary within the mangrove swamp, approximately 12 km from the creek mouth.

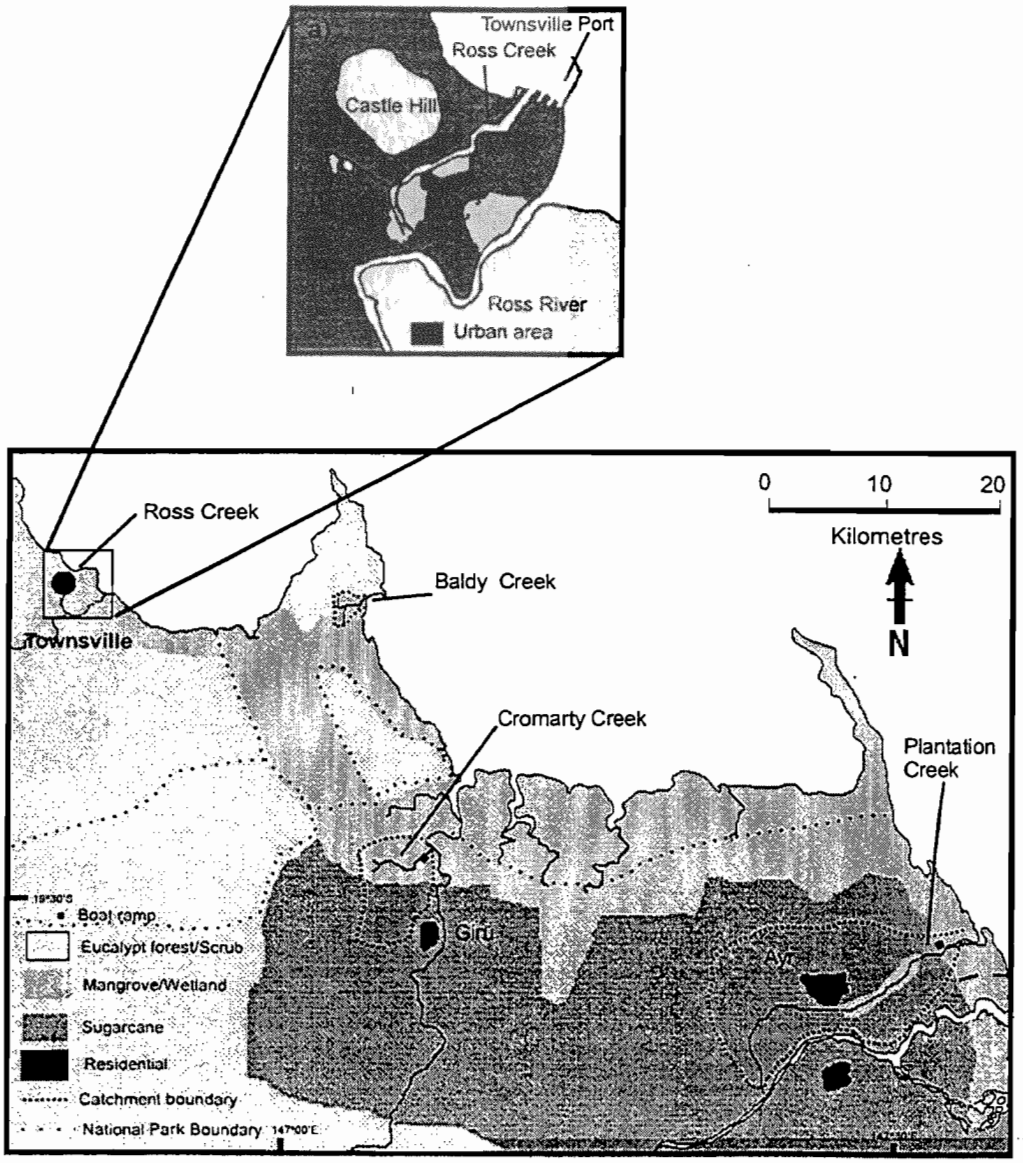


Figure 4.2. Map showing catchment boundaries and land-use surrounding creeks in the Townsville and Burdekin regions sampled during field trials.

Seymour River

The Seymour River is a former major distributary of the Herbert River. It is permanently connected with the main Herbert channel and still carries part of the river flow (Johnson and Murray, 1997). The catchment area includes some of Hinchinbrook Island National Park and lowland agriculture (predominantly sugarcane, Figure 4.3). Some of the sugarcane land in this catchment has been developed in the last 10 years and is likely to contain less organochlorine

insecticide residues than older farming land. The increasing predominance of green-cane harvesting over the last 15-20 years in the Herbert region, suggests that residues from burning (PAHs and dioxins) may also be low in these soils. The Seymour River drains into a mangrove swamp, which extends along approximately 7 km of the river prior to the mouth entering the southern end of Hinchinbrook Channel. Fish were captured in upper reaches of the estuary, approximately 13 km from the river mouth. A sand bar is located at approximately 7 km upstream of the river mouth and restricts tidal movement into the upper part of the estuary. Agricultural land (sugarcane and grazing) is present behind a narrow strip of mangroves lining the bank along this part of the estuary.

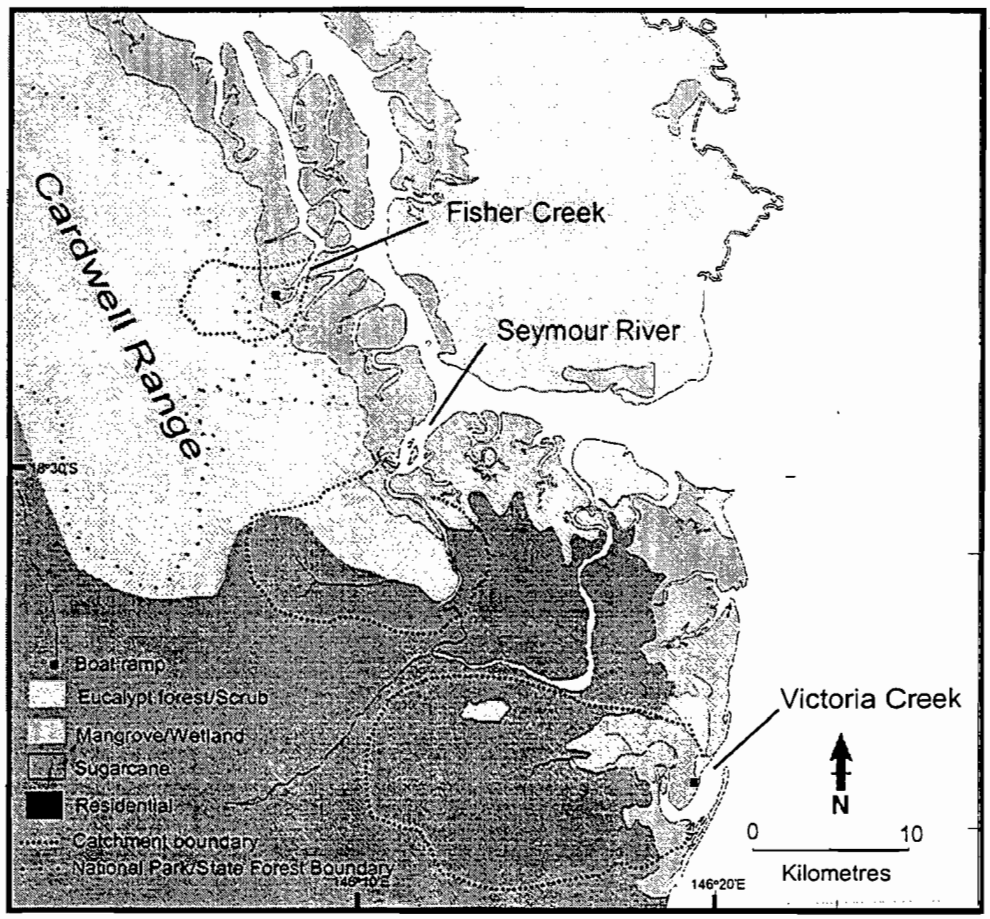


Figure 4.3. Map showing catchment boundaries and land-use surrounding creeks in the Herbert region sampled during field trials.

Plantation Creek

Plantation Creek, a distributary of the Burdekin River, is located on the Burdekin River delta (Figure 4.2). During flood events, diversion of Burdekin River water through Plantation Creek occurs, and flooding of the catchment may occur. In the dry season, water is pumped from

Table 4.1. Description of land-use and general characteristics of study catchments.

Catchment	Sub-catchment	Sub-catchment grouping	Approx area (km^2)	Land-use# (% of catchment area)	Vegetation* (%)	Wetland (%)	Mangrove (%)	Other activities occurring within creek system
Baldy Creek		undisturbed	40		80		20	limited boating
Fisher Creek		undisturbed	41		70		30	recreational boating
Herbert River	Victoria	sugarcane	111	sugarcane (70)	2	71	20	commercial fishing, recreational boating
Herbert River	Seymour	sugarcane	84	sugarcane (40)	38	2	20	recreational boating
Haughton River	Cromarty	sugarcane	45	sugarcane (40)	2	60		recreational boating
Burdekin River	Plantation	sugarcane	157	sugarcane (70) urban (6)		16	12	recreational boating
Ross River	Ross Creek	urban	273	urban (90)	10			shipping port, recreational boating

#Approximate percentage land-use was determined from maps (provided by Jim Tait, Australian Centre for Tropical Freshwater Research) and Geographical Information System (GIS) databases (Herbert Resource Information Centre).

*Vegetation - Eucalypt/Melaleuca forest

the Burdekin River into Plantation Creek to replenish the shallow groundwater aquifers, which supply irrigation water to overlying farmland. Hence, freshwater input to Plantation Creek is not solely confined to periods of rainfall. Most of the sugarcane land drained by Plantation Creek has been used for sugarcane farming for more than 60 years. Plantation Creek passes close to the town of Ayr and receives an unknown contribution of contaminants from urban run-off. A freshwater wetland area (approximately 9 km long) is located just downstream from Ayr and prior to discharge of the creek into mangroves. This wetland may trap sediment and associated contaminants derived from sugarcane and urban land-use in the upper catchment. Sugarcane farms are adjacent to the narrow riparian zone of the reaches of the creek just below the wetland. Cattle grazing occurs on some of the saline wetland behind the mangroves along the lower creek sections. Fish were captured approximately 3 km downstream of the wetland area, and 1 km upstream from the Plantation Creek boat ramp.

Cromarty Creek

Cromarty Creek drains into the Haughton River about 12 km upstream of the river mouth (Figure 4.2). It is a popular for recreational fishing and boating, and is located in an extensive area of freshwater and estuarine wetlands. Variation in the frequency of tidal inundation of the wetlands has resulted in a mix of wetland types. Areas inundated by diurnal tides are dominated by mangroves and areas inundated less frequently (spring tides) are dominated by saltpans and *Spartina* spp. grasslands. Restriction of tidal waters entering and leaving the Cromarty wetlands, and limited freshwater input has resulted in the formation of a slowly flushed local sedimentary depositional basin (G. Blackman, EPA, pers. comm.). The upper parts of the catchment area includes grazing land and farm land which has been used for sugarcane for more than 60 years, the township of Giru, and a sugar mill. Fish were captured along a 2 km length of the creek, approximately 5 km upstream of the Cromarty Creek boat ramp, which is located where Cromarty Creek joins the Haughton River.

4.2.2.3 Urban catchment

Ross Creek drains through the centre of the city of Townsville (Figure 4.2a), which has a population of 140,000 people. The catchment is predominantly urban land although a limited area of salt pan and mangrove swamp exists. A man-made lake system that receives stormwater from the surrounding urban area discharges into the creek. Considerable boating activity occurs within the creek due to presence of a marina, the operation of a ferry service, and the presence of a large commercial port facility at the creek mouth. Fish were captured approximately 5 km upstream from the creek mouth.

4.2.3 Fish collection

Fish were collected from each of the study locations by hook and line. The fish used in the laboratory trials were captured over the period March to April 1998. These fish were maintained in 100 l flow-through aquaria (5 fish in each aquarium), fed *ad libitum* with frozen

prawns, and acclimated for 10 days prior to the commencement of experiments. Water quality parameters during acclimation periods and experiments are given in *Appendix F.*

Fish used in the field studies were captured over the period 20-29 April 1999. Immediately after capture, the fish were killed and their livers dissected out and frozen in liquid N_2. Fish were sexed, their lengths measured, and notes taken of fish condition. After the weights of gutted fish, guts, liver, and gonads were determined in the laboratory, otoliths were removed for aging of the fish. Their condition was determined as (total weight (g)/length^3 (cm^3)) x 100 (Kirby *et al.*, 1999). Liver somatic index (LSI) and gonado-somatic index were determined as (liver weight/total fish weight) x100 and (gonad weight/total fish weight) x 100 respectively (Kirby *et al.*, 1999). Muscle tissue lipid content was determined (section 4.2.7.1). Additionally, organochlorine and PAH residue analysis of muscle tissue from selected individuals from each catchment was undertaken.

4.2.4 Sediment collection

During field studies, surface sediment samples for chemical analyses were collected from 2 locations in each creek at the time and place of fish capture, using a Van-veen grab sampler. Samples were placed in cleaned, solvent-rinsed glass jars, and stored frozen until analysis.

4.2.5 Laboratory exposure trials

Fish were exposed to β–napthoflavone (BNF) and a mixture of hexachlorocyclohexane isomers (HCH) to characterise the response of the P-450 1A system in *A. berda.* The HCH mixture contained approximately 76% (α-HCH), 8% (β-HCH), 11% (γ-HCH) and 5% (δ-HCH).

Fish were immersed in an anaesthetic solution of tricaine methylsulfonate (MS-222, 70 mg L^{-1}) for several minutes prior to being given one intraperitoneal (i.p.) injection of BNF as a solution in corn oil at 10, 20, 40 and 80 mg kg^{-1}, or HCH dissolved in corn oil at 1, 10, 50 and 100 mg kg^{-1}. Five fish were injected at each dose level; 5 fish were injected with the carrier; and 5 fish were used as untreated controls. Four days after injection, fish were killed by cervical incision. Livers were removed immediately, and stored at -80°C until processed. The fish were sexed, weighed, length measured, and notes taken of fish condition.

4.2.6 Biochemical analyses

4.2.6.1 Microsome preparation

A detailed description of microsomal preparation is given in *Appendix G.1.* Briefly, microsomes were prepared by homogenisation of the livers in 0.1 M phosphate buffer [pH 7.4, containing 1 mM dithiothreitol, 1 mM EDTA, 0.1 M KCl, 0.1 M phenanthroline] followed by sequential centrifugation. All steps were performed at 4°C. Centrifugation at 10,000 *g* for 20 mins yielded a post-mitochondrial supernatant (S9). This supernatant was centrifuged for 60

minutes at 100,000 *g* to yield a microsomal pellet. This pellet was resuspended in phosphate buffer (pH 7.4) containing 20 % glycerol (v/v). The S9 fractions and microsomes were stored at -80°C until biochemical analyses. The S9 fraction was used for analyses during the laboratory trials and microsomes for analyses during field studies.

4.2.6.2 Cytochrome P-450 content

Cytochrome P-450 content was determined by the dithionite reduced difference spectral method of Matsubara *et al.* (1976), with modifications by Rutten *et al.* (1987). Microsomal suspensions were diluted 1/10 in 0.1 M phosphate buffer (ph 7.4, 5 ml) containing 20% glycerol (v/v) at room temperature and bubbled with carbon monoxide for 30 sec. After an additional 2 min for stabilization, the baseline spectrum was recorded. Sodium dithionite (final concentration, 4.58 mM) was added to the sample cuvette, and after 3 min the spectrum between 400-500 nm was recorded using a Shimadzu UV 3000 dual wavelength/ double beam recording spectrophotometer. An extinction coefficient of 104 $mM^{-1}cm^{-1}$ was used to calculate total P-450 content (Matsubara *et al.*, 1976).

4.2.6.3 Detoxification enzyme analyses

Detailed descriptions of the enzyme assays, including temperature optimisation and assessment of the linearity of the assays, are given in *Appendix G.2* and *G.3*.

Ethoxycoumarin-O-dethylase (ECOD) assay

ECOD activity was determined using the method of Ullrich and Weber (1972). All assays were conducted at 35°C and pH 7.6. The incubation mixture consisted of an NADPH regenerating system (10 mM magnesium chloride, 200 mM potassium chloride, 6 mM glucose-6-phosphate, 1.25 mM NADP and 100 units G-6-dehydrogenase, 100 µl), 1.3 ml Tris buffer (pH 7.6) and 500 µl of ethoxycoumarin substrate. The reaction was started with the addition of 100 µl of S9 and incubated for 10 minutes prior to stopping the reaction with $Ba(OH)_2$ (0.5 ml) and $ZnSO_4$ (0.5 ml). The resultant precipitate was removed by centrifugation (2000 *g*, 5 minutes). Prior to recording fluorescence, a glycine-NaOH buffer (0.5 ml, pH 10.5) was added to the supernatant (1 ml) in the cuvette, and the solution was mixed. Fluorescence was determined on a Hitachi F-4010 fluorescence spectrophotometer at EX/EM wavelength of 380/452 nm. Assays were performed in triplicate. Hydroxycoumarin concentrations were calculated from a standard regression after correction of readings for blank fluorescence.

Ethoxyresorufin O-dethylase (EROD) analysis

EROD activity was determined using a fluorescence method modified from Burke and Mayer (1975). All assays were conducted at 35°C and pH 7.6. The incubation mixture consisted of an NADPH regenerating system (10 mM magnesium chloride, 200 mM potassium chloride, 6 mM glucose-6-phosphate, 1.25 mM NADP and 100 units G-6-dehydrogenase, 250 µl), 0.5 ml Tris buffer (pH 7.6), 100 µl albumin, and 100 µl of ethoxyresorufin substrate. The reaction was

started with the addition of 100 µl of S9 (laboratory trials) or 25 µl of microsomal suspension (field studies), incubated for 10 minutes (laboratory trials) or 5 minutes (field studies), prior to stopping the reaction with methanol (2.5 ml). The resulting precipitate was centrifuged (2000 *g*, 5 minutes) prior to determination of resorufin on a Hitachi F-4010 fluorescence spectrophotometer. Fluorescence was determined at EX/EM wavelength of 530/584 nm. Assays were performed in triplicate. Resorufin concentrations were calculated from a standard regression after correction of readings for blank fluorescence.

All enzyme activities were expressed as a rate per mg protein or per nmol P-450. Normalisation of EROD activity to total P-450 content (turnover number) gives an indication of the relative contribution of cytochrome P-450 1A to total P-450 content, in that a higher value suggests a relative enrichment of cytochrome P-450 1A (Stegeman *et al.*, 1997). Protein assays were performed on the microsomal suspension using the method of Lowry *et al.*(1951; *Appendix G.4*).

4.2.7 Chemical analyses

4.2.7.1 Fish tissue

Extractable lipid weights were determined gravimetrically. Fish tissue (~ 1 g) was homogenized with $Na_2 SO_4$ and placed in teflon centrifuge tubes with dichloromethane CH_2Cl_2 (10 ml). Tissue samples were sonicated (2 x 5 minutes). Solvent was removed and concentrated to approximately 2 ml. Aliquots (10 µl) of the solvent extract were weighed on a micro-balance. Results were expressed as mg per g dry weight of fish tissue.

Muscle tissue, from selected fish from each catchment, was analysed for organochlorine insecticide residues and PAHs. Fish were selected for analysis on the basis of EROD response. Two fish that had low EROD activity, and 2 fish that had high EROD activity, were analysed from each creek, with the exception of Baldy and Fisher Creeks, from which two fish from each creek were analysed. C. Gaus at the University of Queensland performed these analyses, and detailed methods are given in *Appendix G.5*. Briefly, fish tissue (~ 1 g) was macerated in acetone and allowed to stand overnight to remove excess water. The acetone was decanted, and the tissue rinsed twice prior to extraction with CH_2Cl_2 (150 ml) and saturated NaCl solution (5 ml) in a separating funnel. The solvent was filtered through Na_2SO_4, evaporated to dryness, and lipid weight determined. The crude extracts were separated by gel permeation chromatography. Following fluorosil clean-up of the organochlorine/PAH fraction, samples were analysed by gas chromatography with electron capture detection (organochlorine) and mass spectral detection (PAH). Results were expressed as µg per mg lipid.

4.2.7.2 Sediment

Organochlorine analyses were conducted as described in section 2.2.4.1. PAH analyses were conducted on four and three sugarcane soils, collected previously (section 2.2.1.1) from the Herbert and Burdekin regions respectively, in addition to sediment samples collected from the creeks at the time of fish capture.

Ultra-violet fluorescence was used to determine semi-quantitatively the concentrations of aromatic hydrocarbons present in the sediment samples, using a modification of the method described in UNEP/IOC/IAEA (1992). Briefly, known aliquots of sample extract were placed in a cuvette containing hexane (2 ml). Fluorescence was recorded on a UV spectrophotometer at EX/EM wavelengths of 280/327 nm, 310/360 nm and 380/420 nm in addition to recording a synchronous wavelength scan from EX/EM wavelengths of 255/280-475/500. Fluorescence was recorded in the linearly calibrated range of the fluorescence spectrometer. Standard curves at EX/EM wavelength of 280/327 nm and 310/360 nm were generated using Australian Northwest Shelf light crude oil (Harriett A) and a light Arabian crude oil (ROPME) respectively. Wavelength scans of the sediment extracts from the different creeks were similar and indicated that PAHs present in the samples were derived from a number of sources (e.g. combustion products, petroleum oils). Due to the absence of a spectral match of sediment extracts with the reference oils, approximate oil concentrations were calculated using calibration curves based on both the Harriett A and ROPME oils.

Individual PAH compounds were identified using gas chromatography-mass spectrometry under the conditions employed in section 2.2.4.1. Concentrations were determined using known response factors from a mixture of PAH standards and expressed as ng g^{-1} dry weight of sediment.

4.2.8 Statistical analyses

The significance of correlations between tissue lipid content, condition factor and EROD activity were tested using the software package "SPSS for windows" and a two-tailed t-test of the Pearson correlation coefficient on untransformed data. The remainder of the statistical analyses were performed by Dr D.A.J. Ryan at Agriculture and Agri-Food Canada, Nova Scotia, Canada.

4.2.8.1 Laboratory trials

Preliminary analysis of the untransformed data (EROD and ECOD activity normalised to protein and total cytochrome P-450, and total cytochrome P-450 normalised to protein) was performed using a general linear model (SAS statistical software), which included the effects: dose, injection, sex, and disease. Disease was included as an effect as some fish were observed to have formed lesions at the point of injection over the course of the experiment (4 days). The preliminary analyses indicated the form of the model which was fitted using log

transformed data (to satisfy distributional assumptions) to derive predicted values. Effects were considered positive at the 5% level of significance and all results are presented on the original linear scale.

4.2.8.2 Field studies

The log transformed activities (EROD normalised to protein and total cytochrome P-450, and total cytochrome P-450 normalised to protein) were analysed using a general linear model which included the effects: disturbance regime (agriculture, urban, undisturbed), sex (male, female), reproductive status (active, inactive), lesions (present, absent), and catchment (Seymour River, Victoria Creek, Plantation Creek, Cromarty Creek, Ross Creek). The differences in activities, due to the main effects of interest (disturbance regime and catchment) in addition to effects of reproductive status and sex, were estimated using contrasts. The data were log transformed, as the assumptions of normality and homogeneity of variance were not valid on the untransformed scale. Effects were considered at the 5% level of significance and all results presented on the original scale.

4.3 Results

The characteristics of fish captured for the laboratory trials and during field studies are shown in Table 4.2.

Table 4.2. Characteristics of fish used in laboratory trials and field studies.

Trial/catchment	Dates captured	Fish captured	Gutted weight (g)	Length (mm)	Age (yr)	Additional information
		Total number (females)	mean ± s.d	mean ± s.d		
Laboratory trials						
BNF[1]	Mar-98	29 (4)	125 ± 44	167 ± 19	ND[*]	
HCH[2]	Apr-98	29 (1)	95 ± 35	154 ± 11	ND	
Field Studies						
Baldy	20-Apr-99	18 (4)	132 ± 27	174 ± 12	2-5	
Fisher	28-Apr-99	22 (5)	111 ± 27	168 ± 13	2-5	3 SA[**] females 6 SA males
Victoria	26-Apr-99	16 (1)	113 ± 32	170 ± 13	2-5	2 fish EL[#]
Seymour	29-Apr-99	14 (0)	139 ± 36	174 ± 14	2-4	4 fish EL
Cromarty	23, 27-Apr-99	17 (0)	105 ± 25	166 ± 12	2-3	
Plantation	21, 22-Apr-99	20 (3)	105 ± 22	162 ± 13	2-3	
Ross	17, 25-Apr-99	15 (0)	102 ± 16	163 ± 9	2-4	

[1]β-napthoflavone; [2] mixture of hexachlorocyclohexane isomers; [*]ND-not determined; [**]SA- sexually active; [#]EL-external lesions

4.3.1 Laboratory trials

The response of EROD and ECOD activity (pmol min^{-1} mg^{-1} protein) and EROD turn-over number (nmol min^{-1} $nmol^{-1}$ P-450) to BNF exposure was variable. Despite this, significant quadratic dose-response relationships were observed (Figure 4.4; *Table H.1*). Maximal relative increases, of 10-fold and 7-fold in EROD activity and turnover number, were estimated to occur at doses of 56 and 50 mg kg^{-1} BNF respectively (Table 4.3). A 3-fold increase was estimated to occur in ECOD activity at dose of 51 mg kg^{-1} (Table 4.3). Sex had a significant effect on ECOD turn-over number ($p = 0.016$) and estimates of maximal response were not made. While a significant dose-response relationship was evident for P-450 content ($p=0.04$), this response was not linear or quadratic (*Table H.1*). Sex and disease were indicated as influencing the dose response in all parameters (*Table H.1*). However, as only a low number of female fish (4) and diseased fish (3) were analysed, further work is needed to establish the influence of these factors on the response of the P-450 system in *A. berda*.

Table 4.3. Estimated dose of β-napthoflavone at which maximum EROD and ECOD activity (pmol min^{-1} mg $prot^{-1}$) and EROD turnover number (nmol min^{-1} $nmol^{-1}$ P-450) was estimated to occur, and ratio of maximum activity to activity at no dose.

Parameter	Maximum dose	Ratio of maximum activity (95% CI)
EROD activity	56	10 (4.8, 21)
EROD turn-over number	50	6.8 (2.5, 19)
ECOD activity	51	2.8 (1.7, 4.5)

The response of EROD and ECOD activity and turnover number and P-450 content in fish exposed to HCH was low and variable (Figure 4.5). Significant dose-response relationships were observed for EROD activity ($p = 0.0012$) and ECOD activity ($p = 0.01$) but these were not linear or quadratic (*Table H.1*). A significant quadratic dose response was significant for EROD turn-over number ($p = 0.01$) (Figure 4.5b). A linear dose response was significant for P-450 ($p = 0.02$) and indicated that P-450 content decreased with increasing dose (Figure 4.5d).

4.3.2 Field studies

4.3.2.1 Effect of catchment disturbance on cytochrome P-450 1A activity

Catchment disturbance had a significant effect on EROD activity, turnover number, and P-450 content (Table 4.4). Fish, captured in catchments disturbed by agricultural or urban activity, showed significantly elevated EROD activity as compared with fish captured in the undisturbed catchments (Table 4.5). Fish captured from Ross Creek (urban catchment) showed 2.6-fold higher activity compared to those captured from creeks draining sugarcane land (Table 4.5). A relative increase in turnover number (nmol min^{-1} $nmol^{-1}$ P-450) as compared to EROD activity (pmol min^{-1} mg^{-1} protein) in fish captured from sugarcane

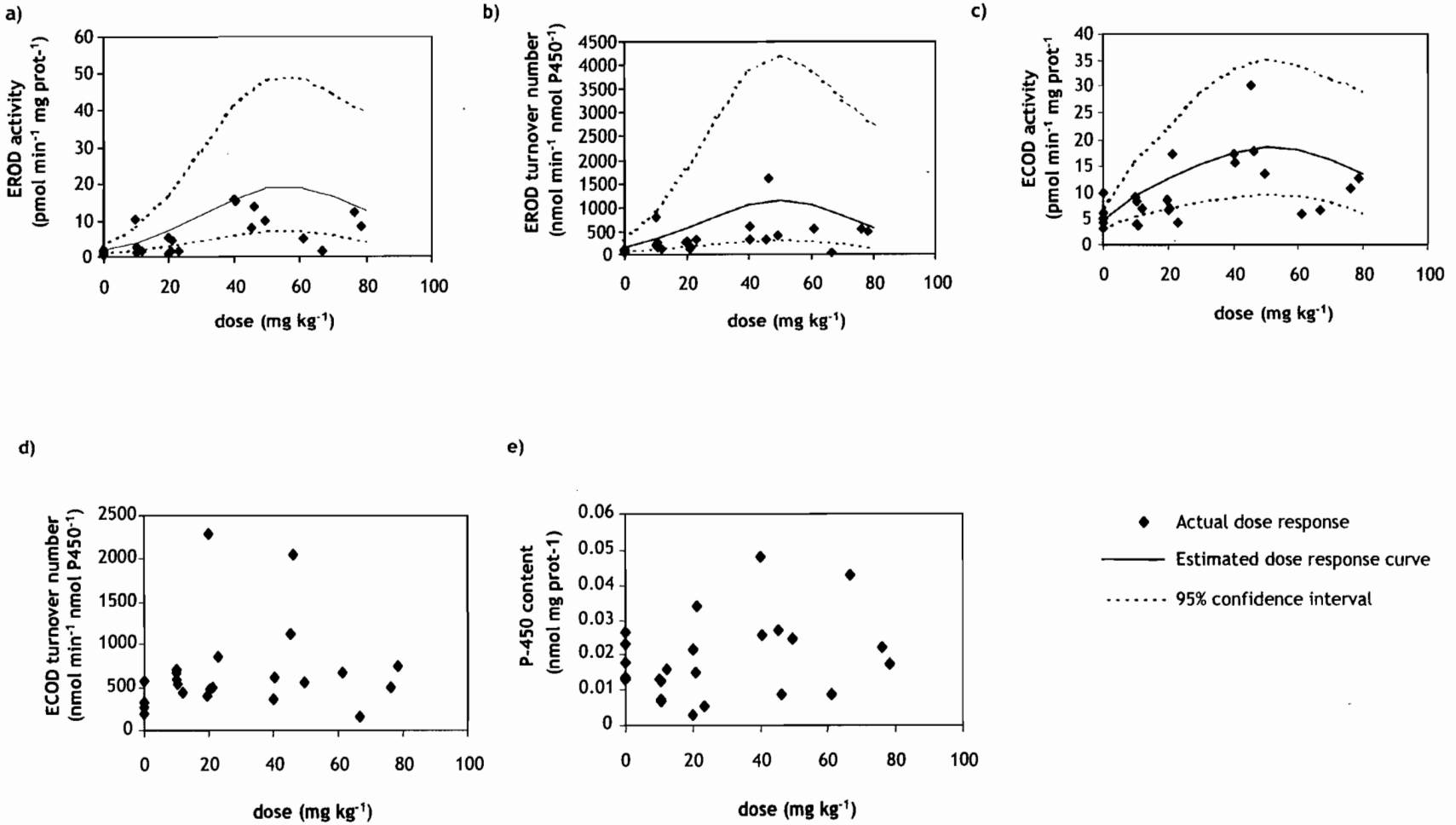


Figure 4.4. Actual and estimated dose response (95% confidence interval) of *A. berda* exposed to different doses of BNF: a) EROD activity; b) EROD turnover number; c) ECOD activity; d) ECOD turnover number and e) P-450 content (nmol mg^{-1} protein). Activity is expressed in units of pmol min^{-1} mg^{-1} protein and turnover number as nmol min^{-1} mg^{-1} protein.

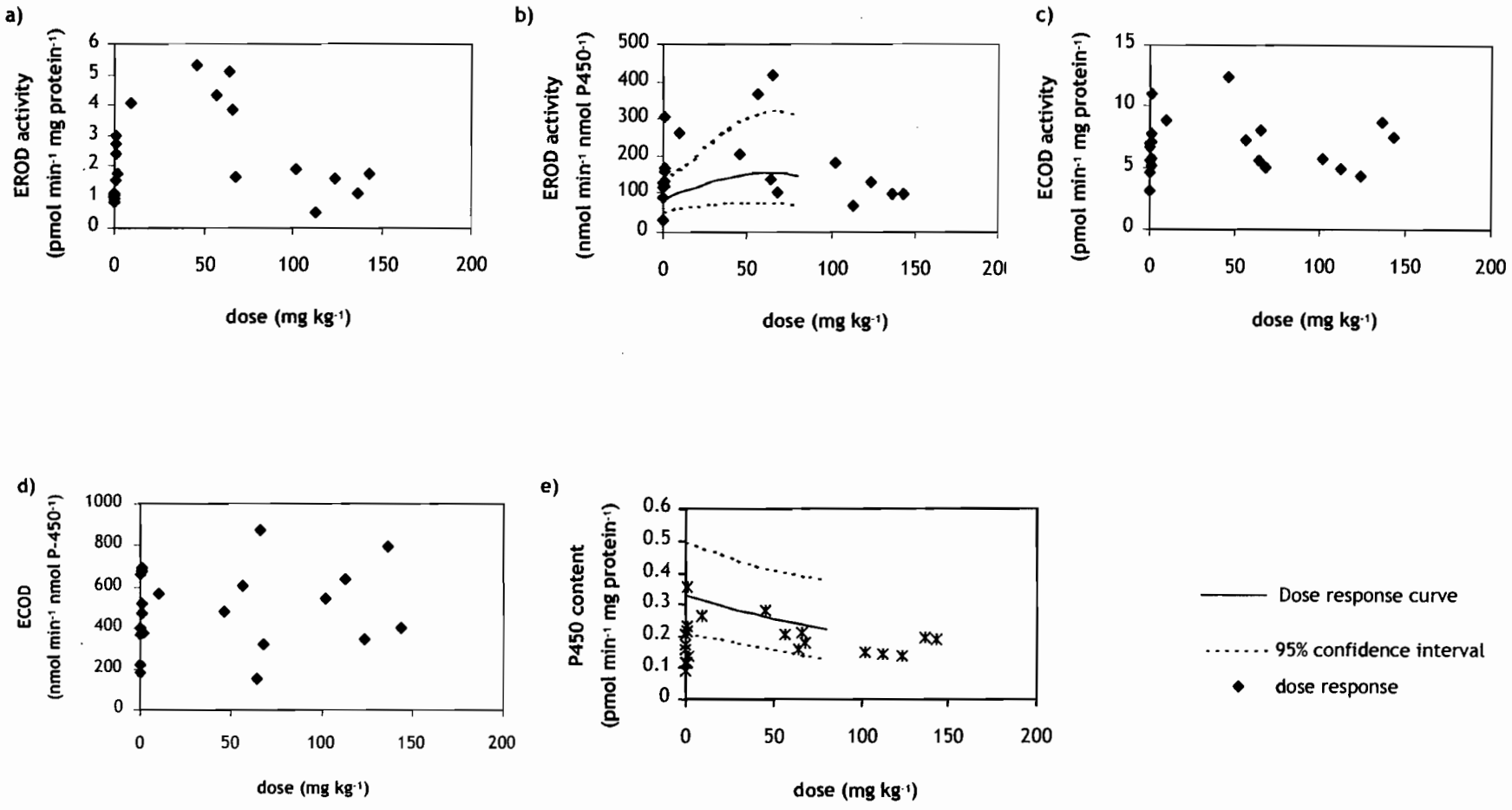


Figure 4.5. Actual response and estimated dose response (95% confidence interval of *A. berda* exposed to different doses of HCH: a) EROD activity; b) EROD turnover number; c) ECOD activity; d) ECOD turnover number; and e) P-450 content (nmol mg^{-1} protein). Activity is expressed in units of pmol min^{-1} mg^{-1} protein and turnover number as nmol min^{-1} mg^{-1} protein.

catchments (3.1-fold and 2.6-fold increase respectively relative to undisturbed catchments; Table 4.5) suggested an enrichment of cytochrome P-450 1A. In contrast, fish captured from the urban catchment showed a decrease in the relative response of turnover number as compared to EROD activity (5.2 fold compared to 6.4-fold increase relative to undisturbed catchments, Table 4.5). These results are not surprising given the wide range of organic contaminants present in the sediments of Ross Creek (Smith *et al.*, 1985; Kross 1997; Inglis and Kross, 2000) and therefore, the high potential for induction of other cytochrome P-450 enzymes (van der Oost *et al.*, 1991; Stegeman *et al.*, 1997). Interestingly, fish captured from sugarcane catchments showed a significantly lowered total cytochrome P-450 content compared to fish captured from undisturbed or urban catchments. This is unusual, as increased EROD activity is typically coincident with increased total cytochrome P-450 content as a result of increased production of cytochrome P-450 enzymes. Fish captured from the urban catchment showed elevated, although not statistically significantly different, cytochrome P-450 content compared to fish captured from the undisturbed catchments (Table 4.5).

Table 4.4. Overall significance of effects (p-values) of disturbance regime, catchment (disturbed catchments only), sex, reproductive status, and lesions, on EROD activity, EROD turnover number and cytochrome P-450 content.

Effect	EROD activity (pmol min^{-1} mg^{-1} protein)	EROD turnover number (nmol min^{-1} $nmol^{-1}$ P-450)	P-450 content (nmol P-450 mg^{-1} protein)
Disturbance regime	0.0001	0.0001	0.0005
Catchment	0.0001	0.0001	0.0245
Sex	0.0070	0.0014	0.41
Reproductive status*	0.0001	0.0012	0.34
Lesions	0.0266	0.4062	0.0844

*inactive versus reproductively active

4.3.2.1 Cytochrome P-450 activity in individual catchments

Significant differences in EROD activity, turnover number, and P-450 content were also observed between individual catchments (Table 4.6), including the two undisturbed catchments, Baldy Creek and Fisher Creek (Figures 4.6-4.8). As significant increases in all three variables occurred in fish captured from all creeks compared to fish captured from Baldy Creek, all increases in these parameters in the subsequent discussion are expressed relative to fish captured from Baldy Creek.

A 2.1-2.9 fold increase in activity normalised to total protein, and a 2.5-4.6 fold increase in EROD turnover number were observed in fish captured from Plantation Creek, Victoria Creek and Seymour River (Table 4.6). EROD activity in fish captured from Seymour River and Plantation Creek was not significantly different from that in fish captured from Fisher Creek.

Table 4.5. Estimates of EROD activity (pmol min^{-1} mg $prot^{-1}$) and EROD turnover number (nmol min^{-1} $nmol^{-1}$ P-450) and P-450 content (nmol P-450 mg^{-1} protein) in sexually inactive male fish collected from undisturbed, sugarcane and urban catchments, and the ratio of disturbed catchments relative to the undisturbed catchments for each of these activities.

Parameter	Catchment grouping		
	undisturbed	sugarcane	urban
No. of fish	40	66	15
EROD activity (pmol min^{-1} mg^{-1} protein)			
mean	88 [a#]	217 [b]	564 [c]
95% CI	71-107	188-249	429 - 742
range	23.2, 229	45, 760	193, 1074
ratio*		2.6	6.4
95% CI		1.9-3.5	4.6-9.1
EROD activity (nmol min^{-1} $nmol^{-1}$ P-450)			
mean	0.41 [a]	1.3 [b]	2.1 [c]
95% CI	0.33-0.52	1.1-1.5	1.6-2.9
range	0.11-0.52	0.32, 5.4	0.91, 4.3
ratio		3.1	5.2
95% CI		2.3 - 4.0	3.6 - 7.5
P-450 content (nmol P-450 mg^{-1} protein)			
mean	0.21 [a]	0.17 [b]	0.26 [a]
95% CI	0.18-0.25	0.15-0.19	0.22-0.32
range	0.12, 0.40	0.03, 0.37	0.14, 0.40
ratio		0.81	1.2
95% CI		0.67 - 1.0	1.0 - 1.6

Values within a row without a common superscript letter are significantly different ($p<0.05$)

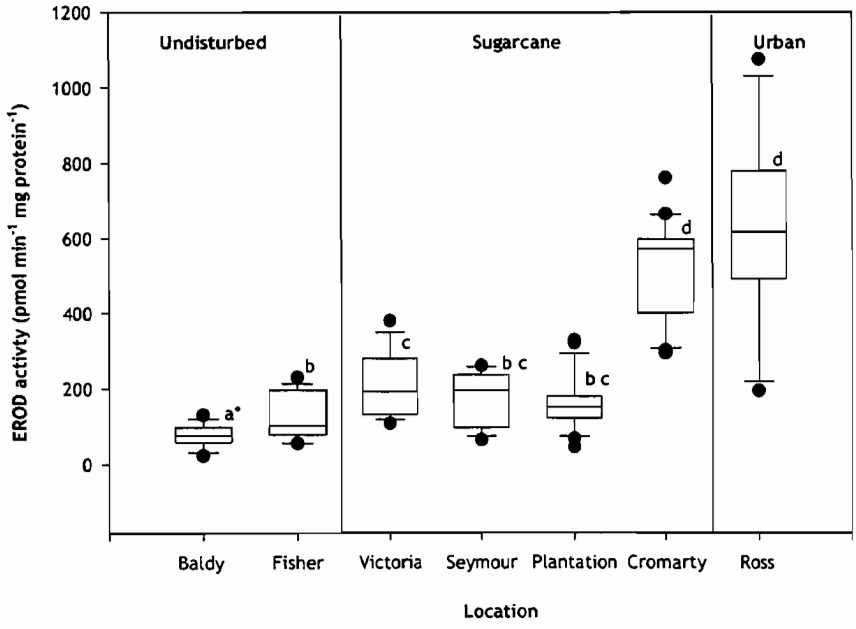
* ratio of activity compared to fish captured from undisturbed catchments

Remarkably high EROD activity was observed in fish captured from Cromarty Creek (7.3-8.6-fold increase, Table 4.6), and was similar to values observed in fish captured from the urban catchment. Fish captured from Ross Creek showed a significant 8.4 fold increase in EROD activity and a significant 7.1-fold increase in turnover number as compared with fish captured from Baldy Creek (Table 4.5, Figures 4.6-4.8). A general trend of decreased total cytochrome P-450 content was observed in all sugarcane creeks, although it was only significant for Plantation Creek and Victoria Creek (both of which have a longer history of agricultural land usage). A slight, although not significant, increased cytochrome P-450 content occurred in fish collected from the urban catchment of Ross Creek.

Table 4.6. Ratio of EROD activity, EROD turnover number and P-450 content in sexually inactive male fish collected from individual catchments and the ratio of each catchment relative to Baldy Creek.

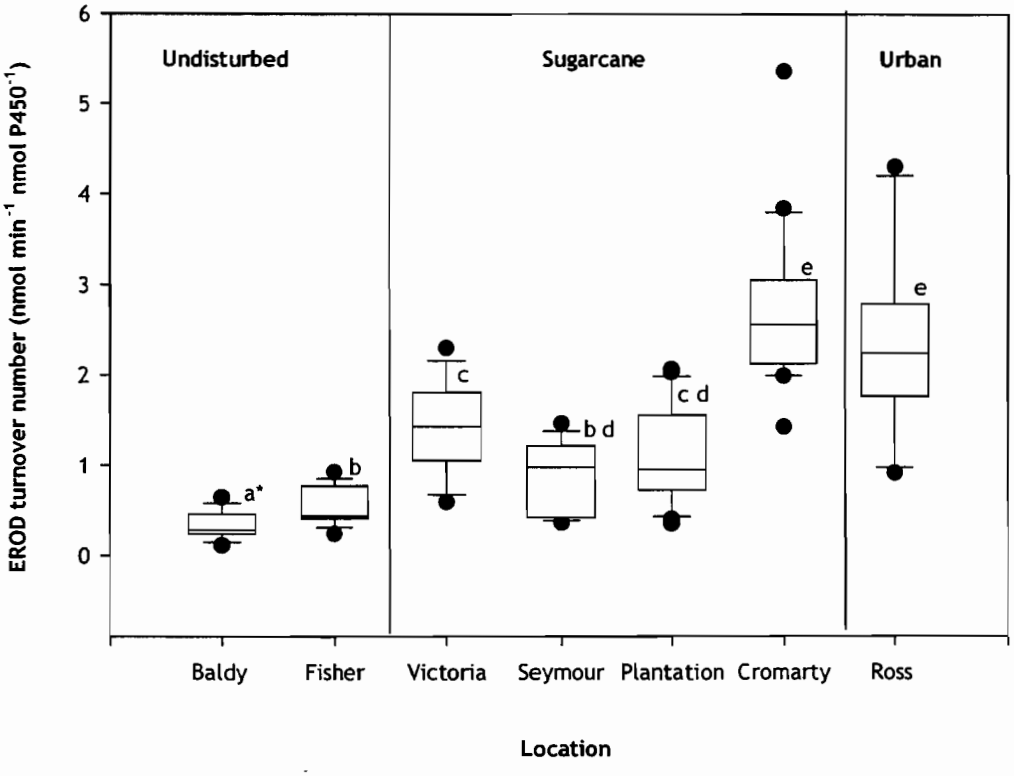
Catchment	No. of fish	EROD activity ratio (95% CI)	Turnover number ratio (95% CI)	P-450 content ratio (95% CI)
Baldy#	14	67 (51-87) (23, 129)	0.31 (0.22-0.40) (0.11, 0.64)	0.22 (0.18-0.27) (0.12, 0.40)
Fisher	7	1.7 (0.9-2.5)	1.9 (1.2-8.4)	0.9 (0.7-1.2)
Victoria	13	2.9 (2.0-4.3)	4.6 (3.1-6.9)	0.6 (0.5-0.8)
Seymour	10	2.4 (1.6-3.6)	2.5 (1.6-3.9)	1.0 (0.7-1.3)
Plantation	17	2.1 (1.5-3.0)	3.2 (2.2-4.6)	0.7 (0.5-0.9)
Cromarty	17	7.3 (5.1-11)	8.6 (5.8-13)	0.8 (0.6-1.1)
Ross	15	8.4 (5.8-12)	7.1 (4.7-11)	1.2 (0.9-1.6)

#Values for Baldy Creek are absolute values (95% CI) and (min, max); EROD activity (pmol min^{-1} mg^{-1} protein); turnover number (nmol min^{-1} nmol $P450^{-1}$), P-450 content (nmol P450 mg^{-1} protein).



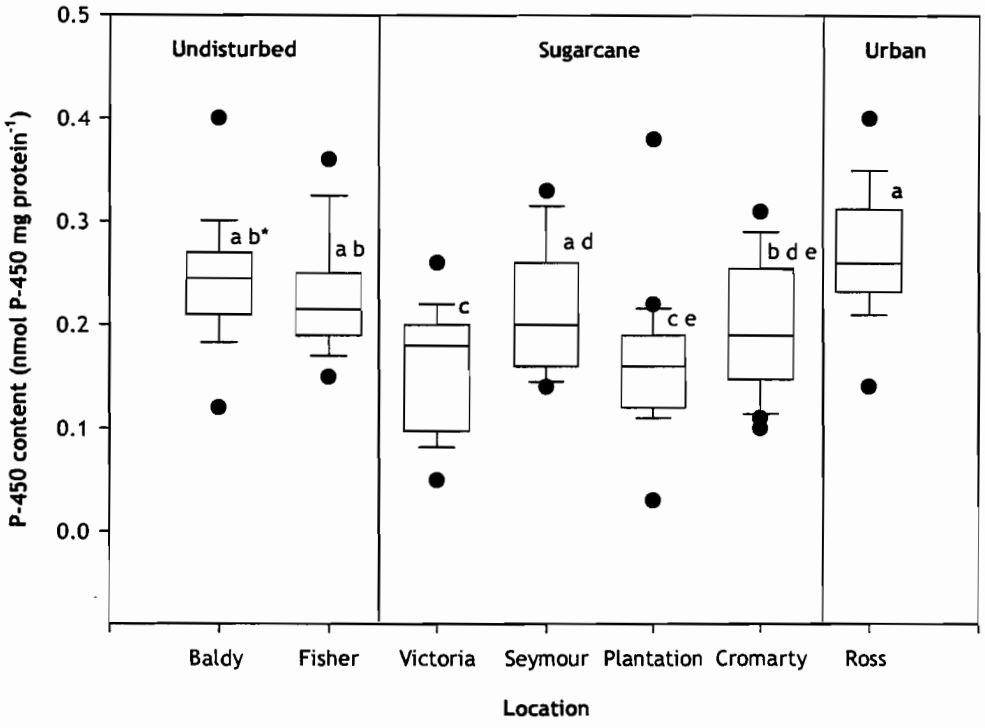
* - boxes without a letter in common are significantly different ($p<0.05$)

Figure 4.6. Box plot of EROD activity (pmol min^{-1} mg^{-1} protein) in fish collected from individual catchments. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.



* - boxes without a letter in common are significantly different ($p<0.05$)

Figure 4.7. Box plot of EROD turnover number (nmol min^{-1} $nmol^{-1}$ P-450) in fish collected from individual catchments. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.



* - boxes without a letter in common are significantly different ($p<0.05$)

Figure 4.8. Box plot of P-450 content (nmol P-450 mg^{-1} protein) in fish collected from individual catchments. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.

4.3.3 Influence of sex, reproductive status, and external lesions on P450 1A activity

Sex and reproductive status had a significant effect on EROD activity and turnover number (Table 4.4), with lower activities observed in females, and reproductively active fish (both males and females; Table 4.7). The influence of reproductive status on EROD activity was particularly evident in the two female fish captured from Fisher Creek, which were within a few hours of spawning, as indicated by hydrated oocytes. EROD activity in these fish was 5.7 and 8.3 pmol min^{-1} mg^{-1} protein (compared to 88 pmol min^{-1} mg^{-1} protein for reproductively inactive female fish from Fisher Creek). This effect was less evident in reproductively active male fish from Fisher Creek in which EROD activity ranged over 21-77 pmol min^{-1} mg^{-1} protein

(compared to 114 pmol min^{-1} mg^{-1} protein for reproductively inactive male fish from Fisher Ck). No significant effect of sex or reproductive status on total P-450 content in *A. berda* was observed in this study (Table 4.4).

Table 4.7. Estimates of EROD activity (pmol min^{-1} mg^{-1} protein), EROD turnover number (nmol min^{-1} $nmol^{-1}$ P-450) and P-450 content (nmol mg^{-1} protein) in sexually active and inactive male and female fish collected from undisturbed, sugarcane and urban catchments.

Catchment grouping	Response			
	Mean (95% CI)			
	Sexually inactive		Sexually active	
	male	female	male	female
EROD activity (pmol min^{-1} mg^{-1} protein)				
undisturbed	87 (71-107)	68 (46-100)	41 (26-66)	17 (10-31)
sugarcane	217 (189-249)	168 (113-251)	102 (59-177)	44 (24-82)
urban	564 (429-742)	438 (272-706)	266 (146-484)	114 (59-224)
EROD activity (nmol min^{-1} nmol-$P450^{-1}$)				
undisturbed	0.4 (0.3-0.5)	0.3 (0.2-0.5)	0.3 (0.1-0.4)	0.1 (0.04-0.15)
sugarcane	1.3 (1.1-1.5)	0.9 (0.6-1.4)	0.8 (0.4-1.4)	0.3 (0.1-0.5)
urban	2.1 (1.6-2.9)	1.6 (0.9-2.6)	1.3 (0.7-2.4)	0.4 (0.2-0.9)
P-450 content (nmol P-450 mg^{-1} protein)				
Undisturbed	0.21 (0.18-0.24)	0.23 (0.17-0.30)	0.17 (0.11-0.24)	0.20 (0.13-0.30)
sugarcane	0.17 (0.15-0.19)	0.18 (0.13-0.24)	0.14 (0.09-0.20)	0.16 (0.10-0.26)
urban	0.26 (0.21-0.32)	0.28 (0.20 -0.40	0.21 (0.13-0.33)	0.25 (0.15-0.41)

Some fish collected from Victoria Creek and Seymour River had external lesions (Table 4.2). These fish were examined by officers of the Queensland Department of Primary Industries and Fisheries who diagnosed 1 fish from Victoria Creek and 2 fish from Seymour River as showing indications of epizootic ulcerative syndrome (EUS). The remainder of fish had bacterial lesions that were thought to be first stage EUS. Significantly lowered EROD activity ($p = 0.001$) and lower, although not statistically significant, total cytochrome P-450 content ($p = 0.08$) occurred in fish with lesions. No significant difference in turnover number was

observed (p = 0.3) indicating that the lowered EROD activity was probably due to reduced production of cytochrome P-450 1A enzyme.

4.3.4 General parameters

Liver somatic index (LSI) and condition factor (CF) varied among different catchments and no trends were evident (Figures 4.9-4.11). With the exception of fish captured from a spawning aggregation, the gonado-somatic index (GSI) for males was less than 0.2, and for females less than 0.7 (*Table H.2*). In fish captured from the spawning aggregation (Fisher Creek), GSI ranged between 0.5-0.6 (males) and 2.5-7.3 (females). Tissue lipid content was variable and showed no correlation with EROD activity or condition factor.

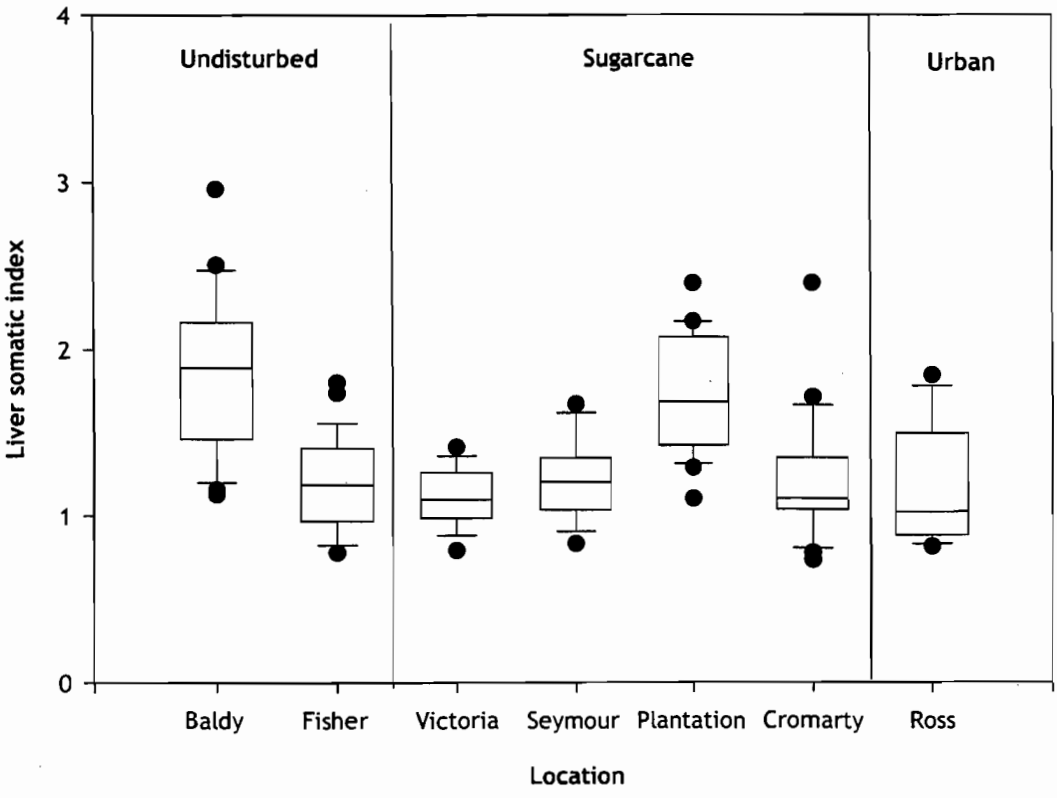


Figure 4.9. Box plot of liver somatic index (LSI) in fish collected from sample locations. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.

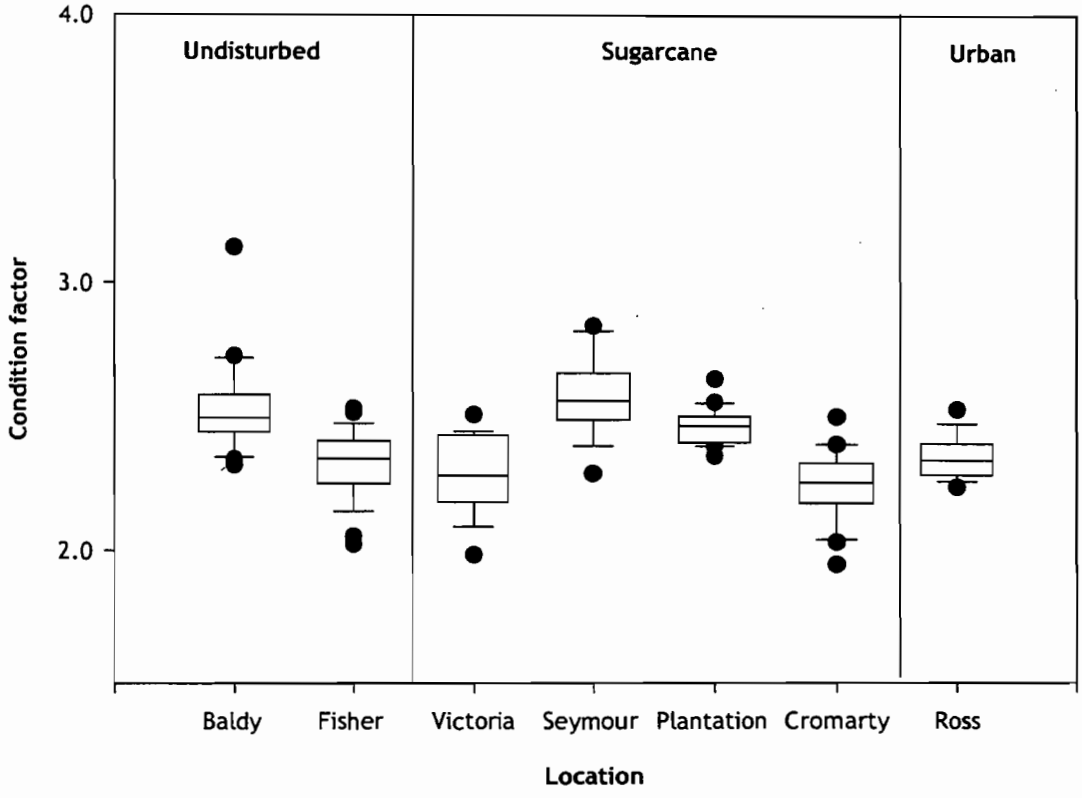


Figure 4.10. **Box plot of condition factor in fish collected from sample locations. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.**

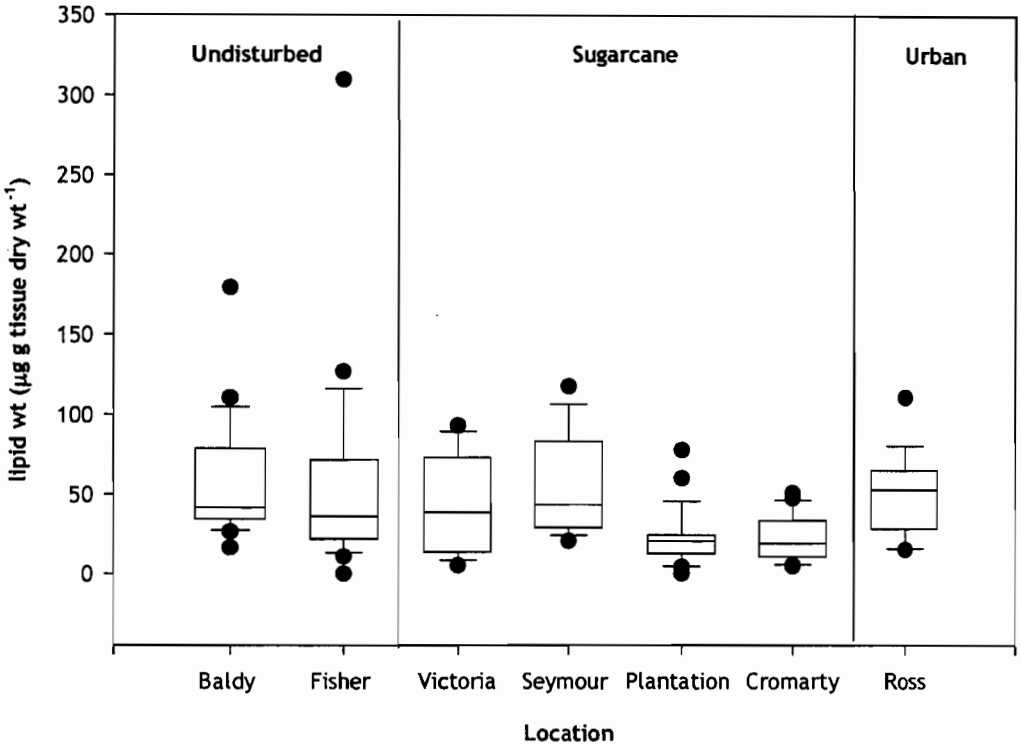


Figure 4.11. Box plot of muscle tissue lipid content (µg g tissue dry wt^{-1}) in fish collected from sample locations. Edges of box show 25th and 75th percentile of data, whiskers show 10th and 90th percentile, solid line indicates median value, solid dots are individual data points lying outside 5th and 95th percentile of data.

PAH and organochlorine concentrations in fish tissue, creek sediments, and selected soil samples surrounding the creeks are shown in Tables 4.8-4.13. There was a low incidence of detection of organochlorine residues in the muscle tissue of fish collected from creeks draining agricultural and undisturbed catchments, with dieldrin being the most frequently detected compound (Table 4.8). Fish collected from Ross Creek had a higher incidence of detection, and generally higher concentrations, of organochlorine residues than fish collected from the agricultural catchments. Interference with lipid material during PAH analysis of fish tissue generally did not enable quantitation of these compounds (Table 4.9). Generally, a greater range of PAHs was detected in fish collected from creeks draining the sugarcane fields, although no trend in the incidence of detection of PAHs in fish collected from these creeks compared to those collected from Ross Creek was readily obvious from the analyses (Table 4.9).

Table 4.8. Incidence of detection and concentration of organochlorine residues (μg mg^{-1} lipid wt) in muscle tissue of fish collected from undisturbed, agricultural and urban catchments.

Compound	Organochlorine concentration (μg mg^{-1} lipid) (incidence/ number of samples)		
	Undisturbed	*Sugarcane*	*Urban*
HCB	nd	nd	nd
α-HCH	nd	nd	nd
lindane	nd	0.02 (1/16)	nd
aldrin	nd	nd	nd
dieldrin	nd	<0.01-2.1	0.18-0.5 (3/4)
heptachlor	nd	0.02-0.035 (2/16)	nd
heptachlor epoxide	nd	nd	0.02(1/4)
DDE	nd	nd	0.06-0.31 (3/4)
DDD	nd	nd	0.05-0.11 (2/4)
DDT	nd	nd	0.04-0.060 (2/4)
endosulfan I	nd	0.035 (1/16)	nd
endosulfan II	nd	nd	0.12-30.1 (3/4)
cis-chlordane	nd	nd	nd
trans-chlordane	nd	nd	nd

nd - not detected

Table 4.9. Incidence of detection and concentration of PAHs (μg mg^{-1} lipid) in muscle tissue of fish collected from undisturbed, agricultural and urban catchments.

Compound	Concentration (μg mg^{-1} lipid) (Incidence of detection/number of samples)		
	Undisturbed	*Sugarcane*	*Urban*
Naphthalene	nd	nd	nd
Acenapthylene	nd	nd	nd
Acenapthene	nd	nd	nd
Fluorene	nd	nd	nd
Phenanthrene	NQ (1/4)	NQ (9/16)	nd
Anthracene	nd	NQ-0.01 (3/16)	nd
Fluoranthene	NQ (3/4)	NQ (7/16)	NQ (4/4)
Pyrene	NQ (3/4)	NQ (10/16)	NQ (3/4)
Benzo (a) anthracene	nd	NQ-0.79 (2/16)	NQ-7.9 (2/4)
Chrysene	nd	nd	nd (1/4)
Benzo (b&k) fluoranthene	0.115 (1/4)	NQ (2/16)	NQ (2/4)
Benzo (e) pyrene	nd	NQ (1/16)	nd
Benzo (a) Pyrene	nd	NQ (2/16)	NQ (2/4)
Perylene	nd	nd	nd
Indeno (1,2,3- c,d) pyrene	nd	nd-7.4 (1/16)	nd
Dibenzo (a,h) anthracene	nd	nd	nd
Benzo (g,h,i) perylene	nd	nd	nd

nd - not detected; NQ-not quantified

Variable low concentrations of organochlorine residues were detected in creek sediments (Table 4.10). Higher concentrations were present in sediments collected from Ross Creek, which also showed high concentrations of oil, as determined by UVF analysis, and PAHs compared with sediments from other creek systems (Figure 4.12, Tables 4.11). Low and variable concentrations of oil and individual PAHs occurred in sediment collected from the other creeks (Table 4.10). Sediment samples collected from Cromarty Creek and Plantation Creek (Burdekin region) showed lower concentrations of oil and PAHs as compared with that collected from Victoria Creek and Seymour River (Herbert region) (Table 4.8). In contrast, sugarcane soils collected from the Burdekin region showed higher concentrations of PAHs than soils from the Herbert region (Table 4.11).

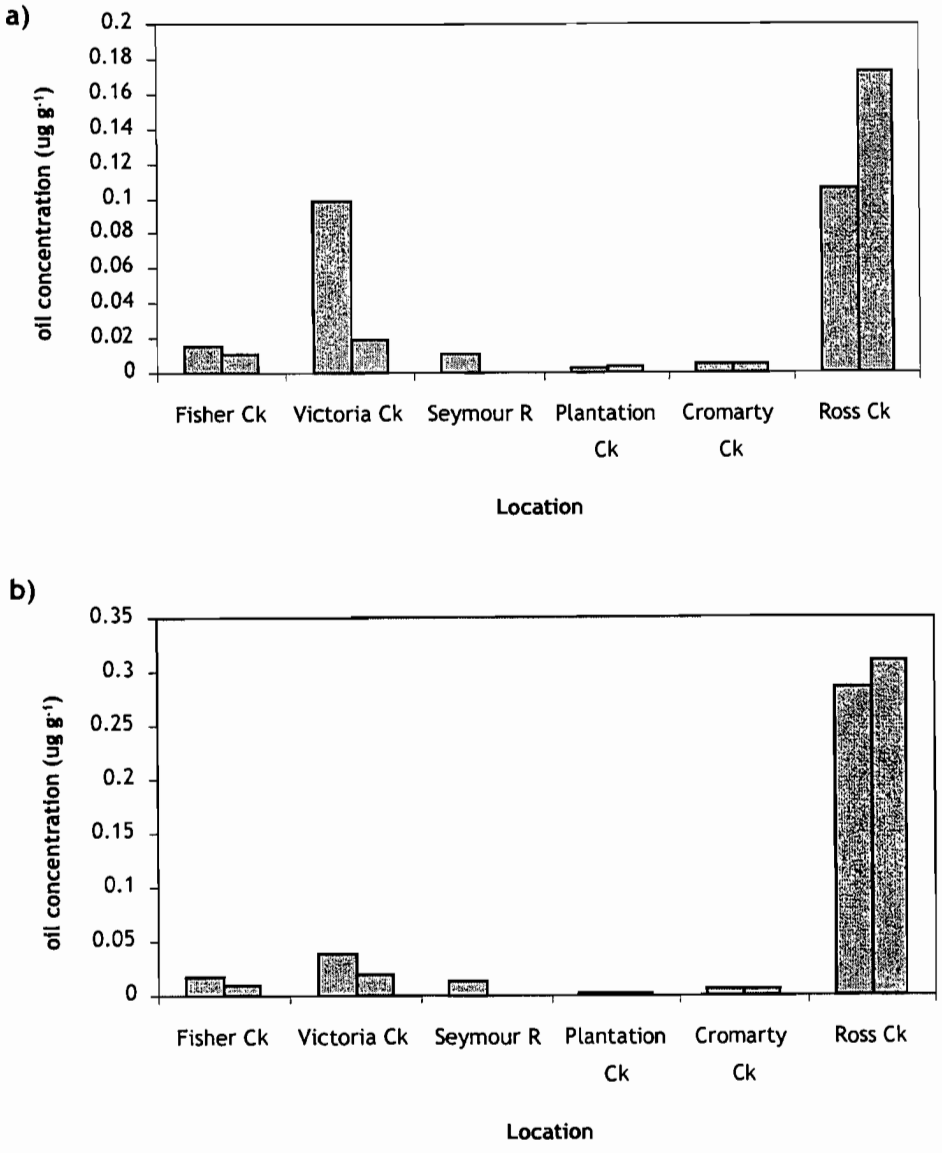


Figure 4.12. Concentration of oil (μg g^{-1}) in creek sediments as determined by UVF and standardisation of readings to a) a light Australian crude oil (Harriett A), and b) a light Arabian crude oil (ROPME).

Table 4.10. Concentration (ng g^{-1}) of organochlorine compounds in samples collected from the study creeks, and sugarcane soils of the Herbert and Burdekin regions.

Compound	Concentration (ng g^{-1})							
	Fisher Ck	*Victoria Ck*	*Seymour R*	*Plantation Ck*	*Cromarty Ck*	*Ross Ck*	*Herbert soils**	*Burdekin soils**
α-HCH	<0.010	<0.010	0.055	<0.010	<0.010	<0.010	<0.010-6.00	<0.010-0.739
β-HCH	<0.010-0.082	0.035-0.085	0.085	<0.010	0.035-0.038	<0.010	<0.010-45.6	<0.010-2.65
γ-HCH	<0.010	<0.010	0.065	<0.010	<0.010-0.033	<0.010	<0.010-3.99	<0.010-1.65
δ-HCH	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010-2.77	<0.010-1.26
heptachlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010-0.146	<0.010-0.207
heptachlor epoxide	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010-0.290	<0.010-18.2
trans-chlordane	<0.010-0.032	<0.025-0.031	0.064	0.021-0.028	0.028-0.048	1.19-2.68	<0.010-0.146	<0.010-10.1
cis-chlordane	<0.010	<0.010	0.066	<0.010	<0.010	0.373-0.995	<0.010-2.87	<0.010-2.75
aldrin	<0.010	<0.010	0.049	<0.010	<0.010	<0.010-0.180	<0.010- 0.850	<0.010-0.112
dieldrin	0.092-0.200	0.185-0.197	0.153	<0.010-0.027	0.074-0.079	3.86-8.19	0.029-27.6	<0.010-3.68
p, p'- DDE	<0.010	<0.025-0.056	<0.010	<0.010	<0.010	<0.010-4.98	<0.010-6.217	<0.010-27.8
p, p'-DDD	<0.010	0.039-0.060	0.052	<0.010	<0.010-0.043	1.60-7.93	<0.010-0.433	<0.010-0.629
p, p'-DDT	<0.010-0.054	<0.025-0.038	<0.010	<0.010	<0.010	2.05-3.19	<0.010-0.411	<0.010-1.53
chlorpyrifos	<0.010-0.031	0.120-0.170	0.274	<0.010	<0.010-0.038	0.838-1.14	<0.010-37.325	<0.010-63.9
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010-0.040
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010-0.363
endosulfan sulfate	<0.010- 0.067	<0.010	0.089	<0.010	0.033-0.040	<0.010	<0.010-0.095	<0.010-0.159
EOM (mg g^{-1})	0.31-0.41	0.24-0.83	0.250	0.05-0.06	0.16-0.20	0.82-1.0	0.01-9.3	0.01-1.5
organic carbon (%)	3.0-3.5	2.2-4.1	3.1	0.7-0.9	2.1-2.2	0.99-2.1	0.51-2.3	0.31-0.95
n	2	2	1	2	2	2	18	23

*results from Table 2.3.

Table 4.11. Concentration (ng g^{-1}) of polycyclic aromatic hydrocarbons (PAH) in samples collected from the study creeks, and sugarcane soils of the Herbert and Burdekin regions.

Compound	Concentration (ng g^{-1})							
	Fisher Ck	*Victoria Ck*	*Seymour R*	*Plantation Ck*	*Cromarty Ck*	*Ross Ck*	*Herbert soils*	*Burdekin soils*
acenapthylene	<0.02	<0.02	<0.02	<0.02	<0.02	0.10-0.26	<0.02	<0.02
Σc2/c3 napthalenes	<0.02	0.04	0.06	<0.02	0.02-0.03	0.84-1.5	<0.02	<0.02
fluorene	<0.02	<0.02	0.06	<0.02	<0.02	0.04-0.11	<0.02	<0.02
c1 fluorene	<0.02	<0.02	<0.02	<0.02	<0.02	0.28-0.78	<0.02	<0.02
phenanthrene	<0.02-0.04	0.02-0.03	0.04	<0.02	<0.02-0.04	0.73-0.86	<0.02	<0.02-0.04
anthracene	<0.02	<0.02	<0.02	<0.02	<0.02	0.18-0.30	<0.02	<0.02
Σc1/c2/c3 phenanthrenes/anthracenes	<0.02	0.02	<0.02	<0.02	<0.02	3.5- 5.2	<0.02 -0.07	<0.02-0.13
fluoranthene	0.02-0.06	0.05	0.06	<0.02	0.03-0.09	2.8-3.1	<0.02	<0.02-0.10
pyrene	<0.02	0.04-0.05	0.06	<0.02	<0.02-0.05	2.2	<0.02	<0.02
c1 pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	1.9-2.5	<0.02	<0.02
benzo (g,h,i) fluoranthene	<0.02	0.09	<0.02	<0.02	<0.02	0.12-0.25	<0.02	<0.02
benzo (a) anthracene	<0.02	0.03	<0.02	<0.02	<0.02	1.6-1.8	<0.02	<0.02
chrysene	<0.02	<0.02	<0.02	<0.02	<0.02	2.4-3.4	<0.02	<0.02-0.05
benzo (b) fluoranthene	0.02-0.11	0.06-0.07	0.05	<0.02	0.05-0.07	2.5-4.3	0.02	<0.02-0.06
benzo (k) fluoranthene	<0.02	<0.02	<0.02	<0.02	<0.02	0.65-1.1	<0.02	<0.02
benzo (a) pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	3.5-6.1	<0.02	<0.02
perylene	<0.02	<0.02	<0.02	<0.02	<0.02	0.74-1.7	<0.02	<0.02
indeno (1,2,3, c,d) pyrene	<0.02	<0.02	<0.02	<0.02	<0.02	4.5-11	<0.02	<0.02
dibenzo (a,h) anthrancene	<0.02	<0.02	<0.02	<0.02	<0.02	2.3-8.1	<0.02	<0.02
benzo (g,h,i) perylene	<0.02	<0.02	<0.02	<0.02	<0.02	3.7-8.4	<0.02	<0.02
n	2	2	1	2	2	2	4	3

4.4 Discussion

4.4.1 Induction of P450 in *A. berda* during laboratory trials

EROD activity, turnover number, and ECOD activity did not respond linearly to increasing doses of BNF in the fish used in the laboratory trials. Quadratic dose-response relationships have been observed due to inhibition of P-450 1A activity at high doses of an inducing agent, which has been attributed to an inability of cells to metabolise inducing agents (Denison and Heath-Pagliuso, 1998). Thus, the quadratic relationships observed for EROD and ECOD activity may be a result of inhibition at higher doses of BNF. Alternatively, the fish dosed at 80 mg kg^{-1} may have received a lower dose than expected. At the concentrations of BNF in corn oil required to dose fish at this level, it was necessary to keep the corn oil warm (50°C) in order to keep BNF in solution. BNF may have come out of solution after injection, which would presumably reduce uptake and therefore, the effective dose.

The significant dose-response of EROD and ECOD to the HCH mixture indicated that induction of the P-450 1A system in *A. berda* did occur as a result of exposure to HCH. However, the biological significance of these responses could not be interpreted, as they were neither linear nor quadratic. The linear dose-response of P-450 content was opposite to that expected, as P-450 content decreased with increasing HCH dose. While further work is needed to characterise the response of P-450 1A in *A. berda* to HCH exposure, it is interesting to note that currently no biomarkers are available to assess biological exposure to HCH isomers (Willett *et al.*, 1998).

The post-mitochondrial supernatant fraction (S9) has been used in previous studies of P-450 1A response (Hodson *et al.*, 1991; Flammarion and Garric, 1997) and was used during initial laboratory trials to assess its application for further work. However, the low EROD activity observed during the laboratory trials (Figures 4.5 and 4.6), and the demonstrated higher response of the microsomal fraction (*Figure G.1c*) resulted in use of the purified microsomal protein during the field studies to increase the sensitivity of the assay. ECOD activity was also investigated as a biomarker for the response of P-450 1A activity, however it was demonstrated to be a less sensitive measure of response. This result has also been previously observed in studies of other fish species (Zhang *et al.*, 1990). Therefore, ECOD responses were not determined in the field studies.

4.4.2 Sources of induction of P-450 1A in *A. berda*

The observed induction of cytochrome P-450 1A in *A. berda* captured in catchments disturbed by agricultural or urban activity, suggest that the fish have been exposed to inducing agents as a result of disturbance from sources including boating activity, and agricultural and urban run-off. The first step in elucidating the sources of inducers of cytochrome P-450 1A is the identification of the inducers. A wide range of chemicals can induce cytochrome P-450 1A.

The best known inducers are planar PCBs, chlorinated dibenzodioxins and furans, and PAHs, primarily those with 3 or more benzene rings (Stegeman and Hahn, 1994). A recent study also identified a wide range of "non-classical" inducers including brevetoxin and the insecticide, carbaryl (Denison and Heath-Pagliuso, 1998). Despite this wide range of possible inducers, a recent study suggested that exposure to PAHs, particularly benzo (b) fluoranthene and benzo (k) fluoranthene, was likely to be the major factor in environmental induction of cytochrome P-450 1A in fish collected from coastal regions of the USA (Gardinali and Wade, 1998). A number of other studies have also suggested that PAHs are the primary source of induction in fish (e.g. Spies *et al.*, 1982; Livingston *et al.*, 1993; Woodin *et al.*, 1997).

The high concentrations of PAHs, including benzo (b) fluoranthene and benzo (k) fluoranthene, in sediments from Ross Creek (Table 4.11) suggests that PAHs are likely to contribute significantly to induction of P-450 activity in fish collected from this system. The low concentrations of PAHs in the other creek systems may also account for the low level of induction in fish collected from these creeks, with the exception of Cromarty Creek. The inducer present in this creek was not identified.

Despite indications from the laboratory trials that inhibition of P-450 activity in *A. berda* may occur at high doses of inducers, no apparent inhibition occurred in fish collected during the field study. Fish were collected from Ross Creek, which was known to be highly contaminated with a wide range of contaminants, including high concentrations of PAHs, (Smith *et al.*, 1985; Kross 1997; Inglis and Kross, 2000) to provide an "environmental maximum" response. Fish collected from this catchment showed the highest level of activity, and contained the highest concentrations of organochlorine residues (Table 4.8). Sediment collected from Ross Creek also contained the highest concentrations of PAH and organochlorine residues (Tables 4.10 and 4.11). The low concentrations of PAHs in muscle tissue of fish collected from Ross Creek is not surprising, despite the high concentrations present in the sediment, given the known ability of fish, and other organisms, to metabolise PAHs (Van der Oost *et al.*, 1994).

Comparison of the relative induction observed in *A. berda* with that observed in other studies using different species is confounded by species-specific differences in cytochrome P-450 1A activity and in sensitivity to inducing agents. Up to one hundred-fold differences in levels of EROD activity between different species captured from one location may be observed (eg. Van der Oost *et al.*, 1991; Spies *et al.*, 1996; Stegeman *et al.*, 1997). Within one species, the relative increase in EROD may range between 2 - 30 fold (eg. Stegeman *et al.*, 1990; Ahokas *et al.*, 1994; Holdway *et al.*, 1995; Spies *et al.*,1996;) for sites considered to be moderately to highly polluted and 1.5-30 fold for sites considered to be low to moderately polluted (eg. Stegeman *et al.*, 1990; Vroljik *et al.*, 1994; Flammarion and Garric 1997). Thus, it is difficult to use of the relative induction of cytochrome P-450 1A in *A. berda* as an indicator of the degree of pollution.

4.4.3 Sources of inducers of cytochrome P-450 1A

Given the location of Ross Creek in the centre of Townsville, and the considerable boating and shipping activity that occurs in this creek, PAHs detected in Ross Creek sediment are likely to be derived from urban run-off, boating and shipping activities.

Sources of PAHs in the other creek systems are less obvious. The major source of PAHs to the coastal environment surrounding heavily urbanized areas of the USA has been attributed to atmospheric deposition of PAHs formed by the combustion of fossil fuels (Collier *et al.*, 1998). While the coastal regions of north Queensland cannot be considered to be heavily urbanized, pre-harvest burning of sugarcane, burning of native vegetation either through fire control measures or natural bushfires, and combustion of fossil fuels (e.g. trucks, cars), could constitute a significant source of atmospheric PAHs. PAHs and dioxins have been found in sugarcane soils (Mueller *et al.*, 1996a). However, the fish analysed were collected prior to the sugarcane harvest season (June-December). Therefore, the contribution of contaminants derived from atmospheric deposition of residues from the burning of sugarcane at the time of fish collection was minimal and limited to movement of soils containing residues deposited during the previous harvest season, into the creek system. However, there is likely to be some contribution from atmospheric deposition of other volatilised residues from urban activities, in particular the use of fossil fuels (e.g. diesel and gasoline combustion).

Lower concentrations of PAHs were present in sediments collected from creeks in the Burdekin region (Cromarty Creek and Plantation Creek) compared with sediment collected from creeks in the Herbert region (Victoria Creek and Seymour River), despite the predominance of pre-harvest burning of sugarcane in the Burdekin region. This may be attributed to the prevailing south-east trade winds that occur during the time of sugarcane harvest (June-December), which may result in shifting the area of deposition of volatilised residues to the north-west of the fires, and away from the coastal streams. Alternatively, the low concentrations of PAHs in creeks from the Burdekin region may be a reflection of local hydrological regimes. Plantation Creek has a freshwater wetland situated above the location of fish collection, and it may trap contaminants associated with erosion of soils elsewhere in the catchment. Cromarty Creek is located in a local sedimentary basin and has limited movement of sediments within the system.

Another source of PAHs within the creek systems is boating activity. One previous study of PAH in sediments of the Great Barrier Reef lagoon suggested that boating activity was the major source of PAHs in the sediment (Smith *et al.*, 1985). Recreational boating is a popular activity in many of the study creeks and commercial fishing activities also occur in Victoria Creek. As such, boating activities may represent an important source of inducers in the study creeks.

Another source of contaminants to the study creeks is movement of sediment into the creeks by a combination of tide-driven landward movement of sediment and long-shore sediment drift (Bryce *et al.*, 1998; Larcombe and Ridd, 1996). This sediment may originate as terrrigenous sediment from rivers further south, or coastal sediments that contain atmospherically deposited residues. The contribution of sediment, and hence sediment-bound contaminants, from such sources, relative to inputs from land-use within local creek catchments, will depend on the degree of tidal flushing within a given creek system; the process is likely to have a greater influence in the lower reaches of an estuary.

The remarkably high P-450 1A activity observed in fish collected from the Cromarty Creek catchment was unexpected. This catchment has a relatively small area disturbed by sugarcane growing than most of the other sugarcane catchments and this land-use is located in the upper regions of the catchment. Additionally, boating activity in Cromarty Creek is no greater than that in creeks draining the other sugarcane catchments. However, it is of interest to note that a rubbish dump, which has received domestic waste, including waste oil, from the town of Giru for over 15 years is located within the Cromarty Creek catchment. Additionally, Cromarty Creek is located within an extensive wetland area and has an unusual hydrological regime (G. Blackman, EPA, pers. comm.), which may be important in determining the exposure of fish to contaminants within this system.

Depending on the source of the inducer in this creek, the observed results may have been due to transient exposure to an inducer. Alternatively, chronic exposure may be occurring. Removal of fish from the source of inducers can result in return of cytochrome P-450 1A to basal levels over a period of 3 weeks (Woodin *et al.*, 1997), although this time-frame will depend on the nature of the inducing agent. Therefore collection of fish at another time could provide an indication of whether transient or chronic exposure to inducers is occurring, and could aid in the identification, and/or the source, of the inducer.

4.4.4 Induction in *A. berda* and relationship to organochlorine exposure

Biological variables (such as sex, spawning status, age) will influence cytochrome P-450 1A activity in fish (Stegeman and Chevion, 1980; Koivussaari *et al.*, 1981; Jiminez and Burtis, 1989). Reduced P-450 1A activity and content is generally observed in females and reproductively active fish (Förlin *et al.*, 1984; Stegeman and Woodin, 1984; Lindstom-Seppa, 1985; Edwards *et al.*, 1988). Reduced activity is generally attributed to the suppression of production of P-450 1A by estradiol-17 β, which is reflected in a lower total P-450 content, (Förlin and Lidman, 1982; Förlin *et al.*, 1984; Stegeman and Hahn, 1984). The magnitude to which these factors influence cytochrome P-450 content and P-450 1A activity in different

species is variable (Förlin, 1980, Koivusaari *et al.*, 1981; Förlin *et al.*, 1984; Lindstöm-Seppa, 1985; Brumley *et al.*, 1995). The present study was not aimed at characterising the effects of sex and reproductive status on P-450 1A activity in *A.berda*. However, the capture, and subsequent analysis, of female fish and reproductively active fish, indicated these fish generally showed lowered P-450 1A activity, although not lower P-450 content (Table 4.7).

Central to the interpretation of environmental induction of P-450 1A in fish as an indicator of the degree of exposure to organic contaminants, is that different compounds elicit different responses. The response depends on the potency of the compound to induce the P-450 1A system, as well as any toxicological effects observed as a result of exposure. Toxicological effects may be mediated by the P-450 system or by unrelated mechanisms. The former includes production of more toxic metabolites (such as for some PAHs; Varanasi *et al.*, 1989), persistent activation of gene expression (such as TCDD; Denison and Heath-Pagliuso, 1998) and reproductive interference by increased clearance of steroids through induction (Kupfer and Bulger, 1980). Alternatively, toxicological effects, such as hepatic lesions and endocrine disruption by environmental estrogens, may occur by mechanisms unrelated to induction of P-450 1A. Whether the toxicological effects observed in fish are mediated by the P-450 system, or by an unrelated mechanism, is dependent upon the inducing agent and/or, in the case of environmental exposure, a co-occurring chemical. Also of note is a recent study that showed a lowered response of P-450 1A of a fish species, *Fundulus heteroclitus*, collected from a highly contaminated location (Elskus *et al.*, 1999). This lowered response was suggested to indicate the development of resistance to chemical inducers.

Alternatively, induction of the P-450 1A system may occur without any detrimental toxic effect. A number of studies have examined correlations between P-450 1A activity and contaminants, either in sediment or body burdens, and/or various indices of fish health (e.g. Goksøyr *et al.*, 1992; Schlenk *et al.*, 1996, Meyers *et al.*, 1998). Unsurprisingly, the results have been variable. For example, Goksøyr *et al.* (1992) found no correlation between PCB concentration and P-450 1A content, but strong correlation between *o, p'*-DDD and DDT with P-450 content. This is despite the fact that the DDT group have been shown not to induce the P-450 system in fish, while numerous PCBs do (Goksøyr *et al.*, 1992). Schlenk *et al.*, (1996) found that healthy fish (as assessed by a health assessment index) showed increased P-450 1A content, while no correlation was found between fish health and EROD activity. In contrast, Meyers *et al.* (1998) found a significant positive correlation between increased P-450 1A activity and increased incidence of hepatic lesions. Similarly, Hodson *et al.* (1992) found a positive correlation between fish health and P-450 1A activity. In the present study, external lesions were found on fish collected from Seymour River and Victoria Creek and indicated that EROD activity was reduced by lowered production of cytochrome P-450 1A. The cause of these lesions was not identified.

In the present study, the liver somatic index and condition factor varied between the catchments, and no trends in relation to land-use or EROD activity were apparent. The condition factor can provide an indication of nutritional status of the fish (Kirby *et al.*, 1999) with a high condition factor indicating well-fed fish. Muscle tissue lipid content may also reflect the nutritional status of a fish with a high lipid content indicating a fish with considerable fat reserves. Organic contaminants that have been absorbed by the fish are stored in fatty tissue, are metabolised slowly and are toxicologically relatively inert. However, under conditions of starvation, fat reserves and hence stored contaminants within the fish are mobilised and the contaminants become toxicologically active and available for metabolism. No correlation between tissue lipid content and condition factor or EROD activity was observed in the present study. Additionally, the low number of detections of PAH and organochlorine residues in fish tissue did not allow correlation of any of these parameters with EROD activity to be established.

The low concentrations of organochlorine residues detected in sediments and fish tissue suggest that the relative contribution of organochlorine insecticide residues to organic contaminant exposure in the sampled fish is low. Given this, and the presence of other inducing agents, it is unlikely that a correlation between organochlorine concentration and EROD activity would be observed in these systems.

4.5 Conclusions

The present study demonstrated the induction of the P-450 1A system under controlled conditions, in an Australian tropical estuarine fish species, *Acanthopagrus berda*, by β-napthoflavone and a mixture of hexachlorocyclohexanes. The post-mitochondrial supernatant (S9) yielded lower enzyme activity than the purified microsomal protein and contributed to the variable results attained in the laboratory experiments. Further work using microsomal protein should be undertaken to fully characterise the nature of the response to exposure by β-napthoflavone and a mixture of hexachlorocyclohexanes, and to interpret its biological significance. The present study illustrated the successful application of P-450 1A induction to identify locations where organic contaminants might be causing potential stress to fish. As the contribution of organochlorine insecticide residues to the total organic contaminant exposure of fish is indicated to be low, P-450 1A induction is unlikely to be a suitable indicator of the exposure of fish to organochlorine residues in the study locations.

PAHs are suggested to be the cause of induction of P-450 1A in fish collected from Ross Creek and, with the exception of fish captured from Cromarty Creek, PAHs may also account for the low level of induction of P-450 1A observed in fish collected from the agricultural catchments. The relative contributions of different sources of inducing agents (such as atmospheric deposition, boating activity, and land-use) were not elucidated. However, it is suggested that the contribution of contaminants derived from land use in agricultural

catchments may not be as significant as the contribution by boating activities or sediment derived from coastal systems. The remarkably high EROD activity observed in fish captured from Cromarty Creek was unexpected and may suggest the importance of local hydrological regimes in determining exposure of fish to contaminants. The cause of induction was not identified and warrants further investigation.

Sex, reproductive status, and fish health were demonstrated to influence P-450 1A activity in *A. berda* both during laboratory trials and field studies. This highlights the necessity for either characterising the influence of these variables, or targeting sampling during field studies so that the influence of these variables is minimal during assessment of temporal trends in P-450 1A activity in *A. berda*.

The present study has demonstrated the potential application of cytochrome P-450 1A induction in *Acanthopagrus berda* as a useful biomonitoring tool for assessing the general organic contaminant exposure of fish collected in the coastal environment of tropical Australia, and provides some preliminary baseline information on the levels of environmental induction of P-450 1A in this species.

Publications

The majority of the data relating to the field studies performed forms the basis of the paper by Cavanagh *et al.* (2000; Appendix I.2)

Chapter 5: Factors influencing insecticide usage in the sugar industry

5.1 Introduction

At the most obvious level, control of insect pests is the major factor driving insecticide usage. However, the choice of the insecticide used and, indirectly, the method of control of an insect pest, are driven by a combination of environmental, economic, and social factors. These factors may be considered in the context of risk, where risk is the probability of a detrimental outcome. In the context of insect control in sugarcane, economic risks are those relating to insect pest control, in terms of efficacy and cost of control, or probability of insect damage. Ecological risks are those relating to ecological impact of control methods, such as mortality or sub-lethal effects on non-target organisms. Human health risks are those that result in detrimental human health impacts to either farm-workers or the wider community through consumption or occupational exposure to insecticides. Economic and ecological risks associated with insect control will generally be regionally specific as a consequence of climatic and geographic variability between regions. Hence the relative importance of different insect pests and control techniques employed is also regionally specific. In contrast, human health risks will largely be independent of region given that the types of potential detrimental impacts are the same for a given insecticide and the magnitude of risk is mainly influenced by the number of people affected in each region. Control measures include not only insecticides but other measures such as cultural and biological control. Adequate assessment of the risks associated with insecticide usage should integrate the economic, ecological, and human health risks associated with each form of control.

Risk assessment is a tool to facilitate informed decision-making (Beer and Ziolkowski, 1995). It can be undertaken at a number of different levels, for example assessment of adverse ecological impacts resulting from insecticide use, or setting environmental priorities at a government policy level. Risk assessment has been used increasingly in the United States and Europe as the basis for environmental management and prioritising environmental issues (Beer and Ziolkowski, 1995; US EPA 1997a-c; US EPA, 1998; Power and McCarty, 1998). Although there is debate about how to best apply it, there is a general consensus that risk assessment is useful in assisting decision-making (Graham and Weiner, 1995; Adams and Power, 1997). Similarly in Australia, there is a general consensus that risk assessment is necessary (Norton *et al.*, 1996) however, its use in current environmental decision-making is almost non-existent. There are "risk-based" draft water quality guidelines (ANZECC, 1999), but only two policy documents pertaining to environmental risk assessment. These are an

Australian standard (AS/NZS, 1999), which provides a generic framework for risk management, and a draft National framework for ecological risk assessment of contaminated sites (Environment Australia, 1997). Additionally, only a few Australian studies have applied risk assessment in an environmental context (Burgman *et al.*, 1999; Harris *et al.*, 1999; van Dam *et al.*, 1999; Walker and Nowak, 1999).

Quantitative assessment is an important aspect of risk assessment, and numerous methodologies exist (e.g. Assmuth, 1996; Thompson and Graham, 1996; Landis and Weigers, 1997; US EPA, 1997b; US EPA, 1998; Havens *et al.*, 1998; Giesy *et al.*, 1999; Krystofowicz, 1999). It is beyond the scope of this chapter to discuss the attributes of different methodologies other than to note that quantitative assessment requires the construction of a model that describes the inputs and variables that influence target risks. However, as with all models, the usefulness of the answers obtained by a risk assessment model is only as good as the construct of the model and the data that goes into it. Furthermore, as risk assessment is a process to facilitate decision-making, the context in which risk assessment is conducted is defined by the management decisions to be made. How effective those decisions are in reducing risks depends on whether the risks, and factors influencing the risks, are adequately identified and incorporated into the assessment. For example, Johnson (1995) noted that economic modelling of fertiliser application on sugarcane typically considered world sugar price as the most significant variable. However, in his survey of risk perceptions of farmers in the Herbert region, weather was the most significant variable influencing fertiliser application. For these reasons, the aim of this chapter is not to provide a quantitative risk assessment *per se*, but to consider the factors that have historically influenced the risks associated with insect control, with a focus on the Herbert and Burdekin sugarcane regions.

Analysis of historical changes in the risks associated with insect control provides constructive insight into the factors likely to drive future risks. Development of different insect control techniques, changes in farming practices and government legislation, and global environmental concerns, have all resulted in changes in insect control methods, including insecticide usage, in the sugar industry over time. This chapter provides an overview of the past changes in insect control and associated risks in the sugar industry, with a specific focus on issues relating to the Herbert and Burdekin regions.

5.2 The changing face of insect control in the sugar industry

Insect pests may be divided into two broad groups: those that damage the foliage or cane stalk (surface pests), and those that damage the root systems of young plants or ratoon shoots (soil pests). Surface pests may cause significant damage occasionally and include locusts, grasshoppers, and cicadas. Soil pests cause the most damage with cane grubs, soldier fly larvae, wireworms, and nematodes the major pests. Cane grub is a generic term for the larvae of nineteen different species of beetle that can cause damage to sugar cane. Of these,

the greyback grub (*Dermolepida alborhirtum*) is the most significant in north Queensland. French's cane grub (*Lepidota frenchi*) is important in northern and central cane-growing regions while a variety of other species including Childers cane grub (*Anitrogus parvulus*) and Southern one-year cane grub (*A. consanguineus*), are significant pests in southern Queensland (Roberston *et al.*, 1995). Cane grubs are the most significant insect pests of sugarcane, and as such, have been a major focus of insect control. Robertson *et al.* (1995) provided an excellent detailed review of past and present methods of cane grub control. The following section provides a brief overview of insect control techniques for all the major insect pests of sugarcane and has been taken from the following sources: Kerr and Bell (1939); King *et al.* (1953 and 1965); Cane Pest and Disease Control Boards Conference Proceedings 1947 and 1950-1966 (BSES, 1947a and 1950a-1966a); Bureau of Sugar Experiment Stations Annual Reports 1947-1987 (BSES, 1946b-1987b); Sturgess (1987) and Robertson *et al.* (1995).

Prior to the introduction of organochlorine insecticides, a variety of insect controls including cultural, biological and chemical techniques were employed in the sugar industry (Figure 5.1). Cultural controls were based on knowledge of the life history of specific insect pests to provide unfavourable conditions for their population growth. These techniques included ensuring adequate drainage of fields (which had the added benefit of improved crop yield), timing of cultivation and planting, hand-collection of cane grubs, burning of post-harvest crop residues, and planting of sugarcane varieties more resistant to insect attack (Mungomery, 1930 and 1934; Kerr and Bell, 1939). Additionally, as cane grubs are the larvae of various beetle species, control of cane grubs through control of the adult stage was also attempted. This included light-trapping, hand-collection of the beetles and destruction of trees that the adult beetles fed upon.

Disease epidemics and indigenous predators and parasites of insect pests were known to reduce cane grub populations (Mungomery, 1930 and 1934; Robertson *et al.*, 1995). However, investigations of biological control largely focussed on the introduction of parasites (Jarvis, 1932; Mungomery, 1934), and vertebrate predators (Low, 1999). Unsuccessful trials using the pathogenic muscardine fungus, *Metharhizium* sp. for cane grub control occurred in 1917, and the Tachinid fly was introduced in 1911 to control the only significant non-indigenous insect pest, the New Guinea weevil borer (Jarvis, 1929; Sturgess, 1987). Indian myna birds were introduced unsuccessfully in the 1880s to control a locust outbreak while outbreaks of cane grubs in the early 1900s led to calls for the introduction of moles and shrews (Boyd, 1902; Robertson *et al.*, 1997; Low, 1999). In 1934 significant outbreaks of cane grubs resulted in the trialing of the European Toad for cane grub control, and release of the "giant toad", *Bufo marinus*, in 1935 (Roberton *et al.*, 1997; Low, 1999).

Chemical control of insect pests prior to the introduction of organochlorines was limited. Lead arsenate and Paris Green (calcium arsenate) were used to control surface pests such as

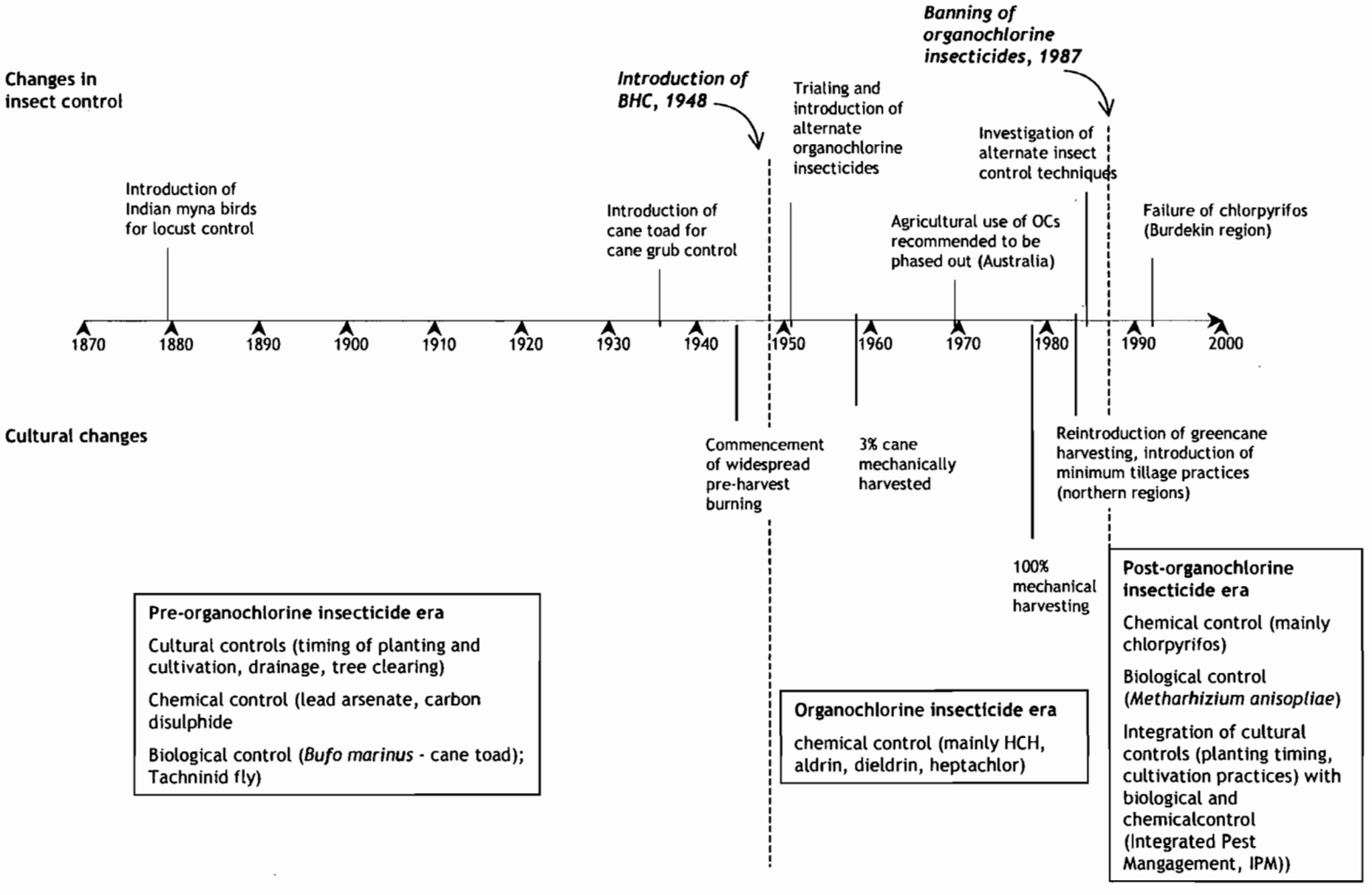


Figure 5.1. Changes, and factors influencing changes, in insect control and cultural techniques in the sugar industry (Source: Compiled from BSES 1950-1996; BSES, 1946a-1996a; King et al., 1953; King et al., 1965; Kerr and Blyth 1993; Robertson *et al.*, 1995).

grasshoppers and caterpillars, while a mixture of carbon bisulphide and paradichlorobenzene was used to fumigate soils for cane grub control (Mungomery, 1934; Kerr and Bell, 1939).

In 1945, a sample of hexachlorocyclohexane (HCH), initially known as "666", was trialed for cane grub control and found to be remarkably effective. Technical HCH contained the $\alpha, \beta, \gamma, \delta$ - HCH isomers in the approximate proportion of 70-75%, 5-7%, 13-15% and 6-8% respectively, and were often erroneously known as "Benzene hexachloride" (BHC). The release of BHC or "Gammexane", another commercial formulation of HCH, for use in sugarcane in 1948 reduced cane grub damage in subsequent years so effectively that it was hailed as the "mortgage lifter" (Sturgess, 1987). By 1949 a commercial formulation designed specifically for use in the sugar industry, was made available. This formulation contained approximately 20% technical HCH in rock phosphate dust. The area treated with HCH formulations increased rapidly from 120 ha in 1947 to approximately 25,000 ha in 1953. Initially HCH formulations were used against all insect pests although, as other organochlorine insecticides became available, their efficacy against different insect pests was tested and recommendations for their use (mode of application, rate) were made (Mungomery, 1952; King *et al.*, 1953; Mungomery, 1954; Wilson, 1955; Wilson, 1958; Mungomery, 1965; Wilson, 1961; Smith, 1962; Hitchcock, 1964). HCH formulations were the most widely used insecticides for cane grub control, while aldrin, dieldrin, and lindane were used preferentially for other insect pests (Table 1.3).

From the mid-1980s spray emulsion formulations of chlorpyrifos were used increasingly for control of wireworms (R. Kerkwyk, Herbert Cane Protection Board, pers. comm.). In 1987 organochlorine insecticides were generally banned from agricultural use and chlorpyrifos became the most widely used insecticide in the sugar industry (BSES, 1989a), either as a controlled-release formulation (SuSCon®) or a spray emulsion (Lorsban®). Controlled-release formulations are primarily used for cane grub control while spray emulsion formulations are used for other insect pests.

In the search for alternate controls of cane grubs, over 30 different insecticides have been trialled since the mid 1980s. However, while organophosphates have provided effective control, pyrethroids and carbamates have not (Robertson *et al.*, 1995). Since the banning of organochlorine insecticides, no insecticides have been registered for use against funnel ant and soldier fly (Agnew, 1997). A microbial insecticide, using the fungal pathogen, *Metarhizium anisopliae*, and a new controlled release formulation of chlorpyrifos are being registered for use in control of cane grubs (D. Logan, BSES, pers comm). The focus of insect control is now on the development and integrated management of different control techniques. Further research includes development of new controlled release and knock-down insecticides for cane grubs; identification of cultural controls that restrict insect pest population growth; selection of sugarcane varieties more resistant to insect attack through

breeding programs or gene technology; and interactions with indigenous parasites and predators, including the interaction between insecticide use and disease (Robertson *et al.*, 1995; Agnew, 1997; Allsopp *et al.*, 1997a and b; Samson *et al.*, 1998).

5.3 The impetus for changes in insect control

Seeking to improve the efficacy of insect control has been the impetus for change in insect control techniques at an industry level. However, since the early 1970s, these changes have been modified by global environmental concerns and export trade issues. The introduction of organochlorine insecticides saw a shift in insect control techniques from a combination of biological, cultural and chemical controls, to almost total chemical control. With the banning of organochlorine insecticides, biological and cultural control techniques are being increasingly used in combination with chemical controls.

5.3.1 Pre-organochlorine insecticide era

Economic concerns, primarily losses due to insect damage of sugarcane and efficacy of control, provided the initial impetus for insect control. Prior to the introduction of organochlorine insecticides, severe and recurrent losses attributed to insect pests were suffered by the sugar industry. Pressure, placed by growers on the government of the day to aid their economic plight resulted in the payment of bounties for the hand-collection of grubs and beetles from 1895 (Sturgess, 1987). In 1911, in response to continued pressure from growers, the government appointed an entomologist to the Bureau of Sugar Experiment Stations, a legislatively established research organisation, in order to find a solution to the grub problem (Sturgess, 1987). This appointment was the commencement of nearly a century of research into control of insect pests of sugarcane.

Early research provided a number of biological and cultural techniques for insect control but they were generally considered to be only moderately effective in reducing insect damage; control of the weevil borer by the Tachnid fly was considered by some authors to be successful (Mungomery, 1935 and 1936). The techniques were generally aimed at preventing insect outbreaks and generally did not provide control in the event of such outbreaks, which were considered to be primarily induced by climatic conditions. Conversely, unfavourable climatic conditions were considered to be an important factor in preventing insect outbreaks. Chemical control by soil fumigation was considered to be the most effective form of control for cane grubs and it could be applied in the event of an outbreak. However, fumigation was expensive and time-consuming, both in terms of monitoring of sugarcane fields to ascertain whether fumigation was warranted and in the application of soil fumigants (Jarvis, 1929; Mungomery, 1962).

5.3.2 Organochlorine insecticide era

The general failure of biological and cultural controls in preventing and controlling insect outbreaks, and the expense of chemical control, continued to provide an impetus for changes in insect control until the trialing of HCH in 1945. From this time to the late 1970s, changes in insect control were driven largely by the introduction of different organochlorine insecticides, and the subsequent testing of their efficacy in controlling different insect pests (BSES, 1952b-1970b). An important feature of organochlorine insecticides was their persistence in the soil, enabling efficacious control of soil pests, in particular cane grubs, for up to the first three years of a cropping cycle. As such, organochlorine insecticides could be applied in a preventative manner at the time of planting. These factors, in addition to the relatively cheap cost and efficacy of insecticides, enabled insecticide application to be easily incorporated into general farming practices, providing cheap and effective control of insects and led to the almost total adoption of chemicals for insect control.

During the late 1960s in the US and Europe, a growing awareness of environmental impacts and human health concerns resulted from the widespread usage of organochlorine insecticides. In 1970, these concerns led the National Health and Medical Research Council in Australia to recommend the phasing out of organochlorine insecticides in Australian agriculture (ASTEC, 1989). The Australian Agricultural Council supported this view and recommended, in 1972, that all agricultural usage of organochlorine insecticides be phased out when suitable alternatives were found (J. Steele, NRA, pers. comm; Commonwealth Government, 1990). The "environmental creed of distorted values clouded the long-term availability of BHC" and provided the impetus for research into alternate methods of insect control in the late 1970s (Sturgess, 1987). New insecticides were the primary focus of research and in the mid 1980s chlorpyrifos, either as a controlled release formulation (SuSCon®) or spray emulsion (Lorsban®), emerged as the most effective although costly, alternative (Hitchcock *et al.*, 1984). The significant cost of controlled release formulations of chlopryrifos provided the impetus for investigation insect control by *Metharhizium anisopliae* (Sturgess, 1987). However, the cheap cost and efficacy of organochlorine insecticides meant that these insecticides remained the primary forms of control of cane grubs.

During the early 1980s, failures of organochlorine insecticides to control cane grub and wireworm occurred (Anon., 1983; Hitchcock 1983; Chandler, 1984). Initially, the failure was attributed to increasing insecticidal resistance of the insect pests. Tests of various cane grub species since early 1970s did not indicate the development of insecticide resistance. Further testing in the early 1980s also indicated that insecticide resistance had not developed, and inappropriate placement of insecticides in the soil profile was suggested to be the cause of failure (Chandler, 1984). No testing of insecticide resistance in wireworms was conducted. As a result of the failures, alternate insecticides were introduced. For example, in the Herbert region, there was an increase in the use of chlorpyrifos for wireworm control from 1984

(Figure 1.10), although no failure of organochlorine insecticides in this region had been reported. In the Burdekin region, where failures of HCH formulations to control greyback grub had been observed, farmers switched to using heptachlor (Figure 1.13), which provided effective cane grub control. Although it is interesting to note that, by the late 1980s, some farmers who had been using heptachlor for a number of years also noted a decrease the efficacy of heptachlor (D. Williams, Inkerman Cane Production Board, pers. comm.). Despite legislative pressure to reduce organochlorine insecticide use, the availability of alternate insecticides, and declining confidence in the efficacy of the available insecticides, organochlorines remained the primary insecticides for insect pests in sugarcane until 1987.

5.3.3 Post-organochlorine insecticide era

5.3.3.1 The beef trade incident, 1987

In May 1987 Food and Safety Inspections Officers of the United States Department of Agriculture found unacceptable residual concentrations of DDT in Australian beef imports (Corrigan and Seneviratna, 1990). Subsequently other organochlorines, primarily dieldrin and heptachlor, were detected. This became a major turning point in the regulation and use of insecticides in Australian agriculture. As a result of the violations, the US Government imposed a four month ban on imports of Australian beef (Ford, 1987) and one shipment of beef contaminated with heptachlor and rejected by US government officials, was subsequently shipped to Hong Kong (Sibbison, 1990). Also at this time, customs officials in Canada and Japan found unacceptable organochlorine insecticide residues in Australian beef imports and their governments threatened to restrict imports (Ford, 1987). The implications of the trade ban and the potential for further trade restrictions were significant for the Australian economy, to which the export of Australian beef contributed, at that time, around $2 billion annually (Corrigan and Seneviratna, 1990).

The major outcome of the violation of chemical residue levels for meat was the enactment of legislation that banned sale, import, and agricultural usage of organochlorine insecticides in 1987. In Queensland, bans were implemented via legislation connected to the Health Act 1937 (Qld. Govt., 1987a). Furthermore, in September 1987, the organochlorine BHC was declared a prohibited chemical in Queensland (Qld. Govt., 1987b). However, restricted sale, import, and use of chlordane, dieldrin, aldrin, and heptachlor was allowed to continue, primarily for termite control (NHMRC, 1992) and use of dieldrin and heptachlor was permitted in the sugar industry for soldier fly and funnel ant control respectively (BSES, 1987c). The conditions of a permit provided that an infestation must exist and that no livestock were in the vicinity of the area to be treated (BSES, 1987c).

5.3.3.2 Chlorpyrifos

Since the banning of organochlorine insecticides, chlorpyrifos has become the dominant insecticide used in the sugar industry (Hamilton and Haydon, 1996). While chlorpyrifos has

afforded effective control of greyback grub and other insect pests in most sugarcane growing areas, it has failed to effectively control greyback grub in the Burdekin region since 1992 and significant damage to sugarcane has occurred (Figure 5.2a; Robertson *et al.*, 1995). Alkaline soils, which cause rapid hydrolysis of chlorpyrifos, and microbial degradation are suggested to be the major causes of observed failures (Chandler *et al.*, 1998; Robertson *et al.*, 1998). A new formulation of chlorpyrifos has been developed to counter-act the high pH of the soils (Chandler *et al.*, 1998) and is currently being assessed for registration (D. Logan, BSES, pers. comm.). The discovery that microbial degradation is a cause of the failure of chlorpyrifos in this region has also led to speculation that earlier failures of BHC and heptachlor may have been due to enhanced microbial degradation of these compounds (D. Logan, BSES, pers. comm.). Given the absence of testing for insecticide resistance in wireworms, it is possible that the failure of aldrin to control wireworms in certain districts may also be attributed to microbial degradation.

The failure of chlorpyrifos to control the greyback grub in the Burdekin region, and its subsequent economic impact, highlighted the necessity for the development of alternate control methods (Robertson *et al.*, 1995). It is interesting to observe that many techniques used prior to the introduction of organochlorine insecticides are now being revisited. These include cultural techniques, such as the timing of planting; biological control using *Metarhizium anisopliae*; use of plant varieties less susceptible to insect damage; and use of post-infestation or "knockdown" insecticides. The "knock-down" insecticides Mocap (ethoprophos) and Rugby (caudofos), are the only insecticides registered for cane grub control, other than chlorpyrifos. However, effective application requires an effective means to apply insecticides as well as adequate assessment of grub numbers at a time suitable for applying insecticides. These limitations on efficacy are the same limitations that were faced during the use of carbon bisulphide in the early 1900s (King *et al.*, 1953; Robertson *et al.*, 1995). Currently, in the Burdekin region, light traps and aerial application of carbaryl are being used in an attempt to alleviate the grub problem by destroying the adult beetles (D. Williams, Inkerman Cane Production Board, pers. comm.). This is despite the known inefficiency of controlling grub numbers through adult beetles (Robertson, 1997; Ward and Robertson, 1999).

There is greater recognition of potential problems faced when relying on a single chemical for insect control. These problems, which include development of insecticide resistance, enhancement of soil microbial populations capable of degrading insecticides and concerns of the environmental impact of insecticides, have provided the impetus for the development of Integrated Pest Management (IPM) techniques for control of cane grubs and other insect pests (Robertson *et al.*, 1995; Samson *et al.*, 1998). Additionally, the absence of chemical controls for some insect pests such as funnel ant, soldier fly, and black beetle has promoted the development of IPM techniques for these pests (Agnew, 1997; Samson *et al.*, 1998).

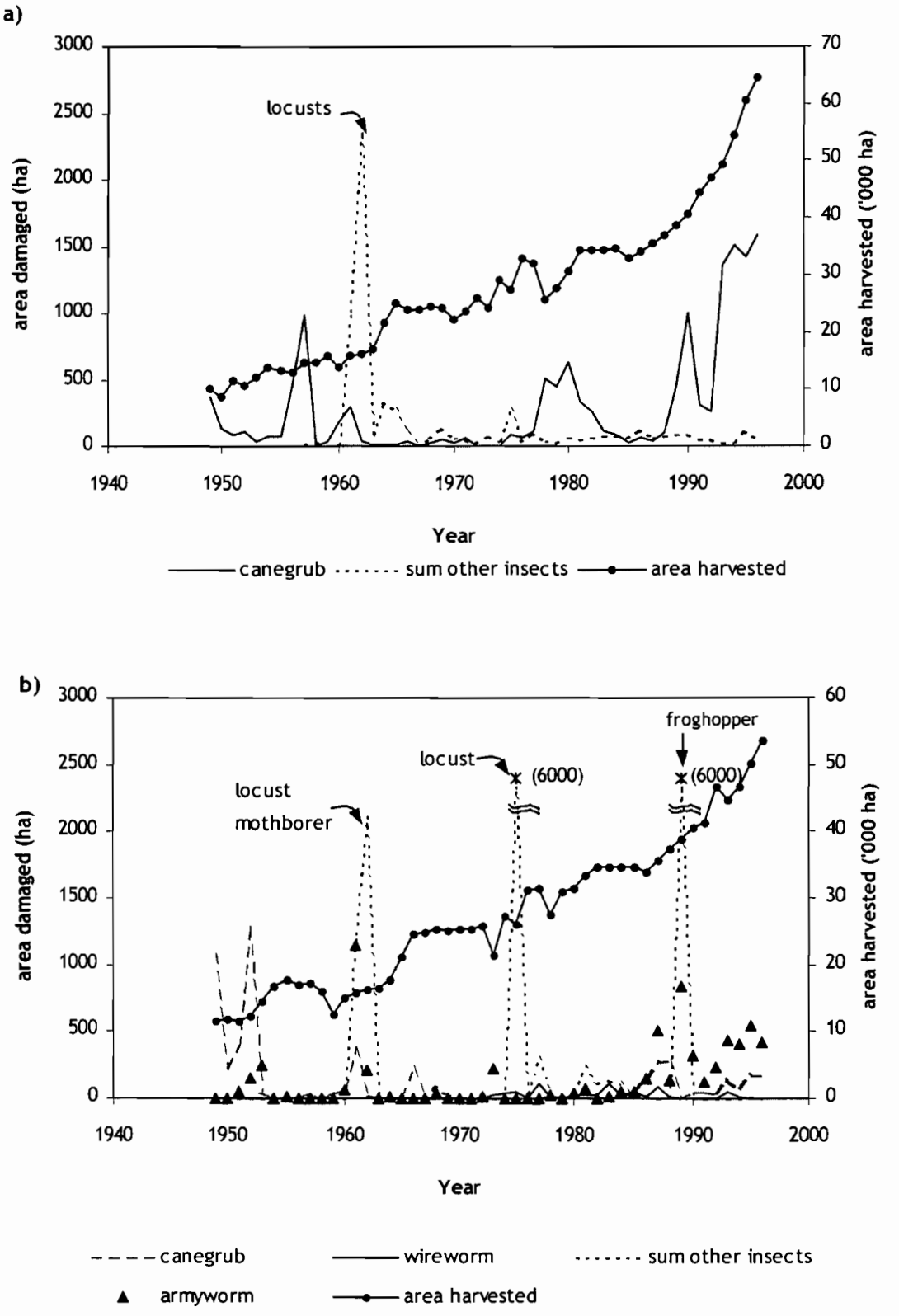


Figure 5.2. Area damaged by different insect pests and area harvested in a) the Burdekin region, and b) the Herbert region. Note: where an insect pest is identified, this insect caused the majority of damage during a particular outbreak (Source: Compiled from BSES (1950a-1996a).

5.4 Risks associated with insect control in sugarcane

The risks associated with insect control in sugarcane may be related to economic, ecological or human health issues. The following section provides an overview of the changes in major types of risks associated with insect control, with a focus on changes in the Herbert and Burdekin regions.

5.4.1 Economic risk

In the context of insect control, economic risk is the risk of economic loss as a consequence of insect damage of the crop. The magnitude of this risk depends on a number of factors including likelihood, frequency, and extent of insect outbreaks; the relative amount of damage caused by insects compared with the total amount of sugarcane harvested; the efficacy of different insect control techniques; and the price received for sugar.

Historically, the likelihood, frequency, and extent of insect outbreaks were considered to depend primarily upon climatic conditions, such as extended dry periods, or unseasonal rainfall (Mungomery, 1934; Mungomery, 1951; Wilson, 1955; Mungomery, 1961; Wilson, 1963, Wilson, 1964). With respect to factors influencing cane grub control, Robertson (1997) suggested that this is simplistic and that factors such as highly virulent and non-persistent diseases may be more important in controlling greyback grub populations. Further work on factors influencing populations of insects, other than greyback grubs are also being undertaken (Fischer and Allsopp, 1997; Samson and Milner, 1997; Samson and Phillips, 1997).

The relative area damaged by insect pests is determined by the area of land used to grow sugarcane and the area of sugarcane damaged by insect pests. Since World War II the sugar industry has expanded considerably, largely driven by trade events, in particular trade agreements negotiated with Britain, Japan and US (Figure 5.3). Expansion was also aided by more efficient farming practices (Kerr and Blyth, 1993) and the advent of cheap, effective and simple to use organochlorine insecticides.

Prior to the introduction of organochlorine insecticides, thousands of hectares of sugarcane was damaged by insect pests, including cane grubs, wireworms, and New Guinea weevil borer (McDougall, 1947; Robertson *et al.*, 1997) and insect control methods employed were not considered to be widely effective. In contrast, organochlorine insecticides were considered to be remarkably effective, as demonstrated by the generally low level of insect damage across Queensland during the period of usage (Figure 5.2). Favourable climatic conditions were generally indicated to be responsible for occasional outbreaks of insect pests during this time (Mungomery, 1951; Mungomery, 1961). Further evidence for the efficacy of organochlorine insecticides comes from a recent study that observed that outbreaks of grubs followed by low numbers of grubs in the subsequent year occurred every 10-13 years since 1870, *excluding*

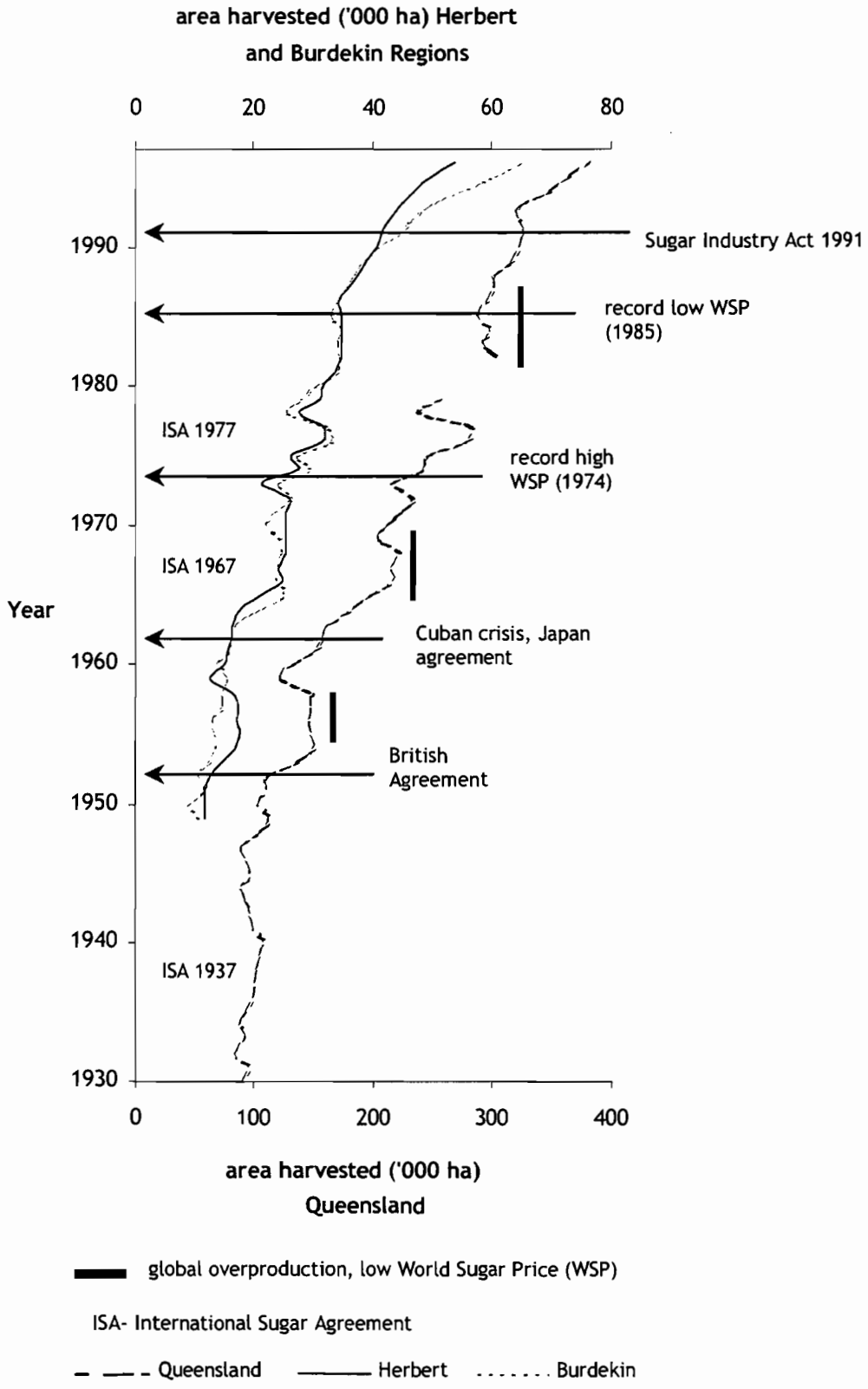


Figure 5.3. Influence of trade and legislative events on the development of Queensland sugar industry, as measured by the area harvested.

the years of organochlorine use (Robertson *et al.*, 1997). This observed cycle was suggested to be due to a highly virulent but non-persistent disease of cane grubs. The banning of organochlorine insecticides has lead to the introduction of insecticides that have been less effective in controlling insect pests in some regions. For example, since 1992 SuSCon has failed to control cane grubs in the Burdekin region and the manufacturer does not support use in this region (Agnew, 1997).

In the Burdekin region, the failure of SuSCon to control cane grubs since 1992 has resulted in significant areas of sugarcane being damaged with annual economic losses estimated at $0.6 - $1.2M (BSES, 1992a-1996a). Over the same period of time insecticides have cost $15,000-$30,000 (BSES, 1992a-1996a). However, although this damage is significant in comparison with previous years, the relative proportion of the area damaged compared with the total area harvested is small (Figure 5.2a). Similarly, the relative economic loss due to insect damage and cost of insecticides is only a small proportion of the total price received for sugar in this region ($265 - $400M). The small proportion of area damaged by cane grubs is largely a result of the expansion of the sugar industry in the Burdekin region into soils that are not susceptible to grub damage (Ward, 1997; Ward, 1998). Geographical variability in locations susceptible to cane grub damage in the Burdekin region was recognised as early as 1939 and there was little concern that the cane-grub would become a district-wide pest (Kerr, 1939). However, the reasons for this geographic variability were not identified and areas prone to grub attack were planted with sugarcane. Currently, some farmers in grub-prone regions have been forced to replant 100% of their crop annually, instead of the usual 25-30%. This increases general farming expenses (e.g. increased fertiliser, fuel costs) in addition to monetary losses due to lower yields or lower cane sugar contents through insect damage (T.Hall, Ayr Cane Production Board, pers. comm.).

Use of the organochlorine insecticides was not always beneficial in reducing insect damage to sugarcane crops and was occasionally suspected of increasing insect damage through an increase in secondary pests or destruction of natural predators of problem insects (Samson et al., 1998). For example, use of heptachlor for cane grub control was linked to outbreaks of cicadas in some fields and use of HCH formulations for soldier fly control was occasionally observed to increase soldier fly populations (Agnew, 1997).

5.4.2 Ecological risks

In contrast to economic risk, the types of ecological risks associated with insect control have changed over time (Table 5.1). Prior to the introduction of organochlorine insecticides, insect control was largely dominated by biological and cultural control techniques. As such, ecological risks were predominantly related to habitat alteration and were localised, such as the removal of 440 ha of forest in the Mourilyan district in 1936 (Sturgess, 1987). However, in comparison to the area of land subsequently cleared for industry expansion (Figure 5.2), the

ecological impact resulting from tree clearing for insect control is insignificant. In contrast, introduction of the "giant toad", *Bufo marinus*, also known as the cane toad in Australia, has led to widespread ecological impacts. Since their introduction in June 1935, cane toads are now widely distributed across northern Australia (Freeland, 1985), including many areas otherwise undisturbed by cropping activities. Their current distribution is considered to be much less than their potential range (van Beurden, 1981) and estimates of the rate of expansion range from 1.07 km yr^{-1} in northern New South Wales to 27 km yr^{-1} in the Northern Territory (Freeland and Martin, 1985). Ecological impacts of the cane toad stem from their high fecundity, their ability to reproduce year round in a variety of ecosystems, the absence of natural predators and parasites in Australia, and the presence of toxins in their skin, which can result in poisoning native fauna such as goannas, frog-eating snakes and quolls (Freeland, 1985). Additionally, cane toads are voracious bee-eaters. Freeland (1985) estimated, based on the number of hives present in Queensland in 1976, that cane toads cost the Queensland bee industry $1 M every five years for preventative measures required to avoid significant loss of bees to cane toads.

Table 5.1. Types of risks associated with insect control techniques.

Insect control	Benefit	Risk
Cultural techniques		
Cultivation	Insect control through dessication	Soil structure decomposition Increased soil erosion
Minimum till	Reduced soil erosion Maintains soil structure Increased incidence of grub parasites	Increased herbicide use Increased incidence in plant disease
Pre-harvest burning	Decreased incidence of some insect pests e.g. New guinea Weevil borer Decreased incidence of plant pathogens	Air pollution Fire escape Decreased incidence of grub parasites
Green cane harvest, retention of crop residues	Decreased soil erosion Increased incidence of plant and grub parasites	Reduced dissolved oxygen in adjacent creeks Indirect increase in rat numbers
Biological control	Reduced ecological impact through decreased use of insecticides	Ineffective control Increased costs
Insecticide application		
Organochlorine insecticides	Effective control of a range of insect pests in all regions	Ecological impacts due to persistence in environment
Chlorpyrifos formulations	Effective control of insect pests in the majority of regions	Ecological impacts

Since the introduction of organochlorine insecticides, insect control techniques have been dominated by insecticide usage. As a consequence, ecological risks have stemmed from the amount of insecticides applied; physico-chemical properties and mode of application of insecticides and their influence on insecticide transport from the site of application and

uptake into non-target organisms; and finally, the acute and chronic toxicity of insecticides to non-target organisms.

The amount of insecticides applied varied both annually and regionally, dependent upon the likelihood of insect damage occurring in each year and the areas treated with insecticides. These factors in turn are dependent upon the regional importance of different insect pests, and geographic variability of insect pests within a region. In the Burdekin region, the greyback grub has been the major insect pest, while wireworm and greyback grub are the main focuses of insect control in the Herbert region. Despite considerable expansion in both the Herbert and Burdekin regions, the areas treated with insecticides in both regions have fluctuated around a constant value since the 1960s (Figures 1.9 and 1.12). In the Burdekin region, the total annual area treated has fluctuated around 3,000 ha. During the early 1960s around 5,000 ha were treated annually while in the early 1980s around 6,500 ha were treated annually (Figure 1.12). Since 1990, the area treated with insecticides has declined. Between 9 and 92 tonnes of HCH formulations are estimated to have been applied annually over 1948-1982, while 3-29 tonnes of HCH and 1.6-7.4 tonnes of heptachlor were estimated to have been applied annually between 1982 and 1987 (Figure 3.2). In the Herbert region, the total annual area treated with insecticides has fluctuated around 10,000 ha from the early 1960s to the early 1990s with a maximum area of 20,000 ha treated in 1975, of which 11,000 ha were treated for locust control (Figure 1.9). From 1993, the total area treated has been around 13,000 ha annually as a result of increases in the area treated for wireworms. Recent expansion of sugarcane into wetland areas (Johnson *et al.*, 1997; Johnson *et al.*, 1999), which are typically more susceptible to wireworm damage, may account for these increases. Despite the increase in area treated for wireworm, in the Herbert region, the area treated with organochlorine insecticides decreased as the chlorpyrifos formlation, Lorsban, was increasingly used for wireworm control (Figure 1.10). Between 12 and 105 tonnes (HCH) and 0.9 and 2.4 tonnes (aldrin) are estimated to have been applied annually in the Herbert region over 1948 - 1987 (Figure 3.3).

Extensive use of organochlorine insecticides in Europe and the United States during the 1950s and 1960s resulted in widely documented ecological impacts, including mass mortality of fish, birds, foxes and reproductive failure of birds (Carson, 1962; Edwards 1976; Brown, 1978). In contrast, no significant ecological impacts as a result of organochlorine insecticide usage were reported in Queensland during the period of usage. At the same time, few studies were undertaken to assess ecological impact of organochlorine insecticides.

The limited number of studies conducted during the 1970s were presumably undertaken in response to environmental concerns of organochlorine insecticide usage in this era. These studies were undertaken in aquatic systems and indicated that low concentrations of pesticides were present. The most comprehensive study was that by personnel of the Bureau

of Sugar Experimental Station who monitored pesticide residue in water and sediment collected from two locations in each of five rivers (Mulgrave, Herbert, Pioneer, Burnett, and South Johnstone) in sugarcane growing regions over the period 1971-1979 (BSES, 1971 and 1979). Concentrations of organochlorine residues were typically below US water quality guidelines. These guidelines were used as indicators for acceptable water quality and no monitoring was conducted after 1979. The US water quality guidelines were significantly higher than current draft values of the ANZECC water quality guidelines (Table 5.2; ANZECC, 1999). Testing of ground-water quality in the Burdekin region during 1975 and 1976, found a low incidence of low concentrations (generally <1 ng l^{-1}) of lindane and heptachlor (Brodie *et al.*, 1986). Two studies that investigated the distribution of organochlorine insecticides in the Great Barrier Reef Environment, found low concentrations of lindane in fish, corals, and molluscs (Olafson, 1978) and low concentrations of DDT and dieldrin in starfish (McCloskey and Deubert, 1972). No studies investigating the ecological impacts of organochlorine insecticides on the terrestrial environment were reported.

Table 5.2. Comparison of 1972 United States Federal Pollution Control Administration water quality guidelines for public water supplies and marine and aquatic organisms with draft Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 1999).

Chemical	Concentration (µg l^{-1})		
	Public water supplies*	Marine and aquatic organisms*	ANZECC
Dieldrin	17	0.05	0.006
heptachlor	18	0.05	0.0003
ΣDDT	42	0.05	
lindane	56	0.05	0.007
aldrin	17	0.05	
chlordane	3	0.05	
HCH		0.05	

*US Federal Pollution Control Administration guidelines.

Subsequent to the period of organochlorine insecticide usage, studies have been conducted on an *ad hoc* basis to determine environmental concentrations of organochlorine insecticide residues in organisms or aquatic systems (e.g. Dutton, 1984; Dyall and Johns, 1984; Russell and Hales, 1993; Rayment *et al.*, 1997). The only other current study published on pesticide distribution in the Herbert and Burdekin regions has focused on the Burdekin River Irrigation Area (Hunter *et al.*, 2000). This region has only been open to sugarcane farming since the late 1980s. Primarily as a consequence of the soil types present in this area, sugarcane grown in this area is generally not susceptible to greyback grub damage and insecticides are rarely

used (Ward, 1997). Low concentrations of herbicides have been the major contaminants detected in water and sediments, and dieldrin has been occasionally detected (Hunter *et al.*, 2000; G. Ham, BSES, pers. comm.). Additionally, research is currently being conducted to understand the transport and fate of pesticides in sugarcane systems with a view to understanding their environmental implications (Anon., 1999; Hargreaves *et al.*, 1999).

Of the organochlorine residues detected by the present study in soils of the Herbert region, dieldrin and lindane most frequently exceeded the ANZECC (1999) guideline "low concentration" (Table 2.17). Two locations exceeding the ANZECC guideline "high concentration" for dieldrin and nine for lindane (Table 2.17). In the Burdekin region, dieldrin, lindane and chlordane most frequently exceeded the ANZECC guideline "low concentrations". Two locations exceeded the ANZECC guideline "high concentration" for lindane and one location exceeded the guidelines for chlordane (Table 2.17). No soils exceeded the concentrations of contaminated sites guidelines for the environmental investigation levels or standard residential settings (Table 2.17).

Recently, global environmental concerns of the ecological impact of organochlorines has been renewed with the discovery that some of these compounds can cause endocrine disruption at low concentrations (e.g. Arnold *et al.*, 1996; Taylor and Harrison, 1999; Ashford and Miller, 1998; Renner, 1998b). Despite this, only one study is currently being conducted in Queensland to evaluate the potential for endocrine disruption in animals arising from the historical usage of organochlorine insecticides (Dr. J. Mueller, pers. comm.).

5.4.3 Human health risks

The types of human health risks have also changed over time in response to changes in insect control. Human health risks largely stem from occupational exposure. Occupational human health risks prior to the introduction of organochlorine insecticides, largely resulted from general farming activities associated with cultural control techniques. Exposure to carbon bisulphide during soil fumigation may have occurred, although its usage was not widespread. For example, a maximum of 500 hectares was treated with carbon bisulphide at the height of its popularity (Mungomery, 1948).

Subsequent to the introduction of organochlorine insecticides, occupational human health impacts stemmed from occupational exposure to insecticides. Health problems including respiratory ailments, skin irritation, dizziness, and headaches were known to have occurred as a result of use of technical HCH-dust formulations. In 1979, occupational health concerns were such that requests for alternate formulations were made by Cane Production Boards to insecticide companies (BSES, 1979a). However, aside from this largely anecdotal evidence, few data exist to substantiate the extent of any occupational health issues.

The only available information on human health problems possibly arising as a result of occupational exposure to organochlorine insecticides used in the sugar industry, comes from McCabe *et al.* (1984). This study was funded by a sugarcane farmer from the Burdekin region who died of leukaemia, which he suspected was due to lifetime exposure to agricultural chemicals, including organochlorine insecticides and the herbicides 2,4-D and 2,4,5-T. McCabe *et al.* (1984) compared human mortality from leukaemia and lymphoma in residents of the urban area of Townsville with residents from cane-farming regions (aggregate of 12 regions, including the Herbert and Burdekin regions). The standardised mortality ratio (SMR) showed a significant increase in mortality from leukaemia in men aged 60 years and over from cane-growing regions (61 deaths, SMR 154) as compared to the same age group from Townsville (10 deaths, SMR 57) for the period 1968-1981. While the absence of data on environmental contamination or exposure did not allow for causal links to be established, McCabe *et al.* (1984) suggested that the increased mortality from leukaemia was in keeping with occupational exposure to a chemical carcinogen with a long latent period (NHMRC, 1992).

While numerous studies have focused on aspects of human exposure to organochlorine insecticides, debate still exists as to their effect on human health. For example, based on an assessment of mouse bioassays, the United States EPA considered aldrin and dieldrin to be the most potent carcinogens known to man (Sielken *et al.*, 1999). In contrast, an epidemiological study of workers from a factory that had produced aldrin and dieldrin concluded that exposure to these organochlorine insecticides did not increase the incidence of cancer (Sielken *et al.*, 1999). Similarly, other studies on workers in factories that produced dieldrin or heptachlor and chlordane concluded there was little evidence for human carcinogenesis (Van Raalte, 1977; Whang and Macmahon, 1979b). Studies on people employed as pesticide applicators and who have been exposed to a range of agricultural chemicals often showed an increase in the incidence of leukaemia, although this could not be attributed to any specific group of chemicals (Whang and MacMahon, 1979a; McCabe *et al.*, 1984; Blair *et al.*, 1983; Brown *et al.*, 1990). A more recent result of the effect of organochlorine insecticides on humans is decreased sperm counts (Silvestroni and Palleschi, 1999).

Despite inconclusive evidence regarding the human health impact of organochlorine insecticides concerns currently relating to organochlorine insecticide usage in the sugar industry are human health concerns stemming from the use of sugarcane land for alternate land uses, such as cattle grazing or residential development (Anon., 1996a). The cattle grazing issues arise from the potential of beef cattle to accumulate unacceptable organochlorine residue concentrations in their fat, which has both trade and human health implications. Maximum acceptable residue levels have been established by the National Registration Authority (NRA) to ensure that consumption of contaminated beef would not

result in detrimental human health effects and that these concentrations will not have significant trade implications (NRA, 2000a).

Concerns of the use of old sugarcane land for grazing can be attributed to the beef trade incident of 1987. A nationwide farm by farm testing program initiated as a result of the beef trade incident, compared organochlorine residue levels in cattle sampled from all states and territories. Cattle from farms in Queensland recorded the second highest number of violations of residual organochlorine concentrations, and the highest number of violations of HCH concentrations (Corrigan and Severitna, 1990). Dieldrin was most often found at unacceptable levels, followed by HCHs, heptachlor, and DDT. As a result of the testing program, 673 herds were quarantined and grazing of cattle on or near old cane land was estimated to account for 40% of HCH residue violations and 13% of dieldrin residue violations (Robertson *et al.*, 1990). The Department of Primary Industries have established guideline concentrations for organochlorine residues in cattle holding pens (DPI, 1997). In the present study, 9 and 2 locations exceeded the Department of Primary Industries guidelines for HCH and dieldrin concentrations respectively in the Herbert region, and no organochlorine insecticide residues exceeded DPI guidelines in the Burdekin region (Table 2.17).

There are also concerns over contamination of horticultural products. For example, potato farmers will not purchase cane farms because of perceived contamination from past use of organochlorines (Anon., 1996a). Additionally, during the present study some farmers in the Burdekin region indicated that their soil had failed to meet peanut industry standards for residual organochlorine insecticide concentrations. Other horticultural industries may also have soil guidelines, which organochlorine residue concentrations in sugarcane soils may or may not exceed. However, no soils from either region exceeded contaminated sites guidelines set for environmental investigation levels, which are the most stringent of contaminated sites guidelines (although these only exist for aldrin + dieldrin combined and ΣDDTs) or guidelines established for a standard residential setting (Table 2.17).

No information is available on the occupational exposure of sugarcane farmers to chlorpyrifos, which is generally considered to be more acutely toxic than the organochlorine insecticides (Rodnitzsky *et al.*, 1975; Gallo and Lawryk, 1991). In the US the use of chlorpyrifos on apples, tomatoes and grapes has recently been revised on the basis of human health concerns (US EPA, 2000). The occupational risk of chlorpyrifos (and other insecticides) will depend on the formulation used (spray emulsion or controlled-release granules) and the safety precautions taken to reduce exposure. The absence of data relating to either current occupational exposure to chlorpyrifos or historical occupational exposure to organochlorine insecticides, including safety precautions taken, does not enable any assessment of the relative occupational health risks associated with insecticide usage.

5.5 Factors modifying the risks associated with insect control

5.5.1 Farming practices

Farming practices change over time in response to issues other than insect control but subsequently impact on insect control. Such changes in the sugar industry include pre-harvest burning of sugarcane, green cane harvesting, retention of post-harvest crop residues on fields (trash blanketing), and minimum tillage cultivation techniques. The widespread adoption of pre-harvest burning of sugarcane was primarily due to man-power shortages during World War II. This practise also reduced the impact of the New Guinea weevil borer, which had caused significant damage in some regions (Jarvis,1929; Mungomery, 1937). Mungomery (1965) noted, with regard to the beetle borer that "so long as pre-harvest burning continues it is unlikely ever to regain its former importance." Since the mid-1970s, green cane harvesting, trash blanketing, and minimum tillage techniques, have been increasingly used in the northern cane growing regions to reduce soil erosion. Since the early 1990s, these conservation techniques have been the dominant farming practices in northern cane regions. Coincident with green cane harvesting and trash blanketing practices becoming the dominant cultivation technique in these regions, there has been an increase in the amount of damage caused by the New Guinea weevil borer in some regions. For example, since 1992 the weevil borer has become the second most important insect pest in the Innisfail region, causing an estimated $0.3-0.5 M damage (BSES, 1992a-1996a). The increase in weevil borer damage has been attributed to green cane harvesting and trash blanketing and the Sugar Research and Development Corporation is currently funding a project to examine best management practices in order to reduce losses (Anon., 2000a; Morton, 2000).

In contrast, conservation farming practices are suggested to have a positive impact on cane grub control. These practices have been observed to enhance the incidence of parasitic microorganisms, such as *Metarhizium anisopliae*, and a parasitic protozoan, *Adelina* sp, that can help control cane grub numbers (Lai-Fook *et al.*, 1997). A lower incidence of parasitic microbes was found in the Burdekin region, where farm management practices (such as pre-harvest burning of sugarcane and frequent field cultivations) are not conducive to the build-up of these parasites.

5.5.2 Perceptions and relative risk

A farmer's perception of the risk of insect damage plays an important role in determining the application of insecticides for preventative purposes, as is undertaken for cane grub and wireworm control. In the Burdekin region, despite the known failure of SuSCon to control the greyback grub, some farmers applied it "just in case". However, overall insecticide usage has decreased in the Burdekin region, despite the increase in the area damaged, largely due to the inefficacy of application (Figures 5.2a and 1.13). In the Herbert region, despite the general absence of grub damage, farmers continue to apply insecticides "just in case".

Similarly, despite the general absence of damage by wireworm in the Herbert region, the area treated for wireworms has continued to increase (Figures 5.2a and 1.10).

The relative cost/benefit of an insecticide, and the price received for sugar may also influence a farmer's decision. For example, SuSCon, at $250/ha, is considerably more expensive than the cost of organochlorine insecticides used for grub control, which was $90/ha in 1985 (Figure 5.4). The price received for sugar by Australian producers fluctuates annually and is largely dominated by export agreements and the world sugar price, which depends on global production and consumption (Figure 5.5). Economic modelling of fertiliser application found that world sugar price to be the biggest factor influencing nitrogen fertiliser application to sugarcane (Anon., 1985). However, a study of risk perceptions of the factors influencing fertiliser application in the Herbert region found that sugarcane farmers considered climate the most significant variable in determining fertiliser application, and did not place a high significance on cane price (Johnson, 1995). The relative importance of climate varied across the region, reflecting climatic variability in different parts of the Herbert River district. Given geographical variability in the importance of insect pests within both the Herbert and Burdekin regions, it is likely that a similar variable response to sugar price and insecticide cost/benefit would be observed.

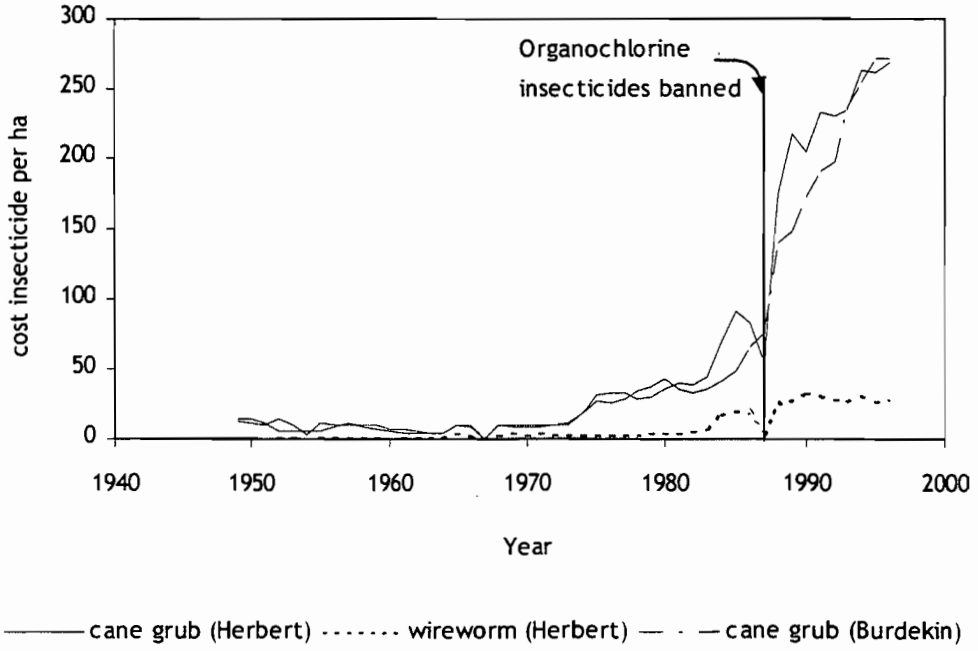


Figure 5.4. Approximate areal cost of insecticides applied for cane grub control (Herbert and Burdekin regions) and wireworm control (Herbert region) since 1949. Note: costs prior to 1970 are expressed £ ha^{-1} subsequent to this time cost is expressed as $ ha^{-1} (Source: compiled from BSES, 1950a-1996a).

The relative importance of insect damage compared with damage from other pests, such as rats, may also influence an individual farmer's decision of insecticide application. In the Herbert region, rats typically cause far more damage than insect pests, for example, estimates of economic losses due to rat damage of sugarcane is $0.3 - $3 M from 1993-1996, compared with estimated losses of $0.04 - $0.15M for insect damage over the same period (BSES, 1993a-1996a). Two native rat species, *Rattus sordidus* and *Melomys burtoni*, cause most of the damage. Control of these rats in sugarcane by rodenticides has been restricted since 1992 by their protection under the *Nature Conservation Act* (Qld) 1992. Several species of owls feed upon these rat species, which may help to regulate numbers (Kay *et al.*, 1994). However, a major decline in populations of a number of owl species in the Herbert area since 1992 is coincident with the introduction of the rodenticide, Klerat (active ingredient: brodifacoum) (Young and De Lai, 1997). The decline in numbers was primarily attributed to secondary poisoning by brodifacoum, although habitat destruction due to expansion of the sugar industry may have also contributed to population declines in some owl species (Young and De Lai, 1997). Subsequent to a change in the rodenticide used and the introduction of owl breeding boxes, owl populations in this area have increased (R. Hunt, CRC Sugar, pers. comm.).

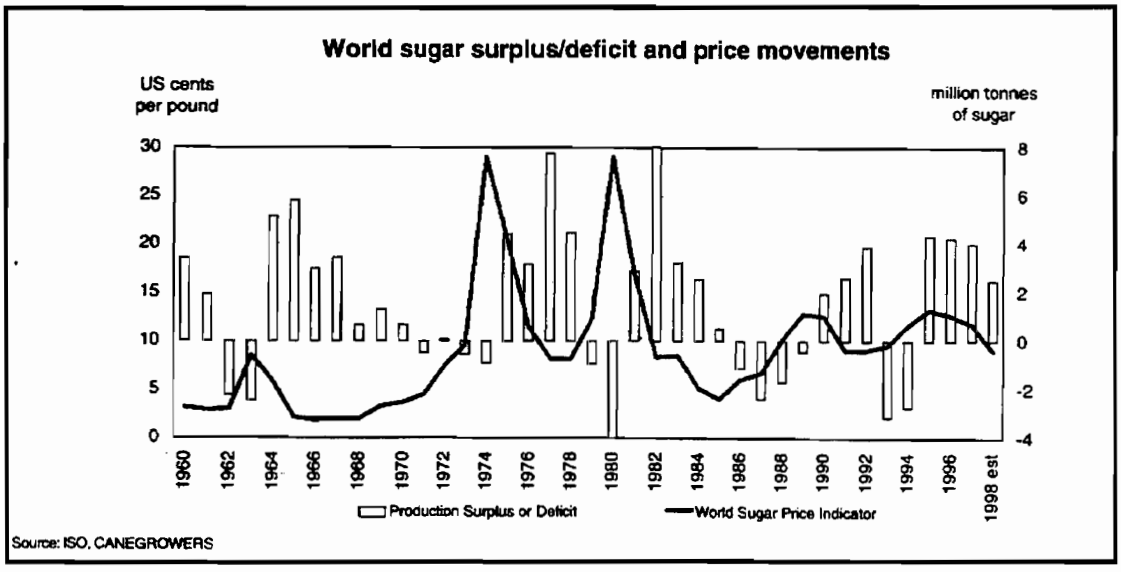


Figure 5.5. Fluctuations in world sugar price and world production and consumption of sugar from 1960 to 1999 (Source: Canegrowers, 1999).

Not surprisingly, industry bodies also play a role in determining insecticide usage. During the early years of organochlorine insecticide use, insect damage to sugarcane was occasionally considered to be exacerbated by a lack of insecticide application due to "the failure of individual growers to anticipate heavy infestations" or ineffective insecticide formulations, and there was active promotion of the use of insecticides (Mungomery, 1949; Mungomery,

1953; Mungomery, 1957). During the 1980s, when greater awareness of the detrimental ecological impacts of organochlorine usage prevailed, minimal insecticide usage was encouraged (BSES, 1988b).

5.5.3 Legislation

5.5.3.1 Pesticide Legislation

Legislation is an important factor in determining the broad-scale use of insecticides by the requirement that all insecticides are registered prior to use. Registration of insecticides comprises two stages: clearance and registration. Clearance is the assessment of a chemical product under conditions required by governing legislation, which includes assessment of the efficacy of insecticides and environmental considerations. Registration follows clearance and largely ensures that the product is appropriately labelled and packaged. In Australia, changes in pesticide legislation have reflected government concerns regarding national economy and, more recently, government and public concerns regarding environmental and human health issues.

Legislation governing the clearance and registration of insecticides was initially produced at a state and territory level. In Queensland, the *Pest Destroyers Act* 1923 (Qld) was the first piece of legislation governing sale of agricultural chemicals. The *Pest Destroyers Act* 1939 (Qld) was the first piece of legislation in Queensland to stipulate any conditions attached to registration. Efficacy of control was the only requirement for pesticide registration (Qld. Govt., 1939L[1]). From 1952, pesticides were required to be registered under the *Agricultural Standards Act* 1952-1987 (Qld), and efficacy of use was the only specified condition of registration (Qld. Govt., 1952L). With respect to human health concerns, specific organochlorine insecticides were acknowledged to be poisons from 1958 and conditions pertaining to their sale and labelling were required by *Poisons Regulations*, which were issued under the *Health Act* 1937 (Qld). Despite the requirement that insecticides were registered prior to use, no legislation existed to govern their use (J. Steele, NRA, pers. comm).

As a result of the 1987 beef trade incident, the *Agricultural and Veterinary Chemicals Act* 1988 (Qld) and the *Chemical Usage (Agricultural and Veterinary) Control Act* 1988 (Qld) were enacted. The former provided for a national system of evaluation, prior to registration, of the suitability of agricultural chemicals for intended purposes. The latter provided for control of the use of a chemical by deeming it an offence to use pesticides for purposes other than that detailed on the label (with the exception of uses allowed under permit). Although a working party of the Australian Agriculture Council had been established in 1986 to develop Commonwealth legislation pertaining to approval procedures (Cwlth. Govt., 1990), the beef trade incident undoubtedly provided an impetus for finalisation of the legislation. This is

evident in the second reading speech by the Federal Minister for Primary Industries and Energy, which acknowledged that the primary benefit of the legislation was to "further strengthen the international standing of Australia's clearance and registration procedures, thereby enhancing the export market potential of our agricultural products." Assurance of the efficacy of use was the next anticipated benefit, followed by "reduction of possible hazards to the public, the environment and users", and "reduction of possible hazards of contamination of agricultural products" (Cwlth. Govt., 1990).

A subsequent review of agricultural and veterinary chemical legislation in 1990, recommended that the national system of clearance of agricultural products be extended to also include product registration (Cwlth. Govt., 1990). In 1995, a body of State, Territory and Commonwealth legislation was enacted to establish this national registration scheme (Cwlth. Govt., 1999). The overseeing body is now the National Registration Authority (NRA) established by the *Agricultural and Veterinary Chemicals (Administration) Act* (1992). It was recognised that a national system of agricultural (and veterinary) chemical product regulation would enhance the "protection of the health and safety of human beings, animals and the environment". However, continuing emphasis of trade issues in relation to agricultural chemical use is evident by the recognition that a system for regulating chemical products is necessary for " the furthering of trade and commerce ..... for the well-being of the economy" (Cwlth. Govt., 1994L; Qld. Govt., 1994L).

Current legislation requires that assessments of human health and ecological risks, and efficacy of use of chemicals, be undertaken prior to registration. An applicant wanting to register an insecticide must supply extensive information to the NRA. Such information includes usage (crop, mode, rate of application), scale of use, persistence in the environment, potential for off-site movement, specificity for target pest(s), and toxicology (both acute and chronic, neurotoxicity, or genotoxicity effects in humans as well as toxic effects on non-target organisms; NRA, 2000a). Additionally, chemicals registered prior to 1995, and which are currently in use, may be periodically reviewed under the Existing Chemicals Review Program (ECRP) or a Special Review Program (SRP). The former reviews older chemicals to ensure "they meet contemporary standards of safety and performance, taking account any new information and scientific data generated since their registration" (NRA, 1998a). The latter reviews chemicals if issues arise that may alter their terms of registration or cause them to be withdrawn. Chemicals for review under ECRP are based on priority of concerns and includes environmental, human health, and trade issues (NRA, 1998a). Since 1995, eleven reviews have taken place, including a recent review of chlorpyrifos (NRA, 2000b). To date, no insecticides have been banned as a result of these reviews, although their uses for some purposes has been restricted. Endosulfan was one of the

[1] References in which the year is followed by the letter L refer to government legislation, and are listed under Legislation in the references.

first chemicals reviewed, largely due to concerns of public health and environmental concerns associated with its use in the cotton industry (NRA, 1998b). Insufficient data were available for a complete assessment of the issues of concern in 1997, knowledge gaps were identified, and restricted use has been approved while further information is gathered for further assessment (NRA, 1998b). Contamination of beef with endosulfan residues resulting from use in the cotton industry during 1998 and 1999 has led to further restrictions in the use of endosulfan (NRA, 1999).

5.5.3.2 Sugar industry legislation

The sugar industry has the distinction of being the most highly regulated Australian agricultural industry. This has impacted indirectly on insecticide usage by its influence on industry expansion. As a net exporter of sugar since 1924, trade events have been the dominant influence on development of the sugar industry (Figure 5.3). From 1929, and until 1991, sugar industry legislation required that land used for sugarcane growing was "assigned" by a central board, which adopted a philosophy of distributing land assignment evenly between sugarcane growing districts (Anon., 1972). The tight regulation is reflected by the general "mirroring" of trends in the area harvested in the Herbert and Burdekin regions with that harvested in Queensland over time (Figure 5.3). The divergence since 1991, of the trend in area harvested in the Herbert and Burdekin regions, from that harvested in Queensland, reflects changes in sugar industry legislation with the introduction of the *Sugar Industry Act (Qld)* 1991. These changes resulted in, amongst other things, the determination of future expansion of sugarcane land being dependent on regional decisions, which are also required to consider environmental impacts of expansion (Qld. Govt., 1991L; Qld. Govt., 1999L). These changes could also influence insect control techniques employed in different regions through the requirement for the consideration of their environmental impact. However, the largely discretionary nature of the required environmental considerations means that these factors are unlikely to be considered (Cavanagh, 2000; Appendix I.3).

5.6 Trade-offs in insect control in the sugar industry

Assessment of a particular target risk can provide a basis for decisions regarding insecticide use in a particular context, however, in reality, insecticide use requires a balance of all risks involved. As a consequence of reducing the target risk in one context, the target risk in other contexts may rise or different risks may result. These "trade-offs" are often unintended and unrecognised and may result in a lesser degree of protection of the environment and human health than intended (Graham and Weiner, 1995). Trade-offs will continue to occur unless decision-makers consider the full set of outcomes associated with each effort to reduce risk (Graham and Weiner, 1995). Changes in farming practices and insect control techniques can result in trade-offs of the risks associated with insect control in the sugar industry. Additionally, trade-offs may occur at legislative or national levels, which then impact on the risks of insecticide usage at a regional level.

While the introduction and adoption of minimum tillage and trash-blanketing has generally been perceived to be a "good thing" there are trade-offs that have occurred. For example, the conditions that are conducive to increasing the incidence of soil insect pest parasites and disease are also conducive for increasing the incidence of plant disease (Matthieson, 1997). Thus, care must be taken to ensure that fields are free of disease before planting new crops. Trash blanketing may have contributed to numerous fish kills in a number of sugarcane growing regions in north Queensland over recent years by their contribution to low dissolved oxygen concentrations in waterways (Veitch, 1999). Low dissolved oxygen concentrations may occur through movement of anoxic water, formed by decomposition of crop residues on the fields, into creeks, and/or the movement of trash from the fields to waterways in times of heavy rain and then subsequent decomposition in waterways.

An increasing number of rats have been observed in the Herbert region, and other northern catchments, in which green cane harvesting techniques are predominant (Anon., 2000). The increasing rat numbers have been coincident with, and attributed to, the increasing area of green cane trash blanketing practices (R. Hunt, CRC Sugar, pers. comm.). Green cane trash blanketing is likely to have contributed only indirectly to increasing rat numbers through an increase in the amount of harbourage (low-lying grasses and weeds) in headlands adjacent to cane fields, although some nesting of rats in crop residues has been observed. In the past headlands were deliberately burned during pre-harvest burning or other occasions to reduce the amount of harbourage available (Knust, 1935; R. Hunt, CRC Sugar pers. comm.). Since the change to green cane harvesting, these headland areas are no longer burned and amount of vegetation available for rat harbourage has increased.

While the increased incidence of rats is an economic concern for sugarcane farmers due to increased damage of sugarcane, it is also a human health concern. In recent years, coincident with increase in rat numbers in the northern cane growing regions, there has also been an increased incidence of leptospirosis, a disease transmitted in the urine of rats, prompting an industry warning (Anon., 2000c). Banana growers are the primary industry sector at the highest risk of contracting leptospirosis (forming 29.5% of cases notified in January to December 1999) while canegrowers comprised only 1.9% of cases for the same period (Anon., 2000d). However, leptospirosis is a major concern for sugarcane farmers in regions prone to rat damage, particularly in the Herbert region (Streamer, 2000). This concern is largely a legacy of historical events. The first Australian outbreak of leptospirosis occurred in sugarcane workers from the Herbert region in 1934 (Alston *et al.*, 1958). During the 1950s, further cases of leptospirosis occurred in sugarcane workers, and people employed in other occupations, although different strains of leptospirosis were specific for different occupations (Johnson, 1950; Derrick *et al.*, 1954; Doherty *et al.*, 1956). Knowledge of transmission of leptopirosis in rat urine led to the enactment of the *Rat Prevention and Destruction*

Regulations (1942). This Act required that rat damaged fields were inspected prior to manual harvesting. If damage was severe, sugarcane fields were required to be burned prior to harvesting. Ironically, it was also during the early periods of pre-harvest burning that the beneficial effect of burning on reducing New Guinea weevil borer numbers was noted (Mungomery, 1937).

In ascertaining the risk of ecological impact, trade-offs exist in the priority of data collection. While there is an absence of information regarding ecological impacts of insecticide usage, past or present, in the Herbert and Burdekin regions, there is also an absence of information on the ecological impacts of general land-use change. Soil incorporation of insecticides in the Herbert and Burdekin sugarcane areas of relatively low relief, in addition to a relatively small area and low rate of application, indicates that the potential for off-site movement and risk of detrimental ecological impact to aquatic systems are both minimal. In contrast, the expansion of the industry has resulted in different, and substantial ecological impacts as a result of land clearing (e.g. Anon., 1995; Anon., 1996a; Anon., 1996b). However, with the exception of the obvious fact of land-use change and associated destruction of habitat, there is a lack of information regarding ecological impacts. Documented increases in sediment and nutrient loads have occurred although no quantitative information exists as to the ecological impacts of these increased loads (e.g. Furnas *et al.*, 1995; Mitchell *et al.*, 1996; Neil and Yu, 1996). In contrast, ecological impacts, in the form of fish kills, have increased in the Herbert region (and other sugarcane growing regions) in recent years. While the direct cause of the fish kills has been attributed to low dissolved oxygen content of the water, the cause of lowered dissolved oxygen content has not been established - although sugarcane growing has been implicated (Veitch, 1998). Thus, in the context of quantifying detrimental ecological impacts in a region, the priority of collecting information regarding the ecological impact of insecticide use needs to be considered in context of the ecological impacts arising from other land-use activities, such as nutrient and soil loss, and land clearing.

Trade-offs have also occurred at legislative or national levels, which have impacted on the risks of insecticide usage at a regional level. For example, at a national level the trade-off of continuing broad-scale agricultural usage of organochlorine insecticides, despite recommendations in the early 1970s for phasing out this use, was the contamination of export beef with its subsequent impacts on trade. Despite the absence of a significant export beef cattle industry in sugarcane growing regions of the Herbert and Burdekin, organochlorine insecticides were still banned from use in these regions (however, it should be acknowledged that the global environmental concerns also contributed to this banning). No significant ecological impacts in the Herbert and Burdekin regions were reported to have resulted from the use of organochlorine insecticides, although there is a distinct lack of data. Since the banning of organochlorine insecticides, there has been a lack of effective grub control in the Burdekin region, which has resulted in an increase in grub damage. Thus, it could be argued

that the re-introduction of heptachlor, under tightly regulated conditions of use, in the Burdekin region may result in an overall reduction of the risks associated with insect control in this region. However, the inclusion of heptachlor as one of the 12 priority contaminants for reduction or elimination of use in the United Nations Persistent Organic Pollutants Treaty automatically precludes any consideration of its re-introduction (Renner, 1998a). Additionally, from an industry perspective, the reintroduction of heptachlor could have significant trade implications, as it may result in current trading partners imposing bans on imports of Australian sugar.

Pesticide regulatory legislation has changed to avoid further detrimental trade impacts resulting from insecticide usage and to address concerns of detrimental environmental and human health impacts. This has resulted in legislation that requires a more rigorous assessment of the potential trade, environmental, and human health impacts of a particular insecticide prior to use. As a consequence of this rigorous assessment, it takes longer to register new pesticides, especially microbial insecticides. In the case of the Burdekin region, the absence of effective insect control has resulted in economic losses to those farmers growing sugarcane in areas susceptible to damage. This trade-off is analogous to the "risk of substitutes" identified by Gray and Graham (1995) in their analysis of the US system of pesticide regulation that operates in a similar manner to Australian legislation. Furthermore, the trade-offs between on-farm and off-farm risks identified by Gray and Graham (1995) has also occurred in the Australian sugar industry by the change in insecticide use to the more acutely toxic, though less persistent organophosphate insecticide, chlorpyrifos. Such a change increases the human health risks faced by farm workers but reduces the human health risk to consumers and the ecological risk to the environment. Other trade-offs in US legislation identified by Gray and Graham (1995) include trading one health risk for another (e.g. cancer risk for impairment of reproductive function); the use of one pesticide for many (e.g. the shift from broad-spectrum insecticide to multiple specifically targeted insecticides); pesticide risk for pest risk (e.g. shift from an effective pesticide to one of a lower efficacy); and pesticide risks for nutrition risks (eg. as a result of increased cost of food through lower yields and higher production costs in the absence of pesticide use). While no formal analysis has been conducted in Australia, it is likely that these trade-offs also exist.

The impetus for change in pesticide use in the US has been human health concerns, primarily cancer risks, despite considerable debate about determination of cancer risk. This debate stems largely from the use of rodent bioassays to determine human health risks (Ames and Gold, 1990 a, b; Gold *et al.*, 1992; Sielken *et al.*, 1999), but also from the absence of determination of the carcinogenicity of natural insecticides (Ames *et al.*, 1990a and b). In comparison, trade issues have dominated regulatory concerns of the agricultural use of insecticides in Australia. This difference may reflect the considerably larger population in the US in that a small detrimental health risk, multiplied throughout the population, results in a

sufficiently large number of affected people to warrant legislative action (Gray and Graham, 1995). Alternately, this may reflect a difference in the interpretation of the typically limited information available to assess potential human health impacts, in addition to the concerns noted above regarding determination of cancer risks. A difference in interpretation of available data occurred in the decision by the NHMRC to allow continued use of organochlorine insecticides as termiticides in Australia after their banning in the US for human health reasons (ASTEC, 1989). Nonetheless, it was US Government concerns of the cancer risk of organochlorine insecticides that were the basis for a change in acceptable residues levels in import beef by the US Environmental Protection Agency in December 1986 (ASTEC, 1989), and which resulted in the 1987 trade ban. At the time there was speculation that this change may have been an attempt to restrict trade (Barnett, 1987). The World Trade Organisation Agreement on Sanitary and Phytosanitary Measures has recognised trade implications inherent in the establishment of acceptable residue levels and requires that residue standards are, as far as practicable, based on international standards, and that measures providing higher protection are scientifically justifiable and are not a disguised restriction on trade (NRA, 1999).

5.7 Implications for future use of insecticides in the Herbert and Burdekin regions

Insect control in the Herbert and Burdekin regions has been, and will continue to be impacted upon by an array of factors that occur at both national and regional levels. Insecticides have dominated invertebrate pest control strategies in the Australian sugar industry since the introduction of organochlorines in1947. National control of the use of insecticides reflects trade, national, and global issues relating to insecticide usage. The phasing out of agricultural usage of organochlorine insecticides in Australia from the early 1970s was a response to global concerns about environmental impacts, as opposed to any documented detrimental impacts occurring in Australia, although these existed (e.g. Olsen and Olsen, 1979; Connell, 1993; Falkenberg *et al.*, 1994). It was not until continued agricultural usage impacted upon the beef export trade that organochlorine insecticides were generally banned. Trade implications are still important considerations in the assessment for registration and continued use of insecticides and other agricultural chemical products. Current pesticide legislation has the potential to force a change in insecticide usage on sugarcane in the Herbert and Burdekin regions in response to events (e.g. trade or global environmental concerns) that are unrelated to insecticide usage in these regions. However, given that a recent Australian Government review of chlorpyrifos, currently the most widely used insecticide in the Herbert and Burdekin regions, did not recommend changes to chlorpyrifos usage for sugarcane growing purposes (NRA, 2000c), it is unlikely that legislative requirements will be modified in the near future. Additionally, despite the legislative requirements that future expansion of the sugar industry takes into consideration environmental consequences of expansion, the largely discretionary

nature of this requirement is such that sugar industry legislation will also have a minimal impact on insecticide usage.

At a regional level, changes in farming practices, specifically the introduction of green cane harvesting and retention of crop residues on fields, have increased the significance of some insect pests, such as the New Guinea weevil borer, although they have also provided a measure of control of cane grub populations. The risks of insect damage and ecological impacts resulting from insect control are regionally specific. Therefore, it is important to obtain data on a regional basis to make an appropriate assessment of the different risks associated with insect control. For example, the greyback grub is the most significant insect pest in the Burdekin region. Despite substantial increases in the area used to grow sugarcane, the area treated with insecticides for grub control has not significantly increased, and in fact, has decreased subsequent to the banning of organochlorine insecticides. Since then however, the area damaged by the greyback grub has increased and at present there are no effective controls for greyback grubs in the Burdekin region, although some products to be registered soon may help to control grub populations (Anon. 2000e; D. Logan, BSES, pers. comm.). The localised nature of grub damage in this region and the absence of other significant insect pests suggests that the risk of significant grub damage to sugarcane is high for those farmers in areas susceptible to cane grub damage, under favourable conditions. In the Herbert region, the total area treated with insecticides has also not substantially increased despite significant increases in the area harvested for sugarcane, although in recent years, the area treated for wireworms has increased.

The general absence of significant insect damage in the Herbert region since the commencement of insecticide usage with the organochlorine insecticides in 1948 suggests the risk of future insect damage to sugarcane is also likely to be low under continued insecticide usage. However, the preventative application of insecticides precludes an assessment of whether significant damage would have occurred in the absence of insecticide use. There is an absence of information regarding ecological impacts of insecticide usage, past or present, in the Herbert and Burdekin regions although the data collected during this study suggests that there is little potential for on-going ecological impacts on aquatic systems resulting from historical usage of the organochlorine insecticides. In contrast, despite the lack of quantitative information on ecological impacts of land-use change, broad-scale habitat destruction, and increases in invasive water-weeds, number of fish kills, and riverine sediment and nutrient loads have been documented. The suggested low risk of significant detrimental ecological impact resulting from historical usage of persistent bioaccumulative insecticides, particularly in contrast to ecological impacts arising from other sources, suggests that future insecticide usage in the Herbert and Burdekin regions will be driven largely by regional issues related to efficacy of control.

The context of a risk assessment of insecticide usage in the sugar industry needs to be considered carefully in order to make an effective assessment. From a sugar industry perspective, the economic, ecologic and human health risks associated with insecticide usage need to be assessed and then compared with those risks associated with other forms of insect control. From an ecological perspective, assessment of the risk of ecological impact arising from insecticide usage needs to be considered on a regional basis and relative to that arising from other sources.

Chapter 6: Conclusions and future directions

6.1 Summary of conclusions

This thesis has investigated three aspects of organochlorine insecticide use in two significant sugarcane growing regions in North Queensland, the Herbert and Burdekin River regions. The first aspect was the distribution of organochlorine insecticide residues in sugarcane soils, and in coastal and riverine sediments in both regions to assess the current distribution of organochlorines and provide information on historical inputs to coastal sediments (Chapter 2). This information was combined with historical information regarding insecticide use in both regions to derive a mass balance of the applied insecticides (Chapter 3). The second aspect was the use of an enzyme assay (ethoxyresorufin *O*-deethylase, EROD) to assess the exposure of a common tropical estuarine fish species, *Acanthopagrus berda*, to a range of organic contaminants and establish a screening tool for exposure to organochlorine insecticide residues (Chapter 4). The third aspect was the examination of factors that have historically influenced the economic, ecological, and human health risks associated with insect control in the sugar industry to provide insight into which factors are important to consider in the quantitative assessment of these risks (Chapter 5).

The main conclusions from each of the chapters are summarised below.

6.1.1 Organochlorine insecticide residues in soils and sediments - implications for contamination of the Great Barrier Reef.

- Easily detectable concentrations of organochlorine insecticide residues were found in surface soils of sugarcane land in the Herbert and Burdekin River regions and reflected historical usage patterns. Hexachlorocyclohexanes (ΣHCH, 2.33 ng g^{-1} (geometric mean); <0.01-57.92 ng g^{-1} (range)) and dieldrin (1.25 ng g^{-1} (geometric mean); 0.03- 27.6 ng g^{-1} (range)) were present at the highest concentrations in sugarcane soils of the Herbert region (section 2.). This reflected the widespread use of HCH formulations for cane grub control and aldrin for wireworm control (section). Hexachlorocyclohexanes (ΣHCH, 0.62 ng g^{-1} (geometric mean); <0.01-3.21 ng g^{-1} (range)), heptachlor epoxide (0.28 ng g-1 (geometric mean); <0.01-18.2 ng g^{-1} (range)) and trans-chlordane (0.16 ng g^{-1} (geometric mean); <0.01-10.9 ng g^{-1} (range)) were most frequently detected in the sugarcane soils of the Burdekin region, reflecting historical usage of HCH formulations and heptachlor for cane grub control (sections 2.3.2; 2.4.2).

- The lower concentrations of organochlorine residues in sugarcane soils of the Burdekin Region may reflect the influence of farming practices (conventional cultivation and irrigation) employed in this region on volatilization losses of insecticides, or a lower rate of insecticide application (section 2.4.2).

- Analysis of the vertical distribution of organochlorine residues in three soil cores collected from the inter-rows of planted sugarcane fields showed that the maximum concentrations of organochlorine residues occurred at a depth of 0-10 cm (section2.). In contrast, maximum concentrations of organochlorine residues in a soil core collected from a recently cultivated field were present at 40-50 cm. Cultivation and soil type may account for the observed difference in organochlorine distribution in this soil core. Generally, less than 5% of the total organochlorine residues present in the top 70 cm were present at 60-70 cm in the soil cores (sections 2.3.3; 2.4.1).

- The clay (< 2 μm) and silt (2-20 μm) size fractions in four soils used to assess the particle size distribution of organochlorine residues contained the highest concentrations of organochlorine residues (section 2.3.4). The concentration of organochlorine residues present in the clay and silt fractions were 2-10 times those of the sand fractions (>20 μm). These size fractions also contained the highest organic carbon content, but no differentiation could be made between the effect of adsorption on mineral (clay) surfaces as compared with that on organic carbon. The presence of high concentrations of organochlorine compounds in the more easily eroded size fraction has significant implications for the widespread distribution of residues in the adjacent aquatic systems (section 2.3.4)

- Low and variable concentrations of organochlorine residues were found in on-farm drains and sediments from creeks draining sugarcane land indicating that some off-farm movement of soil and adsorbed residues is currently occurring, with dieldrin most frequently detected (sections 2.3.5; 2.4.3).

- Dieldrin and γ-HCH concentrations in sugarcane soils of the Herbert region most frequently exceeded ANZECC sediment quality guidelines (ANZECC, 1999) and Department of Primary Industry soil quality guidelines for beef cattle (DPI, 1997). Dieldrin, γ-HCH and chlordane concentrations in sugarcane soils from the Burdekin region most frequently exceeded ANZECC sediment quality guidelines. Dieldrin concentrations in on-farm drains and creek sediments most frequently exceeded ANZECC sediment quality guidelines (section 2.4.4).

- No detectable concentrations of organochlorine residues were found in coastal sediments of either the Herbert or Burdekin region. Together with known sediment transport processes, this absence suggests that no contamination of the Great Barrier Reef as a result of historical application of organochlorine insecticides in these regions is currently occurring (section 2.4.3).

6.1.2 Where did all the organochlorines go? A mass balance for the Herbert and Burdekin Regions.

- Since 1948, 3,900 tonnes of technical HCH (or 0.04% of the total global usage over the period 1940-1990; Li, 1999), 40 tonnes of aldrin, and 46 tonnes of heptachlor have been used on sugarcane in the Herbert and Burdekin regions (section 3.3.1).

- Currently less than 0.01% of the applied amount of individual insecticides is estimated to remain in the sugarcane soils of the Herbert and Burdekin regions. Fifteen years (Herbert region) and 10 years (Burdekin region) may be required for residues currently present in the soils to fall below detectable concentrations (section 3.3.4.1).

- Annual losses of 0.4-64 tonnes of α-HCH, 0.02-13 tonnes of other HCH isomers, and 0.2-2 tonnes of dieldrin to the atmosphere may have occurred annually, if volatilisation is considered to be the major mechanism of removal of organochlorine residues from the sugarcane soils of the Herbert and Burdekin Regions (section 3.3.4.2).

- Alternatively, if degradation processes (biotic and abiotic) were considered to be the major mechanism of removal, half lives of 210-318 days (Burdekin region) and 292-398 days (Herbert region) are required for organochlorine insecticides applied over 1948-1987 to be present at soil concentrations measured in 1997 (section 3.3.3.1).

- At a run-off loss rate of 0.5% of the cumulative amount of residues remaining in the soil each year, degradation rates of individual compounds in the marine environment that are slower than those estimated for degradation in the soil, will result in organochlorine residues being undetectable in coastal sediment of the Burdekin region (assuming a river sediment load of 8.6×10^9 kg). In contrast, marine degradation rates as fast as predicted soil degradation rates, will result in detectable residues in coastal sediments of the Herbert region, although only in sediment derived from soil eroded since mid-1980s. The absence of detectable residues in this region suggests that either degradation rates are faster than those used, or that other processes are important in reducing organochlorine concentrations (section 3.3.4.3).

- At soil concentrations determined in 1997, unrealistically high (15-110 tonne ha^{-1}) soil losses in the Burdekin Region and high, although realistic (<1-6 tonne ha^{-1}) soil losses in the Herbert region are required to produce detectable concentrations of organochlorine insecticide residues in coastal sediments (section 3.3.4.3). This suggests that the absence of organochlorine residues in the surface coastal sediments of these regions is not surprising, and supports the hypothesis that >99% of the organochlorine insecticides

applied in the Herbert and Burdekin regions have been lost through volatilization or degradation processes.

6.1.3 Investigation of the application of enzyme induction in *Acanthopagrus berda* as a screening tool for organochlorine insecticide residue exposure.

- Assessment of hepatic P-450 1A induction, as measured by ethoxy resorufin *O*-deethylase (EROD) assays, in an Australian tropical estuarine fish species *Acanthopagrus berda* (Pikey Bream), collected from creeks draining urban, agricultural and relatively undisturbed catchments proved useful to identify locations where organic contaminants might be stressing fish. The limited movement of *A. berda* between and within creek systems enables a greater degree of specificity of the source of inducers.

- Fish collected from 2 creeks draining relatively undisturbed land (Baldy Creek and Fisher Creek) showed a low level of induction of cytochrome P-450 1A, as measured by EROD activity (67-114 pmol min^{-1} mg^{-1} protein), which contrasted markedly with the high level of activity (564 pmol min^{-1} mg^{-1} protein) observed in fish captured from Ross Creek, which drains through Townsville (section 4.3.2).

- A low level of EROD activity (142-196 pmol min^{-1} mg^{-1} protein) was observed in fish collected from 3 creeks draining sugarcane land (2 in the Herbert region and 1 in the Burdekin region). A fourth creek (Cromarty Creek) draining sugarcane land in the Burdekin region showed unexpectedly high levels of EROD activity (492 pmol min^{-1} mg^{-1} protein), which was similar to that of fish captured from Ross Creek (section 4.3.2).

- PAHs are suggested to be the cause of induction of P-450 1A in fish collected from Ross Creek and fish collected from creeks draining sugarcane catchments, with the exception of those captured from Cromarty Creek. The inducer and source of induction of P-450 1A in Cromarty Creek was not identified, although a landfill dump and recreational boating activity may contribute to the observed induction (section 4.4.2; 4.4.3).

- Sex, reproductive status, and fish health were demonstrated to influence P450 1A activity in *A. berda* with female fish, reproductively active fish and fish with external lesions showing a lower level of activity compared with non-reproductively active male fish (section 4.3.3).

- Laboratory trials to characterise the responses of the P-450 1A system in *A. berda* to a known inducer (β-napthoflavone) and a mixture of HCH isomers indicated significant non-linear dose-responses although, low and variable responses were generally observed.

These low responses were partly attributed to the use of post-mitochondrial supernatant during enzyme assays instead of the more purified microsomal protein (section 4.3.1; 4.4.1)

- The low incidence of detection of organochlorine residues in creek sediment and fish tissue did not enable the relationship between organochlorine exposure in fish and EROD activity to be adequately assessed. The low incidence of detection of organochlorine compounds in the aquatic environments of the Herbert and Burdekin regions combined with the observation that significant induction did occur in fish collected from certain locations, and that this induction is likely to be caused by exposure to PAHs, suggests that EROD activity is not a suitable tool to assess the exposure of fish to organochlorine residues in the study regions. However, EROD activity in *A. berda* provided a useful screening tool to assess the exposure of fish to organic contaminants in a number of different creek systems to identify systems which may be stressed from organic contaminant exposure (section 4.3.4).

6.1.4 Factors influencing insecticide usage in the sugar industry

- Changes in sugarcane farming practices for reasons other than insect control, have had both beneficial and detrimental influences on insect pest populations, and therefore indirectly, on insecticide usage. For example, the introduction of minimum tillage practices and the re-introduction of green cane harvesting and retention of post-harvest crop residues on sugarcane fields for soil erosion control has resulted in an increased incidence of parasites of cane grubs, but also has been attributed to increasing the significance of the New Guinea weevil borer, which was previously of minor concern (section 5.3; 5.5.1).

- Contamination of export beef with organochlorine insecticide residues was the major impetus for legislative banning of agricultural use of organochlorine insecticides in Australia in 1987, although mounting concern of their environmental impact also undoubtedly played a role in the ban.

- Subsequent to banning of organochlorine insecticides, failure of registered insecticides has led to increased damage to sugarcane by insect pests, most notably canegrubs in the Burdekin region. This in turn has led to increasing emphasis being placed on the development of Integrated Pest Management techniques.

- Current pesticide legislative requirements are unlikely to influence insecticide usage in the Herbert and Burdekin regions in the near future. Similarly, despite changes in sugar industry legislation to address concerns of the ecological impact of sugarcane expansion (which could include insecticide usage), these changes are unlikely to influence

insecticide usage. Instead, issues relating to the efficacy of control provided by insecticides or alternate insect control methods are likely to drive insecticide use in the near future (section 5.7).

6.2 Areas for further research

Within each of the aspects investigated in this thesis, scope for further research exists. Listed below are some suggestions for areas of further research.

- Comparison of organochlorine residues in estuarine and wetland sediment cores collected from the coastal regions of catchments with different topographies and climatic conditions from those of the Herbert and Burdekin regions could provide an indication of the importance of soil erosion in determining the distribution of residues in the coastal environment. These comparisons should also take into consideration the application history of organochlorine insecticides within a given catchment, in addition to the current distribution of insecticide residues in the soils of that catchment.

- Mass balance estimates provided useful insights into the relative importance of different loss mechanisms to explain the observed distribution of organochlorine residues in the Herbert and Burdekin regions and thus should be incorporated into process orientated studies of specific catchments and downstream coastal sediments. However, it should be acknowledged that information on the inputs of contaminants, such as organochlorine insecticides, which provided an integral part of the mass balance equations in this thesis, may not always be available.

- Although fish collected from Ross Creek were anticipated to show a relatively high level of P-450 1A induction, the high level of activity in fish captured from Cromarty Creek was unexpected and may indicate that exposure to unknown organic contaminants may be causing stress in these fish. Further work is currently being undertaken to establish whether these fish were exposed to a transient or chronic source of induction and the geographical extent of induction within the Haughton River system in order to identify the inducer, and its source, in this system.

- Additional laboratory trials are required to adequately establish the response of the P-450 1A system in *A. berda* to known inducers such as β-napthoflavone. Use of post-mitochondrial supernatant in enzyme assays did not appear to be successful and further work should use the separated microsomal protein. Further investigation of the response of P-450 1A to the exposure to HCH is warranted, given the current absence of a biomarker for exposure to these compounds (Willett *et al.*, 1998).

- The last chapter of this thesis focussed upon factors that have influenced historical insecticide usage and insect control to provide a broader perspective of the issues facing insecticide use in the sugar industry, and to provide constructive insight into factors likely to drive future insecticide usage. While this discussion was considered from the perspective of risks associated with insect control, there was limited discussion of the application of risk assessment to insecticide usage or insect control, other than to note that the context of the risk assessment needs to be carefully considered. The application of risk assessment in environmental decision-making in Australia is limited and thus, there is considerable scope for further research in the sugar industry.

- Two areas in which risk assessment could be effectively applied in the sugar industry are in the assessment of the relative risk of ecological impact arising from different farming practices, and assessment of the trade-offs that occur as a result of reducing a particular risk. Considerable information exists on aspects of environmental impact of different aspects of sugarcane farming such as fertiliser application and land expansion. There have been limited attempts to assess this information to identify which farming practices are likely to be causing the most impact or to identify knowledge gaps that need to be filled before such assessments can be made. Appropriate risk assessment methodologies can provide the basis for this integration. For example, Landis and Weigers (1997) proposed a regional risk assessment model that ranks different sources of ecological impact, providing direction for decision-makers to reduce the ecological impact of anthropogenic activities.

- Recognition that trade-offs (increases in non-target risks as a result of decreasing a target risk) occur as a result of changing economic and social (ecological and human health) demands or expectations to reduce risk, has highlighted the need for analysis of these trade-offs (Gray and Graham, 1995). In such "risk vs risk" assessments, emphasis is placed on an assessment of all risks (economic, ecological, and human health) associated with a particular practice, as opposed to assessment of a particular risk. The ultimate aim is to provide decision-makers with information that will result in an overall reduction in risk. Assessments of this nature are inherently more subjective, and will necessarily change as community expectations change and more scientific knowledge becomes available. Such assessments have the potential to provide a quantitative basis for the concept of sustainability, which underpins much of the reasons for changes in current sugarcane farming practices. With respect to insecticide usage and insect control in the sugar industry, assessment of the economic, ecological, and human health risks associated with different forms of insect control should be conducted to ensure that any changes do result in an overall reduction of the risks.

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Appendix A: Date of collection and location of samples for organochlorine analyses.

Table A.1. **Date of collection and location of surface soil samples collected from sugarcane fields in the Burdekin region.**

Sample	Sub-region	Sample Type†	Location		Date collected	Previous land use
			S	E		
S071	Giru	SS	19° 34.17'	147° 5.41'	22/12/1997	
S075	Giru	SS	19° 32.02'	147° 7.27'	9/01/1998	
S076	Giru	SS *	19° 32.07'	147° 7.08'	9/01/1998	
S077	Giru	SS *	19° 33.15'	147° 6.86'	9/01/1998	
S078	Giru	SS	19° 33.14'	147° 6.23'	9/01/1998	
S037	Inkerman 1	SS	19° 41.06'	147° 24.36'	11/12/1997	
S038	Inkerman 1	SS	19° 40.96'	147° 24.63'	11/12/1997	
S043	Inkerman 1	SS	19° 39.88'	147° 23.21'	17/12/1997	
S047	Inkerman 1	SS	19° 39.11'	147° 25.72'	17/12/1997	
S084	Inkerman 1	SS	19° 40.50'	147° 23.4o'	23/01/1998	
S045	Inkerman 2	SS	19° 43.80'	147° 24.43'	17/12/1997	
S046	Inkerman 2	SS	19° 42.22'	147° 26.84'	17/12/1997	
S048/SC	Inkerman 2	SS, SC, SF	19° 42.67'	147° 18.45'	17/12/1997	
S021	Invicta 1	SS	19° 33.10'	147° 26.21'	19/06/1997	
S023	Invicta 1	SS #	NR	NR	20/06/1997	
S034/HC	Invicta 1	SS, SC, SF#	19° 38.49'	147° 30.14'	11/12/1997	
S035	Invicta 1	SS	19° 36.65'	147° 26.42'	11/12/1997	
S036	Invicta 1	SS #	19° 36.53'	147° 25.95'	11/12/1997	
S039	Invicta 1	SS	19° 35.87'	147° 24.23'	12/12/1997	
S041	Invicta 1	SS	19° 35.87'	147° 24.23'	12/12/1997	
S025	Invicta 2	SS	19° 36.31'	147° 21.52'	20/06/1997	
S030	Invicta 2	SS	19° 37.27'	147° 22.04''	10/12/1997	
S031	Invicta 2	SS	19° 38.56'	147° 22.63'	10/12/1997	
S032	Invicta 2	SS	19° 39.42'	147° 22.21'	10/12/1997	
S033	Invicta 2	SS	19° 37.02'	147° 22.19'	10/12/1997	
S072	Upper Burdekin	SS *#	20° 13.81'	147° 17.55'	9/01/1998	Tobacco
S073	Upper Burdekin	SS *	20° 16.91'	147° 18.01'	9/01/1998	
S079	Upper Burdekin	SS *	20° 13.77'	147° 16.93'	23/01/1998	
S074	Upper Burdekin	SS	20° 6.76'	147° 16.20'	9/01/1998	
S080	Upper Burdekin	SS	19° 59.64'	147° 15.01'	23/01/1998	Tobacco
S081	Upper Burdekin	SS	20° 0.80'	147° 14.84'	23/01/1998	

†SS-surface soil samples; SC-soil core; SF-size fraction analysis; *samples used for within farm comparison, # samples used for duplicate analyses; NR not recorded.

Table A.2. **Date of collection and location of surface soil samples collected from sugarcane fields in the Herbert region.**

Sample	Sub-region	Sample Type†	Location		Date collected
			S	E	
S005	Abergowrie	SS	18° 32.89'	146° 1.32'	17/06/1997
S007/ LC	Abergowrie	SS, SC, SF	18° 28.26'	145° 54.61'	17/06/1997
S058	Abergowrie	SS	18° 27.62'	145° 54.27'	18/12/1997
S061	Abergowrie	SS	18° 26.28'	145° 52.15'	19/12/1997
S063/ VC	Abergowrie	SS, SC, SF *	18° 29.23'	145° 55.43'	19/12/1997
S015	Macknade	SS *	18° 32.88'	146° 16.83'	18/06/1997
S017	Macknade	SS *	18° 34.00'	146° 16.61'	18/06/1997
S019	Macknade	SS	18° 32.52'	146° 14.02'	18/06/1997
S051	Macknade	SS #	18° 33.3'	146° 14.87'	18/12/1997
S052	Macknade	SS *	18° 33.92'	146° 15.08'	18/12/1997
S053	Macknade	SS	18° 33.92'	146° 15.08'	18/12/1997
S064	Macknade	SS *	18° 33.94'	146° 16.60'	21/12/1997
S067	Macknade	SS *	18° 34.04'	146° 15.78'	21/12/1997
S085	Macknade	SS	18° 34.21'	146° 13.03'	22/12/1997
S086	Macknade	SS	18° 36.23'	146° 13.58'	22/12/1997
S009	Ripple Creek	SS	18° 35.30'	146° 05.05'	18/06/1997
S011	Ripple Creek	SS	18° 37.3'	146° 08.21'	18/06/1997
S001	Stone River	SS	18° 40.04'	146° 0.10'	17/06/1997
S003	Stone River	SS	18° 41.32'	145° 59.18'	17/06/1997
S062	Stone River	SS	18° 41.91'	145° 58.62'	19/12/1997
S059	Victoria	SS *	18° 39.32'	146° 14.96'	18/12/1997
S060	Victoria	SS *	18° 39.34'	146° 14.64'	18/12/1997
S070	Victoria	SS	18° 40.45'	146° 13.14'	21/12/1997

†SS-surface soil samples; SC-soil core; SF-size fraction analysis; *samples used for within farm comparison, # samples used for duplicate analyses; NR not recorded.

Table A.3. **Location and date of collection of sample from an on-farm drainage line in the Burdekin region (ID), Eight-mile Creek, Plantation Creek and an on-farm drainage line located in the Herbert region (HC).**

Sample	Region	Sample Site	Location		Date collected
			S	E	
ID-1	Burdekin	on-farm drain	20° 14.73'	147° 17.75'	9/01/1998
ID-2	Burdekin	on-farm drain	20° 16.91'	147° 18.01'	9/01/1998
ID-3	Burdekin	on-farm drain	20° 13.26'	147° 17.44'	9/01/1998
ID-3a	Burdekin	on-farm drain	20° 13.26'	147° 17.44'	9/01/1998
ID-3b	Burdekin	on-farm drain	20° 13.26'	147° 17.44'	9/01/1998
ID-4	Burdekin	on-farm drain	20° 13.12'	147° 17.26'	9/01/1998
8MC-1	Burdekin	Eight-Mile Creek	20° 16.86'	147° 17.26'	9/01/1998
8MC-2	Burdekin	Eight-Mile Creek	20° 13.12'	147° 17.26'	9/01/1998
8MC-3	Burdekin	Eight-Mile Creek	20° 11.04'	147° 16.94'	9/01/1998
8MC-4	Burdekin	Eight-Mile Creek	20° 9.11'	147° 16.39'	9/01/1998
8MC-5	Burdekin	Eight-Mile Creek	20° 9.11'	147° 16.39'	9/01/1998
PC-1	Burdekin	Plantation Creek	19° 37.02'	147° 21.61'	23/01/1998
PC-2	Burdekin	Plantation Creek	19° 37.29'	147° 22.89'	23/01/1998
PC-3	Burdekin	Plantation Creek	19° 35.18'	147° 23.85'	23/01/1998
PC-4	Burdekin	Plantation Creek	19° 35.11	147° 25.67'	23/01/1998
PC-5	Burdekin	Plantation Creek	19° 32.20	147° 30.21'	23/01/1998
PC-6	Burdekin	Plantation Creek	19° 32.14	147° 30.79'	23/01/1998
HC-1	Herbert	on-farm drain	18° 33.90'	146° 15.08'	18/12/1997
HC-2	Herbert	on-farm drain	18° 33.68'	146° 15.40'	18/12/1997
HC-2a	Herbert	on-farm drain	18° 33.68'	146° 15.40'	18/12/1997
HC-2b	Herbert	on-farm drain	18° 33.68'	146° 15.40'	18/12/1997
HC-3	Herbert	on-farm drain	18° 32.44'	146° 15.61'	18/12/1997

Table A.4. **Location and collection dates of sediment core and surface marine sediment samples collected from the Herbert and Burdekin regions.**

Sample number	Core (C)/ Grab sample (G)	Core length (m)	Water depth (m)	Location S	Location E	Date collected
Burdekin region						
1260	C	3.82	14	19° 17.9'	147° 21.1'	January 1995
1241	C	1.09	4	19° 47.2'	147° 41.9'	January 1995
1248	C	1.54	6	19° 40.4'	147° 38.2'	January 1995
1250	C	2.94	6	19° 22.0'	147° 21.4'	January 1995
Herbert region						
1450	C	2.83	10	18° 32.0'	146° 22.9'	July 1996
1262	C	1.3	5	18° 24.5'	146° 10.3'	June 1995
1451	G	-	4	18° 24.8'	146° 09.7'	July 1996
1453	G	-	3.5	18° 13.7'	146° 09.1'	July 1996
1455	G	-	3.5	18° 13.9'	146° 04.8'	August 1996
1457	G	-	4.5	18° 16.5'	146° 03.3'	August 1996
1458	G	-	3	18° 16.6'	146° 03.1'	August 1996
1468	G	-	17	18° 07.8'	146°.16.6'	August 1996
1470	G	-	10	18° 23.5'	146° 20.7'	August 1996
1473	G	-	58	18° 01.5'	146° 40.7'	August 1996
1477	G	-	126	18° 11.3'	148° 08.3'	August 1996

Appendix B: Method for radionuclide dating

Radiochemical age estimates

Gamma spectrometric measurements of Pb-210, Ra-226, Cs-137, and other isotopes were made on 50-150 grams of dried and ground bulk sediment packed with a 10 tonne hydraulic jack into a custom designed gas-tight plastic container. After storage for 3-4 weeks, the radon daughter in-growth allows direct estimation of Pb-210 from the 46.5 keV gamma emission. Radium 226 was estimated from the gamma photopeaks of Pb-214 at 295 and 351 keV, and Bi-214 at 609 keV. Thermonuclear bomb fallout nuclide Cs-137 was estimated from the 661.6 keV gamma emission of Ba-133. Four planar germanium detectors and one well germanium detector were used inside 1 tonne lead castles with steel liners. The energy spectra of the gamma spectrometers were calibrated with known low activity spikes of suitable nuclides into cleaned silica sand in geometry and mass similar to the sediment samples. Counting errors of these measurements were less than 10%.

Interpretations of the radiochemical tracers of sedimentation history were performed using several sub-models described by Robbins (1978, 1986), which utilize a sediment mixed layer thickness, a decadal-century scale average input of Pb-210, Brisbane measurements of thermonuclear bomb fallout Sr-90 (Cs-137) over 1950-1990, and diffusion coefficients (Kd) for Pb-210 and Cs-137 in marine sediments (Li and Gregory, 1974). Estimates of atmospheric flux of Pb-210 and Cs-137 have been obtained from soil profiles in the Herbert River alluvial floodplain and near the Australian Institute of Marine Science (Brunskill and Pfitzner, unpublished). Confidence in sediment core Pb-210 chronology was enhanced by the use of Cs-137 data and the known history of phosphatic fertiliser application in the adjacent Herbert River valley sugarcane lands, together with the appearance of elevated concentrations of Cd (a contaminant found in the phosphatic fertilisers applied) in the sediment cores (Tesiram and Brunskill, unpublished).

Appendix C: Organochlorine concentration in individual surface soil samples, soil cores and soil fractions.

Table C.1. **Concentration of organochlorine residues (ng g^{-1}), extractable organic matter (EOM) and organic carbon content in surface sugarcane soils collected from different sub-regions in the Burdekin region.**

Compound	Concentration (ng g^{-1})																		
Region	*Invicta*										*Inkerman*								
	S021	S023	S025	S030	S031	S032	S033	S034	S035	S036	S037	S038	S039	S041	S043	S045	S046	S047	S048
α-HCH	0.287	<0.010	0.037	0.098	0.125	0.046	0.179	0.087	<0.010	0.089	<0.010	<0.010	<0.010	<0.010	0.052	<0.010	0.026	<0.010	0.043
β-HCH	1.918	<0.010	0.075	1.133	0.694	0.454	0.421	1.303	<0.010	0.337	0.102	0.109	<0.010	<0.010	0.144	0.276	0.159	<0.010	0.288
γ-HCH	0.828	1.142	0.849	0.311	0.653	0.102	0.910	0.264	<0.010	0.211	<0.010	0.393	0.187	<0.010	<0.010	<0.010	0.148	0.255	<0.010
δ-HCH	0.179	<0.010	<0.010	0.048	<0.010	<0.010	0.051	0.055	<0.010	0.079	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
aldrin	<0.010	<0.010	0.050	<0.010	<0.010	<0.010	<0.010	0.101	<0.010	<0.010	<0.010	<0.010	0.029	0.050	0.038	0.025	<0.010	<0.010	0.030
dieldrin	<0.010	<0.010	0.291	<0.010	0.060	<0.010	<0.010	0.203	<0.010	0.089	0.028	0.079	0.066	0.162	0.215	1.266	<0.010	<0.010	0.960
heptachlor	<0.010	<0.010	0.207	0.050	<0.010	0.073	<0.010	0.166	0.086	0.202	0.047	0.126	0.069	0.059	0.026	0.053	<0.010	0.140	0.113
heptachlor epoxide	<0.010	0.041	5.920	7.000	1.364	2.439	0.817	12.988	0.553	3.528	0.168	6.938	0.282	0.319	0.418	18.190	16.347	0.116	7.186
trans-chlordane	<0.010	0.038	2.907	1.607	0.286	0.601	0.153	5.658	0.698	1.437	0.097	1.599	0.310	0.338	0.258	10.094	4.144	0.120	3.278
cis-chlordane	<0.010	<0.010	0.796	0.552	0.090	0.158	0.044	1.231	0.135	0.390	<0.010	0.744	0.052	0.080	0.056	2.745	1.390	0.036	0.791
p, p'- DDE	1.044	<0.010	0.028	0.074	<0.010	<0.010	0.033	<0.010	<0.010	0.038	0.036	0.046	<0.010	<0.010	0.057	8.602	0.040	<0.010	0.224
p, p'- DDD	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.369	<0.010	<0.010	<0.010
p, p'- DDT	0.053	<0.010	0.053	0.035	<0.010	<0.010	<0.010	0.029	<0.010	<0.010	0.035	<0.010	<0.010	<0.010	<0.010	0.462	0.078	<0.010	0.062
chlorpyrifos	<0.010	<0.010	<0.010	<0.010	<0.010	0.072	<0.010	0.054	<0.010	<0.010	<0.010	0.038	0.035	0.031	0.661	<0.010	0.327	0.178	1.173
hexachlorobenzene	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.046	0.042	0.035	0.049	<0.010	0.045	0.036	0.048	<0.010	0.053	0.041	0.037	0.034
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.040	<0.010	<0.010	<0.010	<0.010	<0.010	0.037
endosulfan II	<0.010	<0.010	0.049	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.026	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	0.085	0.033	<0.010	<0.010	0.058	<0.010	0.053	0.116	0.034	0.103	0.052	0.135	<0.010	<0.010	0.068	<0.010	<0.010
endrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
methoxychlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
Total concentration	4.36	1.28	11.36	11.02	3.39	4.02	2.76	22.20	1.65	6.58	0.62	10.25	1.18	1.26	1.95	42.14	22.79	0.94	14.24
EOM (mg g^{-1})	0.77	1.53	0.98	0.02	0.01	0.01	0.01	0.01	0.01	0.02	0.05	0.04	0.03	0.02	0.02	0.02	0.01	0.03	0.02
organic carbon (%)	0.8	0.9	1.7	0.7	0.8	0.6	0.6	1.2	0.9	1.0	1.1	1.3	1.4	1.2	1.2	1.3	1.0	0.8	1.1

Table C.1 cont. Concentration of organochlorine residues (ng g^{-1}), extractable organic matter (EOM) and organic carbon content in surface sugarcane soils collected from different sub-regions in the Burdekin region.

Compound	Concentration (ng g^{-1})										
Region	*Giru*				*Upper Burdekin*						
	S071	S075	S077	S078	S072	S073	S074	S079	S081	S084	S080
α-HCH	0.151	0.146	0.739	0.084	0.087	0.082	<0.010	<0.010	<0.010	<0.010	<0.010
β-HCH	1.224	0.683	<0.010	0.928	2.651	0.186	<0.010	<0.010	0.031	<0.010	<0.010
γ-HCH	0.358	0.158	0.943	0.723	0.143	0.204	<0.010	<0.010	<0.010	1.645	<0.010
δ-HCH	0.088	0.053	1.259	<0.010	0.051	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
aldrin	0.057	0.042	<0.010	0.112	<0.010	0.069	<0.010	<0.010	<0.010	<0.010	<0.010
dieldrin	3.679	0.423	<0.010	0.357	0.227	0.254	<0.010	<0.010	<0.010	0.047	<0.010
heptachlor	0.036	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
heptachlor epoxide	8.312	0.043	<0.010	<0.010	<0.010	0.055	<0.010	<0.010	<0.010	0.050	0.026
trans-chlordane	1.429	0.028	<0.010	<0.010	0.014	0.069	<0.010	<0.010	<0.010	0.026	<0.010
cis-chlordane	0.660	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'- DDE	0.041	0.035	0.533	0.043	27.843	0.139	15.957	0.182	0.037	16.512	6.204
p, p'- DDD	<0.010	<0.010	0.061	<0.010	0.305	<0.010	0.400	0.026	<0.010	0.629	0.111
p, p'- DDT	0.079	<0.010	0.165	0.067	0.856	0.088	1.187	<0.010	<0.010	1.526	0.342
chlorpyrifos	0.049	0.129	63.905	0.132	0.025	0.028	<0.010	0.042	<0.010	0.108	0.128
hexachlorobenzene	0.045	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.027	<0.010
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.363	<0.010
endosulfan sulfate	0.146	0.159	<0.010	<0.010	<0.010	0.045	<0.010	<0.010	0.092	0.143	0.084
endrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
methoxychlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.034	<0.010	<0.010	<0.010	<0.010
Total concentration	16.35	1.97	67.67	2.51	32.22	1.26	17.60	0.33	0.21	21.10	6.94
EOM (mg g^{-1})	0.02	0.02	0.04	0.02	0.01	0.02	0.01	0.04	0.03	0.02	0.01
organic carbon (%)	0.9	1.7	1.0	1.0	0.3	0.5	0.4	0.8	0.6	0.6	1.2

Table C.2. **Concentration of organochlorine residues (ng g^{-1}), extractable organic matter (EOM) and organic carbon content in surface sugarcane soils collected from different sub-regions in the Herbert region.**

Compound	Concentration (ng g^{-1})												
Region	*Stone River*			*Ripple Creek*		*Abergowrie*					*Victoria*		
	S001	S003	S062	S009	S011	S005	S007	S063	S058	S061	S070	S059	S060
α-HCH	2.303	0.367	0.936	4.102	0.733	4.894	6.000	4.552	4.017	3.367	0.146	2.154	1.427
β-HCH	2.081	0.898	4.360	6.727	0.765	45.641	9.943	13.015	7.267	4.291	0.250	3.812	2.032
γ-HCH	1.027	0.137	0.881	2.649	0.319	3.989	3.307	2.829	2.160	1.875	0.183	1.992	1.448
δ-HCH	0.605	0.103	0.263	1.774	0.164	2.768	2.512	1.894	0.563	1.006	0.066	0.909	1.135
aldrin	0.130	<0.010	0.043	0.079	0.050	0.132	<0.010	0.098	0.077	<0.010	<0.010	0.121	0.058
dieldrin	7.513	7.710	27.645	2.025	2.427	7.053	0.029	11.233	2.611	0.867	0.512	7.506	0.905
heptachlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.073	<0.010	<0.010	<0.010	<0.010	<0.010
heptachlor epoxide	<0.010	<0.010	0.016	<0.010	<0.010	<0.010	<0.010	2.151	<0.010	<0.010	<0.010	<0.010	<0.010
trans-chlordane	<0.010	<0.010	<0.010	<0.010	0.011	<0.010	<0.010	0.439	<0.010	<0.010	<0.010	<0.010	<0.010
cis-chlordane	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.217	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'- DDE	6.217	0.070	0.092	0.446	2.371	0.492	0.097	0.959	0.208	0.132	0.265	0.095	0.027
p, p'- DDD	0.027	<0.010	<0.010	<0.010	0.031	<0.010	<0.010	0.028	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'- DDT	0.226	0.017	0.042	0.047	0.411	0.069	0.092	0.338	0.147	0.149	0.091	0.052	<0.010
chlorpyrifos	1.871	<0.010	0.122	<0.010	<0.010	<0.010	<0.010	0.146	0.329	0.239	0.270	0.770	37.325
hexachlorobenzene	0.031	<0.010	0.020	0.017	0.016	<0.010	<0.010	<0.010	0.030	<0.010	<0.010	<0.010	0.026
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	0.081	0.026	<0.010	<0.010	<0.010	<0.010	0.063	0.045	0.052	0.095	0.078
endrin	<0.010	<0.010	<0.010	0.044	<0.010	0.038	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	0.023	<0.010	0.021	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
methoxychlor	0.065	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.255	<0.010	<0.010	<0.010	<0.010	<0.010
Total concentration	22.10	9.37	34.51	17.97	7.30	65.13	22.01	38.25	17.50	12.00	1.87	17.54	44.52
EOM (mg g^{-1})	9.32	7.72	0.02	4.29	1.49	4.97	1.07	0.02	0.02	0.01	0.03	0.02	0.01
organic carbon (%)	1.11	1.11	0.61	2.00	1.66	1.52	1.29		1.06	1.47	1.13	0.88	0.89

Table C.2 cont. Concentration of organochlorine residues (ng g^{-1}), extractable organic matter (EOM) and organic carbon content in surface sugarcane soils collected from the Macknade sub-region of the Herbert region.

Compound	Concentration (ng g^{-1})								
Region	Macknade								
	S015	S017	S019	S051	S052	S064	S067	S086	S085
α-HCH	<0.025	0.032	1.450	0.295	0.021	<0.025	0.036	<0.025	0.946
β-HCH	0.036	0.069	4.145	0.279	0.034	<0.025	<0.025	<0.025	1.604
γ-HCH	<0.025	<0.025	1.275	0.583	<0.025	0.256	0.127	<0.025	0.677
δ-HCH	<0.025	<0.025	0.718	0.073	<0.025	<0.025	<0.025	<0.025	0.448
aldrin	<0.025	<0.025	0.032	0.146	<0.025	<0.025	<0.025	<0.025	0.039
dieldrin	0.037	0.042	2.111	1.904	1.837	0.178	0.079	0.925	1.151
heptachlor	<0.025	<0.025	<0.025	0.020	<0.010	0.078	<0.025	<0.025	<0.025
heptachlor epoxide	<0.025	<0.025	<0.025	<0.025	0.230	0.295	0.087	0.495	<0.025
trans-chlordane	<0.025	<0.025	<0.025	<0.025	0.850	<0.025	0.094	0.034	0.039
cis-chlordane	<0.025	<0.025	<0.025	<0.025	0.128	0.063	<0.025	<0.025	<0.025
p, p'- DDE	0.059	<0.025	0.296	<0.025	<0.025	0.119	<0.025	<0.025	0.174
p, p'- DDD	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	0.029
p, p'- DDT	<0.025	<0.025	0.052	<0.025	<0.025	<0.025	<0.025	<0.025	0.127
chlorpyrifos	<0.025	<0.025	<0.025	0.097	0.823	0.035	0.162	<0.025	0.261
hexachlorobenzene	<0.025	<0.025	0.033	0.013	<0.025	0.075	<0.025	<0.025	0.074
endosulfan I	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
endosulfan II	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
endosulfan sulfate	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	0.087	<0.025	<0.025
endrin	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
endrin aldehyde	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	0.033
methoxychlor	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025
Total concentration	0.19	0.19	10.13	3.42	3.93	1.10	0.76	2.29	5.60
EOM (mg g^{-1})	2.12	3.14	1.18	0.04	0.07	0.03	0.05	0.03	0.02
organic carbon (%)	0.51	1.56	0.84	1.39	1.89	0.87	1.00	2.26	1.16

Table C.3a. **Concentration of organochlorine residues in cores collected from the Burdekin region.**

Compound	Concentration ng g^{-1}													
	Core HC							Core SC						
Depth (cm)	*0-10*	*10-20*	*20-30*	*30-40*	*40-50*	*50-60*	*60-70*	*0-10*	*10-20*	*20-30*	*30-40*	*40-50*	*50-60*	*60-70*
α-HCH	0.123	0.166	0.208	0.096	0.022	0.064	0.044	0.253	0.055	0.039	0.022	0.017	0.033	0.011
β-HCH	1.930	0.495	0.672	0.489	0.083	0.290	0.143	0.839	0.331	0.183	0.103	0.083	0.064	0.033
γ-HCH	0.375	0.207	0.215	0.109	0.023	0.075	0.050	0.175	0.063	0.043	0.016	0.012	0.028	0.010
δ-HCH	0.119	0.100	0.096	0.068	0.010	0.049	0.025	0.066	0.017	0.011	<0.010	<0.010	0.012	<0.010
aldrin	0.065	0.050	0.064	0.032	<0.010	0.017	<0.010	0.046	0.067	0.046	<0.010	0.023	<0.010	0.022
dieldrin	0.179	0.236	0.209	0.147	<0.010	0.123	0.069	2.630	0.417	0.221	<0.010	0.081	0.044	0.040
heptachlor	0.212	0.217	0.172	0.109	<0.010	0.077	<0.010	0.110	0.031	0.017	<0.010	<0.010	<0.010	<0.010
heptachlor epoxide	3.536	1.746	1.798	0.698	0.074	0.494	0.366	6.286	1.541	0.607	0.057	0.112	0.040	<0.010
trans-chlordane	1.029	1.496	1.194	0.597	0.124	0.459	0.367	2.807	1.057	0.445	0.186	0.115	0.026	0.020
cis-chlordane	0.239	0.318	0.331	0.125	0.036	0.096	0.082	0.804	0.245	0.117	0.058	0.032	0.011	<0.010
p, p'- DDE	0.015	0.035	0.028	0.021	<0.010	0.009	0.014	0.443	0.189	0.111	0.087	0.053	0.022	0.019
p, p'-DDD	<0.010	<0.010	0.256	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
p, p'-DDT	0.097	<0.010	0.029	<0.010	<0.010	<0.010	<0.010	0.074	0.023	0.021	<0.010	<0.010	<0.010	<0.010
chlorpyrifos	0.506	2.130	0.181	0.086	<0.010	<0.010	<0.010	0.073	0.016	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan I	0.035	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.100	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	0.045	0.025	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
HCB	0.064	0.053	0.067	0.030	0.017	0.021	0.015	0.055	0.017	0.009	0.003	<0.010	<0.010	<0.010
endrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
methoxychlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
EOM (mg g^{-1})	0.021	0.029	0.027	0.022	0.004	0.128	0.007	0.049	0.007	0.008	0.007	0.008	0.005	0.006
organic carbon (%)	1.2	1.1	1.1	1.2	1.0	1.0	1.2	1.4	0.9	1.2	0.6	0.5	0.4	0.4

Table C.3b. **Concentration of organochlorine residues in cores collected from the Herbert region.**

Compound	Concentration (ng g^{-1})													
	Core LC							Core VC						
Depth (cm)	*0-10*	*10-20*	*20-30*	*30-40*	*40-50*	*50-60*	*60-70*	*0-10*	*10-20*	*20-30*	*30-40*	*40-50*	*50-60*	*60-70*
α-HCH	9.109	4.027	3.482	2.369	0.408	0.282	0.516	4.776	5.743	5.063	8.491	14.923	2.468	2.040
β-HCH	26.843	9.736	9.078	5.560	1.712	0.949	1.558	7.424	10.233	8.071	13.727	26.650	5.344	4.356
γ-HCH	6.390	3.095	2.328	1.825	0.314	0.203	0.380	3.388	4.141	3.384	5.371	10.189	1.784	1.337
δ-HCH	3.499	1.670	1.915	1.267	0.217	0.139	0.217	1.332	1.794	1.698	2.478	5.783	0.786	0.683
aldrin	<0.010	0.044	0.028	<0.010	<0.010	<0.010	<0.010	0.162	0.077	0.042	0.054	0.045	<0.010	<0.010
dieldrin	33.214	10.658	8.024	1.960	0.633	0.320	0.029	6.835	6.664	3.439	5.101	11.428	2.339	0.202
heptachlor	<0.010	0.038	0.032	<0.010	<0.010	<0.010	0.004	0.146	0.074	0.065	0.106	0.108	0.024	0.013
heptachlor epoxide	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	2.874	3.166	2.160	3.519	4.215	1.173	0.983
trans-chlordane	0.034	0.010	0.009	0.022	0.009	0.007	0.017	0.837	0.862	0.961	1.874	2.090	0.471	0.528
cis-chlordane	0.023	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.290	0.263	0.298	0.573	0.647	0.169	0.211
p, p'- DDE	0.627	0.309	0.426	0.287	0.052	0.042	0.037	0.776	0.559	0.266	0.391	0.342	0.105	0.108
p, p'-DDD	0.098	0.012	0.013	<0.010	<0.010	<0.010	<0.010	0.433	0.449	0.345	0.642	0.609	0.154	<0.010
p, p'-DDT	0.669	0.161	0.201	0.163	0.029	0.024	0.042	0.104	0.046	0.035	0.049	0.060	0.015	0.025
chlorpyrifos	1.535	0.244	0.232	0.022	<0.010	<0.010	<0.010	1.218	0.165	0.629	0.110	0.064	<0.010	<0.010
endosulfan I	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.048	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
HCB	0.022	0.009	0.009	0.007	0.004	<0.010	0.003	0.037	0.026	0.015	0.027	0.031	0.009	0.011
endrin	<0.010	<0.010	<0.010	0.053	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
methoxychlor	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
EOM (mg g^{-1})	0.044	0.011	0.017	0.141	0.007	0.042	0.007	0.095	0.073	0.025	0.220	0.029	0.020	0.004
organic carbon (%)	1.1	0.8	0.8	0.7	0.5	0.4	0.5	1.6	1.3	1.0	0.9	0.9	0.7	0.6

Table C.4a. **Concentration of organochlorine residues (ng g^{-1}) in bulk soil (bulk), different size fractions and vegetal debri (VD) of two soils collected from the Burdekin region.**

Compound	Concentration (ng g^{-1})													
	Soil HC							Soil SC						
Size fraction (μm)	*bulk*	*<2*	*2-20*	*20-63*	*63-125*	*125-500*	*VD*	*bulk*	*<2*	*2-20*	*20-63*	*63-125*	*125-500*	*VD*
α-HCH	0.123	0.220	0.139	0.039	0.044	0.071	43.714	0.253	0.121	0.051	0.055	0.041	0.046	<0.010
β-HCH	1.930	4.093	2.910	0.240	0.270	0.219	46.853	0.839	0.506	0.241	0.141	0.103	<0.010	<0.010
γ-HCH	0.375	0.583	0.502	0.077	0.048	0.132	48.466	0.175	0.105	0.043	0.044	0.030	0.087	<0.010
δ-HCH	0.119	<0.010	0.076	<0.010	0.037	0.044	8.216	0.066	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
aldrin	0.065	0.127	0.151	0.049	<0.010	<0.010	0.637	0.046	0.391	0.059	<0.010	<0.010	<0.010	<0.010
dieldrin	0.179	0.558	0.356	0.120	0.009	0.060	6.937	2.630	1.723	0.185	0.299	0.297	0.080	9.992
heptachlor	0.212	0.337	0.079	0.065	<0.010	<0.010	6.276	0.110	0.216	<0.010	0.078	0.052	<0.010	2.161
heptachlor epoxide	3.536	5.899	6.130	0.920	0.105	0.586	144.452	6.286	8.786	2.668	0.958	1.148	0.146	49.333
trans-chlordane	1.029	2.027	1.763	0.142	0.230	0.119	23.995	2.807	3.815	1.532	0.541	0.639	0.147	<0.010
cis-chlordane	0.239	0.547	0.404	0.036	0.064	0.035	6.619	0.804	1.212	0.438	0.172	0.212	0.080	<0.010
p, p'- DDE	0.015	0.044	0.017	0.006	0.012	<0.010	<0.010	0.443	0.607	0.313	0.092	0.109	0.021	2.092
p, p'-DDD	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.686	<0.010	0.100	<0.010	<0.010	8.021
p, p'-DDT	0.097	0.437	0.189	<0.010	<0.010	<0.010	<0.010	0.074	0.093	<0.010	<0.010	<0.010	<0.010	9.704
chlorpyrifos	0.506	0.402	0.134	0.020	<0.010	0.069	11.315	0.073	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan I	0.064	0.061	0.055	0.018	0.045	<0.010	2.136	0.055	0.094	0.036	<0.010	0.011	0.024	<0.010
endosulfan II	0.035	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.100	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
HCB	0.045	0.671	0.095	<0.010	<0.010	0.147	6.224	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	1.028
methoxychlor	0.021	0.052	0.011	0.005	<0.010	<0.010	1.563	0.049	0.054	<0.010	0.040	0.013	0.018	13.200
EOM (mg g^{-1})	1.221	1.148	1.122	1.154	1.030	1.034	1.190	1.402	0.865	0.040	0.561	0.453	0.400	0.383
organic carbon (%)	1.2	2.2	2.1	0.3	0.4	ND	ND	1.4	3.1	2.6	0.4	0.5	ND	ND

ND - Not determined

Table C.4b. **Concentration of organochlorine residues (ng g^{-1}) in bulk soil (bulk), different size fractions and vegetal debri (VD) of two soils collected from the Herbert region.**

Compound	Concentration (ng g^{-1})													
	Soil LC							Soil VC						
Size fraction (μm)	*bulk*	*<2*	*2-20*	*20-63*	*63-125*	*125-500*	*VD*	*bulk*	*<2*	*2-20*	*20-63*	*63-125*	*125-500*	*VD*
α-HCH	9.109	2.483	3.490	1.442	2.060	0.081	84.544	1.172	2.653	1.075	2.167	0.106	27.298	<0.010
β-HCH	26.843	28.422	13.452	3.626	5.020	0.213	201.417	5.144	4.895	1.368	3.364	0.167	43.530	<0.010
γ-HCH	6.390	3.602	2.722	0.862	1.334	0.055	48.043	1.056	1.753	0.596	1.277	0.060	15.031	<0.010
δ-HCH	3.499	1.729	1.956	0.693	1.073	0.023	40.197	0.402	0.785	0.302	0.676	0.031	8.849	<0.010
aldrin	<0.010	0.411	0.104	0.037	0.027	<0.010	0.582	0.240	0.107	<0.010	0.091	<0.010	<0.010	<0.010
dieldrin	33.214	17.749	4.558	2.053	4.555	0.238	271.399	8.407	3.732	1.086	2.635	0.261	68.036	9.992
heptachlor	<0.010	1.062	<0.010	0.070	0.063	0.024	0.905	0.110	0.067	0.032	<0.010	<0.010	<0.010	2.161
heptachlor epoxide	<0.010	26.004	0.068	<0.010	0.024	<0.010	0.324	3.208	1.828	0.484	1.072	0.071	22.587	49.333
trans-chlordane	0.034	6.257	0.088	0.186	0.111	0.035	1.496	0.885	0.693	0.212	0.339	<0.010	<0.010	<0.010
cis-chlordane	0.023	1.410	0.024	0.037	0.022	<0.010	0.473	0.376	0.227	0.085	0.125	<0.010	<0.010	<0.010
p, p'- DDE	0.627	0.524	0.539	0.098	0.164	0.023	5.957	0.759	0.471	0.378	0.336	0.036	5.956	2.092
p, p'-DDD	0.098	0.042	0.051	0.022	0.028	<0.010	0.558	0.632	<0.010	0.095	<0.010	0.177	7.358	8.021
p, p'-DDT	0.669	1.044	0.303	1.061	1.283	0.032	5.248	0.077	0.105	0.029	0.109	<0.010	0.548	9.704
chlorpyrifos	1.535	3.795	0.237	0.205	0.334	<0.010	15.661	0.544	0.347	0.051	0.295	<0.010	<0.010	<0.010
endosulfan I	0.022	0.347	0.013	0.023	0.008	<0.010	0.314	<0.010	0.012	0.013	0.010	<0.010	<0.010	<0.010
endosulfan II	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endosulfan sulfate	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
HCB	<0.010	0.299	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010
endrin aldehyde	<0.010	0.911	0.097	0.708	0.441	0.117	1.161	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	1.028
methoxychlor	0.04	0.06	0.01	0.01	0.01	0.01	0.77	0.17	0.11	0.03	0.08	0.07	4.91	13.200
EOM (mg g^{-1})	1.221	1.148	1.122	1.154	1.030	1.034	1.190	1.402	0.865	2.6	0.561	0.453	0.400	0.383
organic carbon (%)	1.1	3.5	3.1	0.3	0.5	ND	ND	1.6	2.7	2.7	0.5	0.9	ND	ND

ND - Not determined.

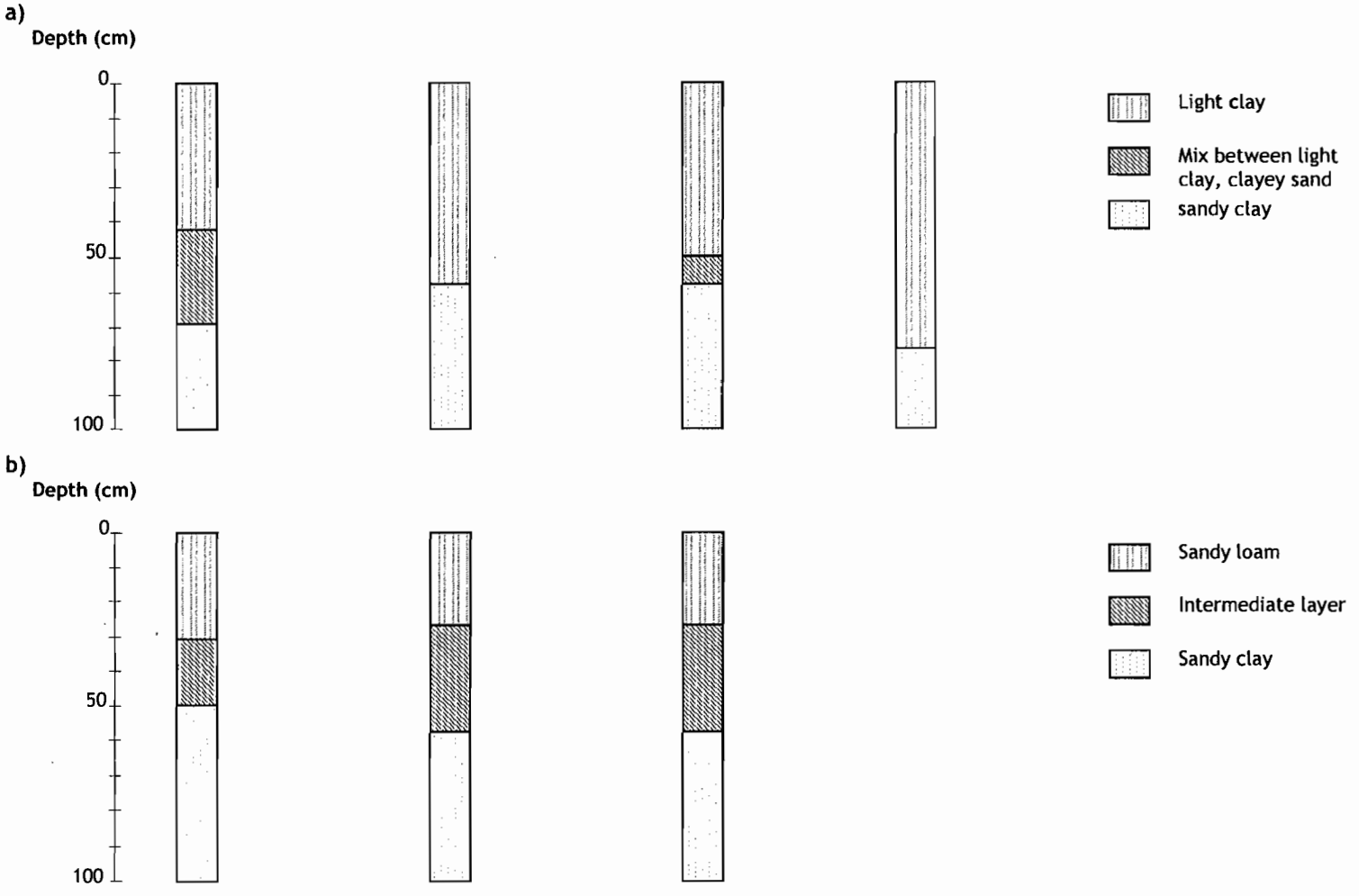

Figure C.1a. **Soil texture profiles of soil cores collected from the Burdekin region a) HC, and b) SC.**

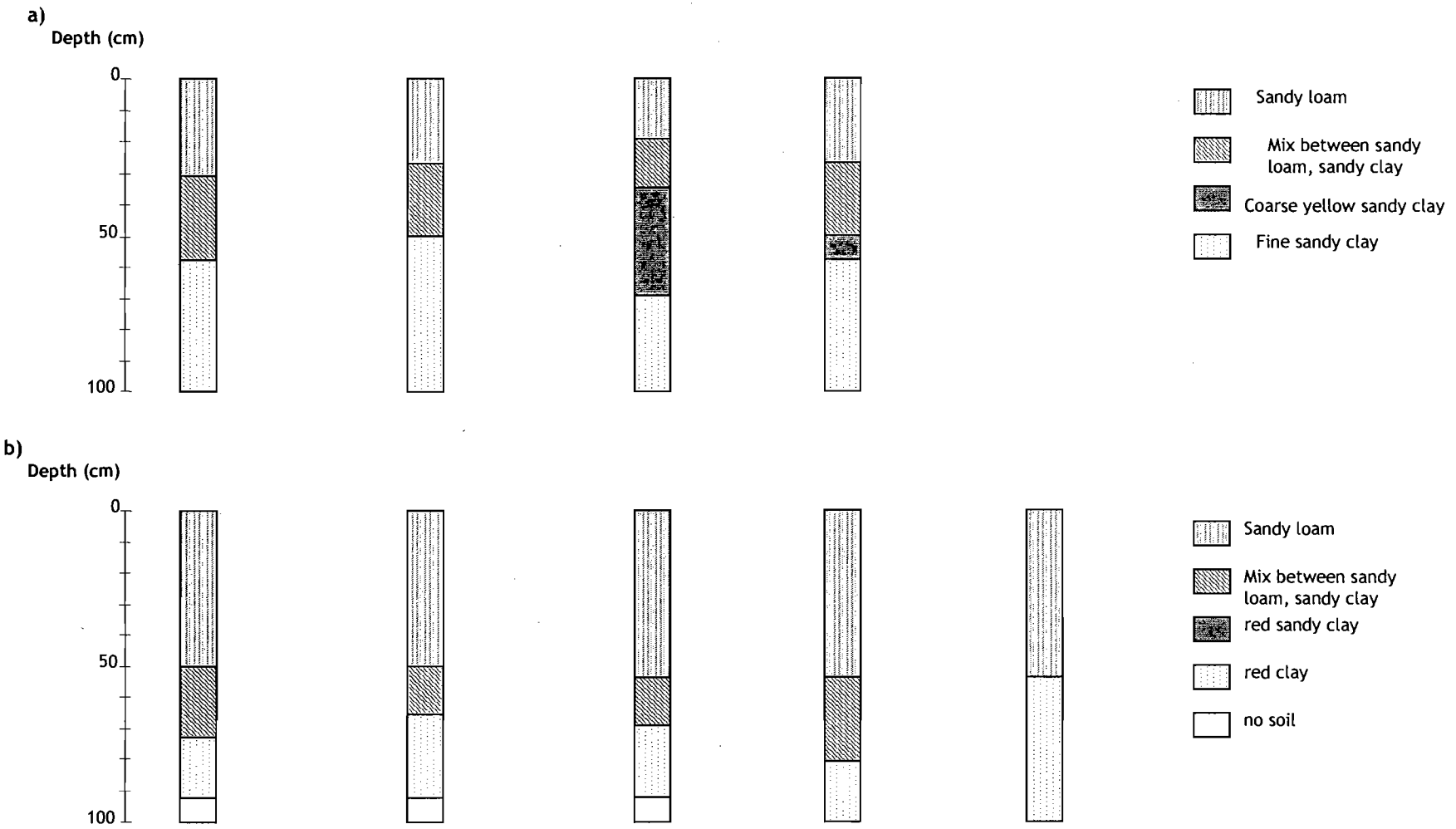

Figure C.1b. **Soil texture profiles of soil cores collected from the Herbert region a) LC, and b) VC.**

Appendix D: Example of spreadsheet models

D.1 Individual field calculations

Herbert Region

Chemical a-HCH

Half-life model parameters

amt isomer (kg/ha)	10.491
soil density (g cm-3)	1.5
soil depth (m)	0.1
kg soil/ha/depth	150000
1/2 life	256

Half-life model results

Last year of application	surface soil concentration ng/g
1987	3.59582
1986	1.33843
1985	0.49819
1984	0.18543
1983	0.06902

Dissipation model parameters

mixed layer (cm)	30
undisturbed layer (cm)	70
kg soil/ha/mixed layer	450000
kg soil/ha/undisturbed layer	600000
half-life (days)	307
No. half-lives per year	1.189
volatilisation (%)	0
run-off (%)	0.5
leaching %	1.30

% composition HCH

a-HCH	72
b-HCH	6
g-HCH	15
d-HCH	7

Amt applied (kg/ha)

α-HCH	10.491
β-HCH	0.8742
γ-hCH	2.1856
δ-HCH	1.0199
aldrin	0.2802
heptachlor	2.2467

Dissipation model results

Last year of application	Mixed layer concentration (ng/g)	Undisturbed layer concentration (ng/g)
1987	1.72284	0.22225
1986	0.72468	0.10349
1985	**0.30482**	**0.04786**
1984	0.12822	0.02201
1983	0.05393	0.01007

Table D.1. Results page for environmental half-life model (section 3.2.2.1) and dissipation model (section 3.2.2.2), showing parameters used to determine environmental half-life and estimates of degradation losses of α-HCH from the Herbert region.

Table D.2. Example of spreadsheet calculations for environmental half-life model (section 3.2.2.1. Parameters shown in *Table D.1* were used to generate these numbers.

Year of application	Amount applied (mg ha^{-1})	Year diff (1997-year)	# half-lives	Annual concentration remaining in 1997 (ng g^{-1})	Cumulative concentration remaining in 1997 (ng g^{-1})	Equivalent year of last application
1949		48	68.4	0.0000	0.0000	
1950		47	67.0	0.0000	0.0000	
1951		46	65.6	0.0000	0.0000	
1952	10490688	45	64.2	0.0000	0.0000	
1953		44	62.7	0.0000	0.0000	
1954		43	61.3	0.0000	0.0000	
1955		42	59.9	0.0000	0.0000	
1956		41	58.5	0.0000	0.0000	
1957	10490688	40	57.0	0.0000	0.0000	
1958		39	55.6	0.0000	0.0000	
1959		38	54.2	0.0000	0.0000	
1960		37	52.8	0.0000	0.0000	
1961		36	51.3	0.0000	0.0000	
1962	10490688	35	49.9	0.0000	0.0000	
1963		34	48.5	0.0000	0.0000	
1964		33	47.1	0.0000	0.0000	
1965		32	45.6	0.0000	0.0000	
1966		31	44.2	0.0000	0.0000	
1967	10490688	30	42.8	0.0000	0.0000	
1968		29	41.3	0.0000	0.0000	
1969		28	39.9	0.0000	0.0000	
1970		27	38.5	0.0000	0.0000	
1971		26	37.1	0.0000	0.0000	
1972	10490688	25	35.6	0.0000	0.0000	
1973		24	34.2	0.0000	0.0000	
1974		23	32.8	0.0000	0.0000	
1975		22	31.4	0.0000	0.0000	
1976		21	29.9	0.0000	0.0000	
1977	10490688	20	28.5	0.0002	0.0002	
1978		19	27.1	0.0000	0.0002	
1979		18	25.7	0.0000	0.0002	
1980		17	24.2	0.0000	0.0002	
1981		16	22.8	0.0000	0.0002	
1982	10490688	15	21.4	0.0255	0.0257	
1983		14	20.0	0.0000	0.0257	
1984		13	18.5	0.0000	0.0257	
1985		12	17.1	0.0000	0.0257	
1986		11	15.7	0.0000	0.0257	
1987	10490688	10	14.3	3.5701	3.5958	**1987**
					1.33843	**1986**
					0.49819	**1985**
					0.18543	**1984**
					0.06902	**1983**

Table D.3. **Example of spreadsheet calculations for dissipation model (section 3.2.2.2). Parameters shown in Figure D.1 were used to generate these numbers.**

Year of application	Equivalent year of last application	Amount applied (mg ha^{-1})	Mixed layer calculations						Undisturbed layer calculations			
			Amount leached (mg)	Amount in run-off (mg)	Amount degraded (mg)	Amount volatilised (mg)	Cumulative amount remaining (mg)	**Concentration (ng g^{-1})**	Cumulative amount leached (mg)	Amount degraded (mg)	Cumulative amount in undisturbed layer (mg)	**Concentration (ng g^{-1})**
1949			0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1950			0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1951			0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1952		10490688	136378.944	52453.440	5889162.226	0.000	4412693.390	9805.985	136378.944	76559.109	59042.177	98.404
1953			57365.014	22063.467	2477155.667	0.000	1856109.242	4124.687	116407.191	65347.557	50395.859	83.993
1954			24129.420	9280.546	1041964.877	0.000	780734.398	1734.965	74525.279	41836.289	32264.033	53.773
1955			10149.547	3903.672	438281.219	0.000	328399.960	729.778	42413.580	23809.730	18362.000	30.603
1956			4269.199	1642.000	184354.033	0.000	138134.728	306.966	22631.199	12704.486	9797.665	16.329
1957		10490688	138174.695	53144.114	5966706.980	0.000	4470796.938	9935.104	147972.361	83067.311	64061.285	106.769
1958			58120.360	22353.985	2509773.282	0.000	1880549.312	4178.998	122181.645	68589.165	52895.778	88.160
1959			24447.141	9402.747	1055684.810	0.000	791014.614	1757.810	77342.919	43418.029	33483.866	55.806
1960			10283.190	3955.073	444052.228	0.000	332724.122	739.387	43767.056	24569.532	18947.956	31.580
1961			4325.414	1663.621	186781.490	0.000	139953.598	311.008	23273.370	13064.982	10075.679	16.793
1962		10490688	138198.341	53153.208	5967728.041	0.000	4471562.009	9936.804	148274.020	83236.653	64191.881	106.986
1963			58130.306	22357.810	2510202.770	0.000	1880871.123	4179.714	122322.187	68668.061	52956.622	88.261
1964			24451.325	9404.356	1055865.466	0.000	791149.977	1758.111	77407.947	43454.534	33512.019	55.853
1965			10284.950	3955.750	444128.217	0.000	332781.060	739.513	43796.968	24586.324	18960.906	31.602
1966			4326.154	1663.905	186813.453	0.000	139977.548	311.061	23287.060	13072.667	10081.606	16.803
1967		10490688	138198.652	53153.328	5967741.485	0.000	4471572.083	9936.827	148280.258	83240.155	64194.582	106.991
1968			58130.437	22357.860	2510208.425	0.000	1880875.360	4179.723	122325.019	68669.651	52957.848	88.263
1969			24451.380	9404.377	1055867.844	0.000	791151.759	1758.115	77409.228	43455.253	33512.573	55.854
1970			10284.973	3955.759	444129.218	0.000	332781.810	739.515	43797.546	24586.648	18961.156	31.602
1971			4326.164	1663.909	186813.874	0.000	139977.863	311.062	23287.320	13072.813	10081.718	16.803

Table D.3 cont.

Year of application	Equivalent year of last application	Amount applied (mg ha^{-1})	Mixed layer calculations						Undisturbed layer calculations			
			Amount leached (mg)	Amount in run-off (mg)	Amount degraded (mg)	Amount volatilised (mg)	Cumulative amount remaining (mg)	**Concentration (ng g^{-1})**	Cumulative amount leached (mg)	Amount degraded (mg)	Cumulative amount in undisturbed layer (mg)	**Concentration (ng g^{-1})**
1972		10490688	138198.656	53153.329	5967741.662	0.000	4471572.216	**9936.827**	148280.374	83240.220	64194.632	**106.991**
1973			58130.439	22357.861	2510208.500	0.000	1880875.416	**4179.723**	122325.071	68669.680	52957.871	**88.263**
1974			24451.380	9404.377	1055867.876	0.000	791151.783	**1758.115**	77409.251	43455.266	33512.583	**55.854**
1975			10284.973	3955.759	444129.231	0.000	332781.820	**739.515**	43797.557	24586.654	18961.161	**31.602**
1976			4326.164	1663.909	186813.879	0.000	139977.868	**311.062**	23287.325	13072.816	10081.720	**16.803**
1977		10490688	138198.656	53153.329	5967741.665	0.000	4471572.217	**9936.827**	148280.376	83240.221	64194.633	**106.991**
1978			58130.439	22357.861	2510208.501	0.000	1880875.417	**4179.723**	122325.072	68669.680	52957.871	**88.263**
1979			24451.380	9404.377	1055867.876	0.000	791151.783	**1758.115**	77409.252	43455.266	33512.584	**55.854**
1980			10284.973	3955.759	444129.231	0.000	332781.820	**739.515**	43797.557	24586.654	18961.161	**31.602**
1981			4326.164	1663.909	186813.879	0.000	139977.868	**311.062**	23287.325	13072.816	10081.720	**16.803**
1982		10490688	138198.656	53153.329	5967741.665	0.000	4471572.217	**9936.827**	148280.376	83240.221	64194.633	**106.991**
1983			58130.439	22357.861	2510208.501	0.000	1880875.417	**4179.723**	122325.072	68669.680	52957.871	**88.263**
1984			24451.380	9404.377	1055867.876	0.000	791151.783	**1758.115**	77409.252	43455.266	33512.584	**55.854**
1985			10284.973	3955.759	444129.231	0.000	332781.820	**739.515**	43797.557	24586.654	18961.161	**31.602**
1986			4326.164	1663.909	186813.879	0.000	139977.868	**311.062**	23287.325	13072.816	10081.720	**16.803**
1987		10490688	138198.656	53153.329	5967741.665	0.000	4471572.217	**9936.827**	148280.376	83240.221	64194.633	**106.991**
1988			58130.439	22357.861	2510208.501	0.000	1880875.417	**4179.723**	122325.072	68669.680	52957.871	**88.263**
1989			24451.380	9404.377	1055867.876	0.000	791151.783	**1758.115**	77409.252	43455.266	33512.584	**55.854**
1990			10284.973	3955.759	444129.231	0.000	332781.820	**739.515**	43797.557	24586.654	18961.161	**31.602**
1991			4326.164	1663.909	186813.879	0.000	139977.868	**311.062**	23287.325	13072.816	10081.720	**16.803**
1992			1819.712	699.889	78579.438	0.000	58878.828	**130.842**	11901.432	6681.112	5152.456	**8.587**
1993			765.425	294.394	33052.834	0.000	24766.175	**55.036**	5917.881	3322.123	2562.012	**4.270**
1994			321.960	123.831	13902.999	0.000	10417.385	**23.150**	2883.973	1618.977	1248.551	**2.081**
1995			135.426	52.087	5848.012	0.000	4381.860	**9.737**	1383.977	776.924	599.161	**0.999**

Table D.3 cont.

Year of application	Equivalent year of last application	Amount applied (mg ha^{-1})	Mixed layer calculations						Undisturbed layer calculations			
			Amount leached (mg)	Amount in run-off (mg)	Amount degraded (mg)	Amount volatilised (mg)	Cumulative amount remaining (mg)	**Concentration (ng g^{-1})**	Cumulative amount leached (mg)	Amount degraded (mg)	Cumulative amount in undisturbed layer (mg)	**Concentration (ng g^{-1})**
1996			56.964	21.909	2459.847	0.000	1843.140	**4.096**	656.126	368.330	284.055	**0.473**
1997	**1987**		23.961	9.216	1034.684	0.000	775.279	**1.723**	308.016	172.911	133.348	**0.222**
	1986		10.079	3.876	435.219	0.000	326.105	**0.725**	143.427	80.516	62.093	**0.103**
	1985		4.239	1.631	183.066	0.000	137.170	**0.305**	66.333	37.237	28.717	**0.048**
	1984		1.783	0.686	77.003	0.000	57.698	**0.128**	30.501	17.122	13.205	**0.022**
	1983		0.750	0.288	32.390	0.000	24.269	**0.054**	13.955	7.834	6.041	**0.010**
	Total (kg)		**1.883**	**0.724**	**81.318**	**0.000**				**1.864**	**1.438**	

D.2 Catchment-scale calculations

Herbert

Chemical	a-HCH	% composition HCH		Annual volatilisation estimates (tonnes)	
isomer	0.72	α-HCH	72	Max	0
total app (tonnes)	1668.10	β-HCH	6	Min	0
Environmental half-life model		γ-hCH	15	mean	0
half-life	256	δ-HCH	7		
amt remaining (kg)	1.9239				
% of applied	0.0001				

Dissipation Model Parameters		Concentration in coastal sediment	
Half-life	307	Sediment load (MT)	1.43
# half-lives per year	1.1889	half-life (days)	307
% vol	0	#half life per year	1.188
% run-off	0.5	1997	0.0253
%leached	1.3	max	0.0384

Model results

Totals	Amount	% of total applied
Remaining (kg)	3.0397	0.0002
Volatilised (tonnes)	0.0000	0.0000
Degraded (kg)	1611.7856	96.6237
Run-off (tonnes)	14.3558	0.8606
Leached (tonnes)	37.3251	2.2376

Table D.4. **Results sheet for catchment scale calculations for the amount of α-HCH estimated to remain in the Herbert Catchment using the environmental half life model and dissipation model; maximum, minimum and average amounts volatilised (dissipation model); and the amount present in coastal sediment assuming a river sediment load of 1.43 MT and a degradation half-life in the coastal environment of 307 days.**

Table D.5. Example of spreadsheet calculations using the Environmental half-life model and dissipation model for catchment-scale calculations.

Year	Amount HCH applied (mg ha^{-1})	Amount individual isomer applied	Environmental half life model			Dissipation model					Catchment run-off model		
			Year diff (1997-year)	# half-lives	Annual amount remaining in 1997 (kg)	Amount leached (kg)	Amount in run-off (kg)	Amount degraded (kg)	Amount volatilised (kg)	Annual amount remaining (kg)	# half-lives	Amount remaining in coastal sediments	Sediment concentration (µg kg^{-1})
1948			49										
1949	816.43	587.83	48	68.44	0.0000	7.6418	2.94	329.9898	0.00	247.26	57.07	0.0000	0.0000
1950	14967.98	10776.95	47	67.01	0.0000	143.3146	55.12	6188.6622	0.00	4637.11	55.88	0.0000	0.0000
1951	32748.80	23579.13	46	65.59	0.0000	366.8111	141.08	15839.7631	0.00	7231.48	54.69	0.0000	0.0000
1952	52962.21	38132.79	45	64.16	0.0000	589.7355	226.82	25466.1591	0.00	19081.55	53.50	0.0000	0.0000
1953	113436.52	81674.29	44	62.73	0.0000	1309.8260	503.78	56561.3525	0.00	42380.88	52.31	0.0000	0.0000
1954	84657.65	60953.51	43	61.31	0.0000	1343.3471	516.67	58008.8728	0.00	43465.50	51.12	0.0000	0.0000
1955	55884.00	40236.48	42	59.88	0.0000	1088.1257	418.51	46987.8163	0.00	35207.53	49.93	0.0000	0.0000
1956	45815.59	32987.23	41	58.46	0.0000	886.5318	340.97	38282.5178	0.00	28684.73	48.75	0.0000	0.0000
1957	43817.40	31548.53	40	57.03	0.0000	783.0323	301.17	33813.1693	0.00	25335.89	47.56	0.0000	0.0000
1958	47633.04	34295.79	39	55.61	0.0000	775.2118	298.16	33475.4609	0.00	25082.85	46.37	0.0000	0.0000
1959	38704.51	27867.25	38	54.18	0.0000	688.3512	264.75	29724.6166	0.00	22272.37	45.18	0.0000	0.0000
1960	37086.29	26702.13	37	52.75	0.0000	636.6685	244.87	27492.8370	0.00	20600.12	43.99	0.0000	0.0000
1961	39215.81	28235.38	36	51.33	0.0000	634.8615	244.18	27414.8079	0.00	20541.66	42.80	0.0000	0.0000
1962	74002.49	53281.79	35	49.90	0.0000	959.7048	369.12	41442.3003	0.00	31052.32	41.61	0.0000	0.0000
1963	65416.37	47099.79	34	48.48	0.0000	1015.9774	390.76	43872.2858	0.00	32873.09	40.42	0.0000	0.0000
1964	52761.72	37988.44	33	47.05	0.0000	921.1999	354.31	39779.5682	0.00	29806.45	39.23	0.0000	0.0000
1965	61871.71	44547.63	32	45.63	0.0000	966.6031	371.77	41740.1860	0.00	31275.53	38.05	0.0000	0.0000
1966	88426.06	63666.77	31	44.20	0.0000	1234.2498	474.71	53297.7967	0.00	39935.53	36.86	0.0000	0.0000
1967		0.00	30	42.77	0.0000	519.1619	199.68	22418.6283	0.00	16798.07	35.67	0.0000	0.0000
1968	83976.53	60463.10	29	41.35	0.0000	1004.3951	386.31	43372.1344	0.00	32498.33	34.48	0.0000	0.0000
1969	83790.64	60329.26	28	39.92	0.0000	1206.7587	464.14	52110.6663	0.00	39046.03	33.29	0.0000	0.0000
1970	89512.91	64449.30	27	38.50	0.0000	1345.4392	517.48	58099.2168	0.00	43533.19	32.10	0.0000	0.0000

Table D.5. cont.

Year	Amount HCH applied (mg ha^{-1})	Amount individual isomer applied	Environmental half life model			Dissipation model					Catchment run-off model		
			Year diff (1997-year)	# half-lives	Annual amount remaining in 1997 (kg)	Amount leached (kg)	Amount in run-off (kg)	Amount degraded (kg)	Amount volatilised (kg)	Annual amount remaining (kg)	# half-lives	Amount remaining in coastal sediments	Sediment concentration (μg kg^{-1})
1971	90431.39	65110.60	26	37.07	0.0000	1412.3693	543.22	60989.4166	0.00	45698.79	30.91	0.0000	0.0000
1972	83311.60	59984.35	25	35.64	0.0000	1373.8809	528.42	59327.3932	0.00	44453.45	29.72	0.0000	0.0000
1973	82138.54	59139.75	24	34.22	0.0000	1346.7116	517.97	58154.1629	0.00	43574.36	28.53	0.0000	0.0000
1974	74776.15	53838.83	23	32.79	0.0000	1266.3714	487.07	54684.8849	0.00	40974.87	27.35	0.0000	0.0000
1975	91458.76	65850.31	22	31.37	0.0000	1388.7273	534.13	59968.4959	0.00	44933.83	26.16	0.0000	0.0000
1976	82395.14	59324.50	21	29.94	0.0001	1355.3582	521.29	58527.5423	0.00	43854.13	24.97	0.0000	0.0000
1977	74968.43	53977.27	20	28.52	0.0001	1271.8082	489.16	54919.6571	0.00	41150.78	23.78	0.0000	0.0000
1978	69231.94	49847.00	19	27.09	0.0003	1182.9711	454.99	51083.4625	0.00	38276.35	22.59	0.0001	0.0001
1979	82446.55	59361.52	18	25.66	0.0011	1269.2923	488.19	54811.0156	0.00	41069.37	21.40	0.0002	0.0001
1980	84973.49	61180.92	17	24.24	0.0031	1329.2538	511.25	57400.2910	0.00	43009.49	20.21	0.0004	0.0003
1981	59763.35	43029.61	16	22.81	0.0058	1118.5084	430.20	48299.8104	0.00	36190.59	19.02	0.0008	0.0006
1982	28132.50	20255.40	15	21.39	0.0074	733.7979	282.23	31687.1106	0.00	23742.85	17.83	0.0012	0.0008
1983	48913.96	35218.05	14	19.96	0.0345	766.4918	294.80	33098.9091	0.00	24800.70	16.64	0.0029	0.0020
1984	52083.58	37500.17	13	18.54	0.0987	809.9114	311.50	34973.8692	0.00	26205.59	15.46	0.0069	0.0048
1985	39340.08	28324.86	12	17.11	0.2003	708.8958	272.65	30611.7809	0.00	22937.12	14.27	0.0138	0.0097
1986	35305.20	25419.74	11	15.68	0.4830	628.6392	241.78	27146.1128	0.00	20340.32	13.08	0.0280	0.0196
1987	29639.56	21340.48	10	14.26	1.0894	541.8505	208.40	23398.3723	0.00	17532.18	11.89	0.0549	0.0384
1988	0.00		9	12.83		227.9183	87.66	9842.0468	0.00	7374.55	10.70	0.0527	0.0368
1989	0.00		8	11.41		95.8692	36.87	4139.8557	0.00	3101.95	9.51	0.0505	0.0353
1990			7	9.98		40.3254	15.51	1741.3457	0.00	1304.77	8.32	0.0484	0.0339
1991			6	8.55		16.9621	6.52	732.4614	0.00	548.83	7.13	0.0465	0.0325
1992			5	7.13		7.1347	2.74	308.0949	0.00	230.85	5.94	0.0446	0.0312
1993			4	5.70		3.0011	1.15	129.5938	0.00	97.10	4.76	0.0427	0.0299

Table D.5. cont.

Year	Amount HCH applied (mg ha^{-1})	Amount individual isomer applied	Environmental half life model			Dissipation model					Catchment run-off model		
			Year diff (1997-year)	# half-lives	Annual amount remaining in 1997 (kg)	Amount leached (kg)	Amount in run-off (kg)	Amount degraded (kg)	Amount volatilised (kg)	Annual amount remaining (kg)	# half-lives	Amount remaining in coastal sediments (kg)	Sediment concentration (µg kg^{-1})
1994			3	4.28		1.2623	0.49	54.5110	0.00	40.84	3.57	0.0410	0.0287
1995			2	2.85		0.5310	0.20	22.9289	0.00	17.18	2.38	0.0393	0.0275
1996			1	1.43		0.2233	0.09	9.6446	0.00	7.23	1.19	0.0377	0.0263
1997			0	0.00		0.0939	0.04	4.0568	0.00	3.04	0.00	0.0361	0.0253
Totals (tonnes)		**1668.11**			**0.0019**	**37.325**	**14.356**	**1611.78**	**0.000**			**0.0005**	

Appendix E: Distribution of organochlorine compounds in soil cores

Table E.1. **Distribution of selected organochlorine compounds, expressed as a percentage of the surface (0-10 cm) concentration, in soil cores collected from the Burdekin and Herbert regions (Source: Table A.3).**

Core depth	Percentage distribution							
	α-HCH	β-HCH	γ-HCH	δ-HCH	dieldrin	heptachlor epoxide	trans-chlordane	cis-chlordane
Burdekin								
HC								
10-20	135.5	25.6	55.1	84.1	132.3	49.4	145.3	132.8
20-30	169.5	34.8	57.5	80.9	116.8	50.8	116.0	138.5
30-40	77.9	25.3	29.0	57.5	82.2	19.7	58.0	52.1
40-50	18.2	4.3	6.3	8.4	0.0	2.1	12.1	15.0
50-60	52.2	15.0	19.9	40.8	68.6	14.0	44.6	40.2
60-70	36.2	7.4	13.3	20.8	38.5	10.4	35.6	34.4
SC								
10-20	21.8	39.5	36.0	26.0	15.9	24.5	37.7	30.5
20-30	15.3	21.8	24.4	17.4	8.4	9.7	15.9	14.6
30-40	8.7	12.3	9.2	0.0	0.0	0.9	6.6	7.2
40-50	6.7	9.9	6.7	0.0	3.1	1.8	4.1	4.0
50-60	13.0	7.7	16.1	17.7	1.7	0.6	0.9	1.4
60-70	4.2	3.9	5.8	0.0	1.5	0.0	0.7	0.0
Herbert								
LC								
10-20	44.2	36.3	48.4	47.7	32.1			
20-30	38.2	33.8	36.4	54.7	24.2			
30-40	26.0	20.7	28.6	36.2	5.9			
40-50	4.5	6.4	4.9	6.2	1.9			
50-60	3.1	3.5	3.2	4.0	1.0			
60-70	5.7	5.8	5.9	6.2	0.1			
VC								
10-20	120.2	137.8	122.2	134.7	97.5			
20-30	106.0	108.7	99.9	127.5	50.3			
30-40	177.8	184.9	158.5	186.0	74.6			
40-50	312.4	359.0	300.7	434.2	167.2			
50-60	51.7	72.0	52.6	59.0	34.2			
60-70	42.7	58.7	39.4	51.3	3.0			

Appendix F: Water quality parameters

Table F.1. Summary of water quality parameters during fish laboratory exposure trials.

Trial*	Temperature (°C)	pH	Dissolved oxygen (%)	Conductivity (mS)
BNF	29 - 30.4	7.7-8.2	78 - 101	52.1- 54.6
HCH	28.2-31.3	7.7 - 8.3	83-104	52.6 - 56.5

BNF- β-napthoflavone; HCH - mixture of hexachlorocyclohexanes.

Appendix G: Detailed biochemical analyses

G.1. Microsomal preparation

Homogenising buffer

0.1 M K_2HPO_4 (base) and KH_2PO_4 (acid) containing;

1 mM Dithiothreitol (0.1542 g/L)

1 mM EDTA (0.2923 g/L)

0.1 M KCl (7.456 g/L)

0.1 M Phenanthroline (0.01982 g/L)

Add acid to base until pH reaches 7.4

Resuspension buffer

0.1 M Phosphate buffer (pH 7.4) containing glycerol (20 % v/v)

Method

Weigh the liver while frozen, add ice cold (4°C) homogenising buffer (20% liver wt/v) and homogenise with 3-4 passes of the homogeniser. Homogenate is centrifuged at 10,000 g for 20 min to yield post-mitochondrial supernatant (S9) and a pellet containing mitochondria and other cell debri. Transfer S9 to new centrifuge tubes and centrifuge at 100,000 g for 60 min. The resultant pellet contains the microsomes. Decant supernatant (cytosol) and resuspend microsomal pellet in resuspension buffer. Store at -80°C. The S9 fraction was used for enzyme assays during the laboratory trials. Microsomes were used for enzyme analyses during field investigations.

G.2. Detoxification Enzyme Analyses

G.2.1. Ethoxyresorufin-O-deethylase (EROD) assay

G.2.1.1. Optimisation

This assay is a modification of the method of Burke and Mayer (1975). The assay was optimised for incubation temperature during initial laboratory trials, and linearity of the assay over 20 minutes assessed for both laboratory trials and field studies. Incubation temperature was optimised over 20-50°C using an incubation time of 10 minutes and 100 µl of post-mitochondrial supernatant (S9). Optimal activity occurred at 35°C (Figure 1a) and this temperature was subsequently used for all assays. Linearity of the reaction over 20 minutes was assessed by continuous measurement of fluorescence produced during *in situ* reactions in a cuvette in the fluorescence spectrometer and timed assays using an incubation temperature of 35°C and 100 µl of S9 or microsomes.

Resorufin production by the S9 fraction from fish used in laboratory trials was linear over 20 minutes, and an incubation time of 10 minutes was subsequently used during analyses of the S9 fraction. A drop in resorufin production occurred after 10 minutes when the microsomal fraction was used (Figure 1b), suggesting substrate limitation was occurring. Despite a higher level of enzyme activity occurring in the microsomal fraction as compared with the S9 fraction (Figure 1c), the S9 fraction was used during enzyme analysis of fish used in laboratory trials due to the small amount of material available for analysis.

The observation of substrate limitation during assays in which microsomes were used was even more marked in microsomes from fish captured during field studies that showed a high level of activity (Figure 1d). Due to this observed limitation, a smaller volume of microsomal protein (25 µl) and a shorter incubation time (5 minutes) was used during enzyme analysis of microsomes from fish captured during field studies.

Ethoxyresorufin subtrate

Dissolve a small amount of ethoxyresorufin in 1:1 methanol:DMSO to give stock solution (~0.5 mM). Dilute stock solution 1:50 in 0.1 M Tris buffer (pH 7.6) to give working solution. Scan working solution between 400 and 800 nm to record the absorbance maximum at 482 nm to verify substrate concentration. Stock solution may be frozen at -20°C until use. Ethoxyresorufin concentration (nmol ml^{-1}) = A482*1000/22.5

Resorufin standard

Dissolve resorufin (5.3 mg) in 0.01 N NaOH (10 ml). Dilute this solution (100 µl) to 5 ml with 0.1 Tris buffer (pH 7.6) to give working standard. Scan working standard between 500 and 800 nm to record absorbance at 572 nm to verify standard concentration. Make solution up daily. Resorufin concentration (nmol ml^{-1}) = A572*1000/40.

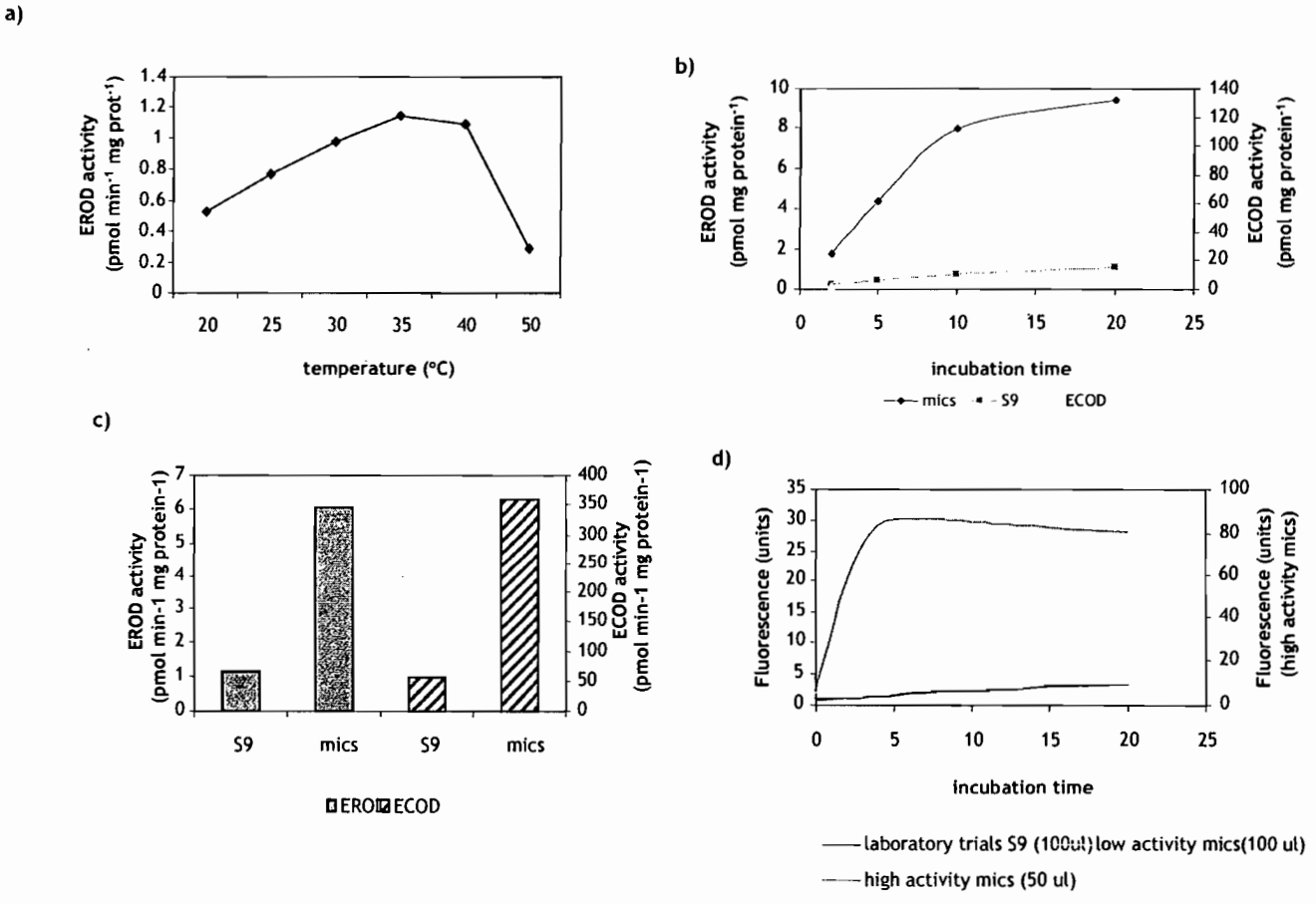

Figure G.1. a) Temperature response of enzyme assay; b) influence of incubation time on enzyme response; c) comparison of EROD and ECOD activity of post-mitochondrial supernatant (S9) and microsomes; and d) linearity of enzyme response in fish captured for field studies -note non-linearity of high activity microsomes after 4 minutes

Co-factor solution

Part A

100 mM magnesium chloride (203.3 mg)

2000 mM potassium chloride (1491.2 mg)

60 mM Glucose-6-phosphate (182.5 mg)

Dissolve in MQ water (10 ml). Pipette aliquots (1 ml) into eppendorf tubes. Freeze at -20°C.

Part B

12.5 mM NADP (98.4 mg)

1000 units G-6-dehydrogenase

Dissolve in MQ water (10 ml). Pipette 1 ml aliquots into eppendorf tubes and freeze at -20°C.

Working cofactor solution

Dilute A (1 ml) and B (1 ml) to 10 ml with 0.1 M phosphate buffer (4 ml, pH 7.4) and MQ water (4 ml) just prior to use. Store on ice.

Bovine serum albumin (BSA)

Dissolve BSA (120 mg) in MQ water (100 ml)

Procedure

Table G.1. **Volume of reagents used in EROD assays.**

Reagent	Std 1	Std 2	Std 3	Std 4	Std 5	Sample (lab trials)	Sample (field)
Buffer	0.45	0.375	0.4	0.35	0.25	0.45	0.525
BSA	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Cofactor	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Ethoxyresorufin	0.1	0.1	0.1	0.1	0.1	0.1	0.1

1. Add buffer, cofactor substrate and standard to disposable glass tubes at volumes shown in *Table G.1.* Standards are analysed in duplicate, samples in triplicate in addition to a blank
2. Preincubate tubes at 35°C for 2 min in a shaking water bath.
3. Start reaction with S9 (100 µl) or microsomal preparation (25 µl) and incubate for 10 mins (S9) or 5 mins (microsomes). Microsomes are not added to standard or blanks.
4. Stop reaction with the addition of methanol (2.5 ml). Vortex immediately and place tubes on ice. S9 or microsomal suspension is added to standards and blanks and tubes vortexed.
5. Remove resultant precipitate by centrifugation (2000 *g*, 5 min).
6. Supernatant (1.0 ml) is placed in spectro cuvette. Record fluorescence at EX/EM wavelength of 530/585 nm.
7. Determine the concentration of resorufin in samples from linear regression of the standards.

G.2.2. Ethoxycoumarin-*O*-deethylase (ECOD) assay

This assay is based on the method of Ullrich and Weber (1972). This assay was linear over 20 minutes using the post-mitochondrial supernatant from fish used in laboratory trials (Figure 1b) and an incubation time of 10 minutes was used. Incubation temperature was not optimised for this reaction specifically. Based on the temperature optimisation of the EROD assay, an incubation temperature of 35°C was used.

Ethoxycoumarin substrate

Dissolve ethoxycoumarin (15.2 mg) in methanol (0.35 ml) and add to pre-heated (50°C) 0.1 M Tris buffer (39.5 ml).

Hydroxycoumarin standard

Dissolve hydroxycoumarin (10.1 mg) in ethanol (12.5 ml) and dilute 1:50 in MQ water. 1:10 dilution of this solution gives the working standard.

Co-factor solution

Part A

100 mM magnesium chloride (203.3 mg)

2000 mM potassium chloride (1491.2 mg)

60 mM Glucose-6-phosphate (182.5 mg)

Dissolve in MQ water (10 ml) and pipette aliquots (1 ml) into eppendorf tubes. Freeze at -20°C.

Part B

12.5 mM NADP (98.4 mg)

1000 units G-6-dehydrogenase

Dissolve in MQ water (10 ml). Pipette 1 ml aliquots into eppendorf tubes and freeze at -20°C.

Working cofactor solution

Dilute A (1 ml) and B (1 ml) to 10 ml with 0.1 M phosphate buffer (4 ml, pH 7.4) and MQ water (4 ml) just prior to use. Store on ice.

5% Zinc sulphate

Dissolve $ZnSO_4.7H_20$ (50g) in MQ water (1L)

Saturated Barium Hydroxide

Add $Ba(OH)_2$ to boiling water whilst stirring until no more will dissolve. Filter whilst hot and store filtrate in a stoppered bottle.

Buffer

0.1 M Tris buffer (pH 7.4)

Glycine-NaOH buffer

Dissolve glycine (37.54 g) in MQ water (500 ml) and adjust pH to 10.5 with 1 M NaOH. Dilute to 1 L with MQ water.

Procedure

Table G.2. **Volume of reagents used in ECOD assays.**

Reagent	Std 1	Std 2	Std 3	Std 4	Std 5	Sample
Buffer	1.3	1.275	1.25	1.2	1.1	1.3
Cofactor	0.1	0.1	0.1	0.1	0.1	0.1
Ethoxycoumarin	0.5	0.5	0.5	0.5	0.5	0.5

1. Add buffer, cofactor substrate and standard to disposable glass tubes at volumes shown in *Table G.2*. Standards are analysed in duplicate, samples in triplicate in addition to a blank.
2. Pre-incubate tubes at 35°C for 2 min in a shaking water bath.
3. Start reaction with the addition S9 (100 µl). S9 is not added to standard or blank tubes.
4. Incubate tubes for 10 min prior to stopping the reaction with $Ba(OH)_2$ (0.5 ml) and $ZnSO_4$ (0.5 ml). Add S9 (0.1 ml) to standard and blank tubes. Vortex all tubes and place on ice.
5. Remove resultant precipitate by centrifugation (2000 *g*, 5 min)
6. Remove supernatant (1.0 ml) and mix with glycine-NaOH buffer (0.5 ml) in cuvette.
7. Record fluorescence at EX/EM wavelength of 380/452 nm.
8. Determine the concentration of hydroxycoumarin in samples from linear regression of the standards.

G.3. Protein determination

This method is based on Lowry *et al.* (1951).

Mixed reagent

Reagent A: 1% $CuSO_4.5H_2O$

Reagent B: 1% NaK tartrate.$4H_2O$

Reagent C: 2% Na_2CO_3 in 0.1 M NaOH.

Working solution

Mix reagent A (1 ml), reagent B (1 ml) and reagent C (98 ml) in a conical flask

Folin-Phenol reagent

Dilute 2N Folin-Phenol 1:1 with MQ water

Bovine Serum Albumin (BSA)

Dissolve BSA (2 mg) in MQ water (10 ml)

Procedure

***Table G.3.* Volumes of reagents used during protein analyses.**

Reagent	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6	Sample
BSA	0	0.01	0.025	0.05	0.1	0.15	0.2
MQ water	0.2	0.19	0.175	0.15	0.1	0.05	0
Mixed reagent	2.1	2.1	2.1	2.1	2.1	2.1	2.1

1. Dilute microsomes 1/100 - 1/200 in MQ water (to give protein 5-40 μg protein/0.2 ml).
2. Add standard and samples and mixed reagent at volumes shown in *Table G.3* and stand at room temperature for 10 minutes.
3. Pipette Folin reagent (0.2 ml) into each tube and vortex.
4. Incubate tubes in the dark for 1 hr.
5. Record absorbance at 750 nm.

G.4. Fish tissue analyses

(Tissue analyses were conducted by C. Gauss at University of Queensland)

Tissue samples (~ 10 g) were macerated for 2 minutes in acetone (100 ml) using a Sorvall mixer. After 24 hours samples were centrifuged at 2,500 RPM and 10°C for 10 min and the acetone decanted from the sample. Sample was rinsed twice by the addition of acetone and centrifugation. Samples were transferred to separating funnels and CH_2Cl_2 (150 ml) and NaCl saturated solution (5 ml) added. Mixture was shaken for 2-3 minutes prior to filtration of the CH_2Cl_2 fraction through Na_2SO_4 and collection in weighed round bottom flasks. The solvent extract was evaporated to dryness and the flasks were weighed to determine lipid content of the sample.

CH_2Cl_2 (3 ml) was added to the round bottom flasks, and the extract filtered through Millex Gel Permeable Chromatograph (GPC) filters and washed through with additional CH_2Cl_2 (4 ml). The filtrate was fractionated on a Gel Permeable Chromatograph to yield oil and PAH/OC fractions. The PAH / OC fraction was reduced to near dryness on a rotary evaporator and transferred to hexane and cleaned up on a Florisil column (Florisil (20 g) and Na_2SO_4 (2 cm)). PAHs and OCs were sequentially eluted with 6% diethylether/hexane (v/v, 120 ml) and 15% acetone/hexane (v/v, 120 ml). Samples were reduced to 3-5 ml on a rotary evaporator, transferred to tapered test tubes and further reduced under N_2 to 1 ml volumes. Samples were then analyzed using a GC equipped with an ECD detector.

Appendix H: Statistical results from fish work

Table H.1. **Significance (p-value) of sources of variability in dose response of EROD and ECOD activity and turnover number and P-450 content in fish exposed to β-napthoflavone (BNF) and a mixture of hexachlorocyclohexane isomers as analysed using a general linear model.**

Source of variability	P-values					
	BNF			HCH		
	DF	Type I F	Type III F	DF	Type I F	Type III F
EROD activity						
(pmol min^{-1} mg protein^{-1})						
disease	23	0.0001	0.0004			
sex	23	0.1504	0.9289			
injection	23	0.019	0.1411	20	0.0001	0.0005
dose	23	0.0001	0.0001	20	0.9347	0.0001
dose*dose	23	0.0035	0.0035	20	0.0008	0.0004
dose*dose*dose				20	0.0012	0.0012
EROD turnover number						
(nmol min^{-1} nmol P-450^{-1})						
Disease	23	0.0001	0.1448			
sex	23	0.2301	0.7956			
injection	23	0.3499	0.1732	20	0.0001	0.0001
dose	23	0.0043	0.0037	20	0.9346	0.0184
dose*dose	23	0.0226	0.0226	20	0.0153	0.0153
ECOD activity						
(pmol min^{-1} mg protein^{-1})						
Disease	23	0.0001	0.0322			
sex	23	0.0236	0.1543			
injection	23	0.0079	0.9454	20	0.0001	0.0001
dose	23	0.0018	0.0027	20	0.8886	0.0155
dose*dose	23	0.0208	0.0208	20	0.7447	0.0126
dose*dose*dose				20	0.0132	0.0132
ECOD turnover number						
(nmol min^{-1} nmol P450^{-1})						
Disease	23	0.0001	0.487			
sex	23	0.0371	0.4201			
injection	23	0.3599	0.1899	20	0.0001	0.0001
dose	23	0.41	0.003	20	0.5205	0.9404
dose*dose	23	0.0426	0.0132	20	0.8383	0.9547
dose*dose*dose	23	0.0962	0.0235	20	0.9325	0.9325
dose*sex	23	0.0156	0.0156			
P-450 content						
(nmol P-450 mg protein^{-1})						
Disease	23	0.0001	0.0879			
sex	23	0.9203	0.5615			
injection	23	0.4208	0.6069	20	0.0001	0.0001
dose	23	0.0788	0.1394	20	0.0212	0.0212
dose*dose	23	0.8024	0.0466			
dose*dose*dose	23	0.038	0.0384			

Table H.2. **Significance of bivariate correlations between muscle tissue lipid weight (LW, μg g^{-1} dry wt), EROD activity (EROD, pmol min^{-1} mg $prot^{-1}$), EROD turnover number (EROD TO, pmol min^{-1} mg $prot^{-1}$) and condition factor (CF) as determined by the Pearson correlation coefficient.**

Location	No.	Correlation coefficent				
		LW v CF	LW v EROD	LW v EROD TO	CF v EROD	CF v EROD TO
Baldy Creek	18	-0.198	0.585*	0.597**	-0.392	-0.263
Fisher Creek	17	0.124	0.059	0.081	-0.349	-0.093
Victoria Creek	12	0.047	-0.476	-0.745**	0.298	-0.203
Seymour River	13	0.151	0.082	0.055	0.162	-0.165
Plantation Creek	17	-0.143	-0.205	-0.299	-0.229	-0.122
Cromarty Creek	17	0.161	0.114	-0.41	0.177	0.576*
Ross Creek	17	-0.214	0.328	0.034*	-0.02	0.543*

*significant at $p<0.05$

**significant at $p<0.01$

Appendix I: Selected publications arising from thesis work.

Appendix I.1: Cavanagh, J.E, Burns, K.A, Brunskill, G.J. and Coventry, R.J. (1999). Organochlorine pesticide residues in soils and sediments of the Herbert and Burdekin River regions - implications for contamination of the Great Barrier Reef. *Marine Pollution Bulletin* **39(1-12)**, 265-275.

Appendix I.2: Cavanagh, J.E., Burns, K.A., Brunskill, G.J., Ryan, D.A.J. Ryan and Ahokas, J. (2000). Induction of hepatic cytochrome P-450 1A in Pikey Bream (*Acanthopagrus berda*) collected from agricultural and urban catchments in far north Queensland. *Marine Pollution Bulletin* (In press).

Appendix I.3: Cavanagh, J.E. (2000) Comparison of the environmental regulation of land management in the Sugar Industry under the *Sugar Industry Act* 1991 (Qld), the Sugar Industry Bill 1999 and the *Integrated Planning Act* 1997 (Qld). *Environmental Planning and Law Journal*, **17(2)**, 118-125.

Cavanagh, J.E, Burns, K.A, Brunskill, G.J. and Coventry, R.J. (1999). Organochlorine pesticide residues in soils and sediments of the Herbert and Burdekin River regions - implications for contamination of the Great Barrier Reef. Marine Pollution Bulletin 39(1-12), 265-275.

Cavanagh, J.E., Burns, K.A., Brunskill, G.J., Ryan, D.A.J. Ryan and Ahokas, J. (2000). Induction of hepatic cytochrome P-450 1A in Pikey Bream (Acanthopagrus berda) collected from agricultural and urban catchments in far north Queensland. Marine Pollution Bulletin 41(7-12): 377-384.

Cavanagh, J.E. (2000) Comparison of the environmental regulation of land management in the Sugar Industry under the Sugar Industry Act 1991 (Qld), the Sugar Industry Bill 1999 and the Integrated Planning Act 1997 (Qld). Environmental Planning and Law Journal, 17(2), 118-125.