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WRC Report No. 795/1/00



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by

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Final report to the Water Research Commission on the Project "An Assessment of the quality of water supplies in the rural Western Cape with regard to agrichemical pollutants."

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WRC Report No: 795/1/00 ISBN No: 1 86845 674 9

# PREFACE

This study is the first South African investigation into the presence of pesticides in ground and surface water at low levels of contamination currently of concern to the global community. It builds on previous research conducted in this area, but with particular emphasis on being able to measure organic pesticides at very low concentrations (parts per billion) which are levels to which international standards for pesticides are increasingly moving. Also central to this project has been the recognition of the need to develop capacity, particularly amongst historically disadvantaged research institutions through collaborative research. The support of the Water Research Commission for this approach has been particularly important in the success of this project, which has consolidated collaborative relationships between Units and Departments at the University of Cape Town, and the Peninsula Technicon in the environmental health field. We hope that the project's important findings will also find appropriate insertion into current policy changes in relation to environment and health in South Africa, thereby contributing to sustainable approaches to development in our country.

#### NOTES ON TERMINOLOGY:

Throughout the report, we use the term 'pesticide' to refer to all chemicals used for the control of pests, weeds, or plant diseases, including agents used in agriculture, public health and vector control. For a more detailed description of the different types and classification of pesticides, readers are referred to texts cited in the bibliography. Another term used in this report is 'detects', used here as is commonly applied in the literature to indicate analytical results where a specific pesticide has been identified on gas chromatography or other methods.

The study also makes use of the term 'Quantification Limits' to indicate the concentration in water above which results from the Peninsula Technicon laboratory is confident to provide a quantitative estimate of the concentration of the pesticide in question. Where pesticides have been detected at levels below Quantification Limits, the results are presented in full, but qualified with acknowledgement that the results lie below the limits of quantification.

The term EEC is used to refer to the European Economic Community as well as to other acronyms/ titles for the transnational legislative body that aims to merge European policy and trade initiatives, variously called the European Community (EC) or European Union (EU). In this document, we have retained the original acronym EEC under which the first pesticide standards were issued, to refer to all permutations of European governance affecting water standards, even though the EEC has been subsumed under a new term the European Union (EU) in this past decade.

Preface

# ACKNOWLEDGEMENTS

The research in this report emanated from a project funded by the Water Research Commission entitled:

"An assessment of the quality of water supplies in the rural Western Cape with regard to agrichemical pollutants." [Project number K5/95]

The Steering Committee responsible for this project consisted of the following:

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The financing of the project by the Water Research Commission and the contribution of the members of the Steering Committee is gratefully acknowledged. The project was only possible with the co-operation of many individuals and institutions. The authors therefore wish to record their sincere thanks to the following:

Prof T Robins of the University of Michigan School of Public Health and the Fogarty Centre for International Research Development - supporting Mr Solomon's study visit to UM and UMS laboratories in late 1996. Mr J Walters - Wenkem Mr C Dain - Zenica Mr G Hodges - Agrevo Mr J Levings - Two-a-day Co-operative, Grabouw Mr Watkins - Mechanical Engineering, UCT World Health Organisation - donated WHO STANDARDS Mr S van Niekerk and J van Zyl - Elsenberg Agricultural College Mr A Jacobs - Infruitec Dr O Sisulu and Dr G Joubert - CSIR Mr J Weaver, K Pietersen and G Tredoux - Environmentek Dr T Mashuku and Mr M van der Merwe, ARC laboratories Mr K Hearshaw -State Forensic Laboratory Ms H van der Westhuizen, E Truter, M Loubscher - Department of Health, West Coast Region, Malmesbury Mr K Hartman, UNIFRUCO Ms A Louw - Department of Water Affairs and Forestry The Hex River Producers Association

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# **DEFINITION OF ACRONYMS**

	1
ACOEM	American College of Occupational and Environmental
	Medicine
ADI	Acceptable Daily Intake
ARC	Agricultural Research Council
CV	Coefficient of Variation
DEAT	Department of Environmental Affairs and Tourism
DWAF	Department of Water Affairs and Forestry
DWEL	Drinking Water Equivalent level
DWLOC	Drinking Water Level of Comparison
EPA	Environmental Protection Agency
EEC	European Economic Community
EC	European Community
ECD	Electron Capture Detector
FOPA	Food Quality Protection Act
GC	Gas Chromatography
GC-NPD	Gas Chromatography with Nitrogen Phosphorous Detector
GC-FCD	Gas Chromatography with Electron Capture Detector
GC-MS	Gas Chromatography using Mass Spectrometry
GL	Guide Levels
GV	Guideline Value
HA	Health Advisory
HPLC	High Pressure Liquid Chromatography
IARC	International Agency Research Cancer
IPCS	International Programme on Chemical Safety (IPCS)
LOAFLS	Lowest Observed Adverse Effect Level
IRC	Loose Reservoir Cartridge
MAC	Maximum Allowable Concentration
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
ND	Not Detected
NS	Not Sampled
NOAFL	No Observed Adverse Effect Level
OFCD	Organisation for Economic Co-operation and Development
ODW	Office of Drinking Water
OPP	Office of Pesticides Programmes
PIC	Convention on Prior Informed Consent
POPe	Persistent Organic Pollutants
PENTECH	Peninsula Technicon
0A	Quality Assurance
00	Quality Controlled
SE SE	State Forensic
SWDA	Safe Drinking Water Act
TDI	Tolerable Daily Intake
INFP	United Nations Environment Programme
IISEPA	United States, Environmental Protection Agency
USGS	United States Geological Survey
WHO	World Health Organisation
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# EXECUTIVE SUMMARY

#### BACKGROUND

A 3-year investigation into the presence of pesticides in rural water sources in the Western Cape was undertaken with the financial support of the Water Research Commission from 1997 to 1999. The study was undertaken by the University of Cape Town's Occupational and Environmental Health Research Unit in collaboration with the Departments of Analytical Chemistry and Chemical Engineering at the Peninsula Technicon.

The study arose out of a concern for the lack of data in South Africa on the presence of pesticides in rural water sources, and the important policy implications that pesticide pollution of water would have for rural development. South Africa is a significant user of pesticides in agriculture and public health and available evidence suggest the potential for environmental contamination is high. Moreover, the infrastructure to monitor and control pesticides reaching water is poorly developed.

#### MOTIVATION

Because low level exposures to pesticides over prolonged periods are increasingly being suspected of being associated with adverse chronic health impacts, such as cancer, reproductive impacts, immune deficiencies and neurological diseases, attention to the ascertainment of low levels of contamination is important. Many social, economic and environmental factors in rural settings in South Africa may increase the risk experienced by farm workers and rural farmers from pesticides. Moreover, with the government's stated policy of increasing participation of black farmers in rural agriculture, and the absence of an adequate infrastructure to protect new entrants from harmful human and environmental exposures to pesticides, the need to ensure safety in relation to pesticides is accentuated. When considering the benefits of pesticides to agricultural production, the adverse impacts related to environmental contamination are often externalised or go unrecorded in the absence of any surveillance.

In South Africa, data on pesticides in rural water sources are sparse. Previous local research results have been constrained by relatively high detection limits used in previous analyses. Nonetheless, one study demonstrated significant residue levels of a range of locally used pesticides in farm dams in the Western Cape and a number of epidemiological studies have provided indirect evidence that environmental exposures, including waterrelated routes, may be important causes of pesticiderelated morbidity in South Africa. Thus some empirical evidence does exist to support the need for further examination of the quality of rural water sources in South Africa with regard to pesticides. Given the sparsity of the data, and the importance of such data to public policy, this study aimed to address the gap related to monitoring data on pesticides in water in South Africa.

#### OBJECTIVES

The objectives of the study were:

- To identify rural water sources in the Western Cape at high risk of contamination by means of:
  - review of secondary data
  - field observation
  - interviews with rural health care providers, farmers and environmental officer, technical officers and other agricultural personnel.
- (2) To ascertain the presence of, and to quantify chemical pollution at "high-risk" sites, relating the presence of these chemicals to different routes of contamination, and to spraying patterns on farms.
- (3) To establish the reliability and validity of methodologies for accurate determination of pesticides in rural water and the practicability of

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detection levels for determining low levels of agrichemicals in water.

- (4) To characterise more broadly the extent to which farm agrichemicals contaminate rural water supplies on farms and in rural towns in the Western Cape, taking account of seasonal variations related to spraying patterns and other confounding factors.
- (5) To identify additional sources of individual exposure, particularly non- occupational routes such as the reuse of pesticide containers, spray drift into and onto dwellings, and the unsafe domestic use of pesticides.
- (6) To describe the water sources available to farm workers, farmers and their families for drinking and ablution.
- (7) To estimate total dietary intake of agrichemicals of rural residents from water pollution, and to compare this to international standards.

#### METHODS

The project was undertaken in a phased approach.

Phase I was concerned with:

- a) the identification of sites in the rural Western Cape thought to be of concern from the perspective of potential contamination of water sources, and the identification of appropriate sampling points within the study sites
- b) the choice of specific pesticides and metabolites for analysis
- c) soliciting local stakeholder cooperation
- d) establishing reliable and accurate analytical methods for pesticide analyses, including establishment of quality control and quality assurance protocols
- e) formalising protocols for field sample collection
- f) piloting of farm-based questionnaires, and
- g) review of the literature, an activity that continued throughout the project.

Phase II involved the regular sampling of the selected sites, implementation of quality assurance protocols, and ongoing liaison with stakeholder groups. Phase III involved the completion of farm-based user surveys, as well as the analysis and write up of the findings.

Three study areas were chosen for sampling - the Hex River Valley, the Grabouw/Vyeboom area, and the Piketberg region. The basis for selecting these areas was that they represented a spread of farming activities in the region and presented a climatic and hydrological profile that was most compatible with the best likelihood of finding pesticides in ground water. In that sense, the three sites were "worst-case" scenarios, selected so as to maximise the possibility of detections, and were not representative of all agriculture in the region.

Analyses were conducted at the Analytical Chemistry laboratories at PENTECH for the main pesticides of concern, endosulfan and chlorpyritos following standardised methods of extraction and analyses. Levels of quantification achieved in the laboratory (0.05  $\mu$ g/c for chlorpyritos and 0.1  $\mu$ g/c for endosulfan isomers and endosulfan sulphate) were substantially lower than previously reported in the South African literature, and compatible with monitoring needed for low level exposures of concern in other countries.

Parallel analyses, using similar methods, were run at the State Forensic (SF) laboratories for 31 pesticides, including endosulfan and chlorpyrifos, as quality assurance (QA), and to detect substances for which the PENTECH laboratories were not adapted. Samples were also shared with the laboratories of the Agricultural Research Council (ARC) as part of a QA programme. Overall, QA analyses suggested that for the two pesticides of concern, the PENTECH laboratories were achieving adequate quality assurance.

Field sampling was conducted on an approximately weekly basis with each study area being visited on a monthly basis. Sites were chosen in each area to cover a spectrum of ground and surface water of different description and use purposes including a range of sources used for drinking. Standard field sampling methods were followed at all times.

Data collection commenced in the Hex River region in April 1998, and in the other areas over the next few months, and continued through to May 1999, so as to allow characterisation of a full year's cycle of farming activity. Concomitant with sampling, data were collected on spraying patterns in the region, and on river flow, temperature, rainfall, water pH and turbidity. Particular attempt was made to increase the frequency of sampling in relation to trigger rains in late autumn.

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#### RESULTS

The findings demonstrated a significant spread of detections throughout all three regions for both chlorpyrifos and endosulfan. Concentrations were generally very low (between 0.05 and 1 µg/l), but there were exceptions with levels in excess of 10 µg/l. Chlorpyrifos was detected most frequently in Piketberg. 62 (66%) out of 94 times sampled compared to Hex River, 96 (52%) out of 184 times and Grabouw 51 (49%) out of 104 times. Endosulfan was found most frequently in Grabouw, 72 (69%) out of 104 times compared to Hex River 85 (46%) out of 184 times and Piketberg, 37 (39%) out of 94 times. Of importance is the observation that the problem is not confined to the Hex River but is ubiquitous in all 3 study areas chosen for investigation. Out of 382 samples, there were 30% detects above the EU limit of 0.1 µg/t for chlorpyrifos and 37% for endosulfan.

The temporal trends were compatible with the role of high irrigation wash-out of both endosulfan and chlorpyrifos in the regions, with seemingly significant ingress of pesticides brought through the Berg River into the Piketberg area. Other factors such as soil characteristics, shallow water tables and intensive spraying probably explain the presence of these pesticides in water. Detections were also consonant with spraying patterns, but less so with rainfall.

The data were consistent in that sub-surface drains were commonly contaminated and that certain sites were clearly active as "hot-spots" as a result of their siting and vulnerability to run-off. Contamination of surface water in dams also emerged as an issue, particularly in the Grabouw/Vyeboom area, often consistent with periods of local application, suggesting direct entry of pesticides from spray activity into dam waters. These findings are consistent with previous research on farm dams in Grabouw.

Compared to international findings, the frequency of detections in this study are consistent with results from field studies of rivers in agricultural areas in Spain and California, but higher than results obtained from routine surveillance (Texas, California). This discrepancy might arise because the likelihood of detections is lower with sporadic testing as occurs in routine surveillance. Moreover, the concentrations detected in this study for endosultan and chlorpyrifos were consistent with the international literature, with maximum averages in comparable studies of the order of magnitude of 0.3 to 0.4 DA µg/t for both endosulfan and chlorpyrifos. Maximum levels found in this study, on the other hand, appeared substantially higher (about to 80 to 90 orders of magnitude higher) than found in two Californian studies that provided enough detailed data for comparisons.

It should be borne in mind that this study purposively sought out sites where probabilities of pesticides reaching water were highest and is therefore not representative of the overall situation with regard to pesticide pollution by agricultural pesticides. In contrast, most of international studies cited above were typically conducted on integrated samples representative of the target population.

#### HEALTH IMPLICATIONS

A number of sampling points where water is used for drinking were consistently contaminated, albeit at low levels. Modeling of the contribution of consumption of water from these points to hypothetical daily intake suggested that sources represent very low proportions (generally less than 1%) of the Acceptable Daily Intake. The pesticide concentrations in these water sources therefore do not appear to represent levels of immediate threat to human health. However, given scientific uncertainty inherent in risk assessment, and the increasing evidence that endocrine disrupting effects occur at concentrations far lower than other toxic effects, these concentrations should warrant greater attention. Moreover, current risk assessment procedures do not adequately address toxicity of combinations of chemicals, as is often found in water monitoring results in both developed and developing countries, and as was the case in this study.

Data in this study has also suggested that farm residents may experience other important indirect routes of exposure to pesticides, including potential spray drift by virtue of living in proximity to orchards or fields, use of pesticides at home and swimming in contaminated dams. Given an environment of poor nutrition, and many other factors increasing the vulnerability of adults and children on farms, risk from low concentrations of pesticides in drinking water that may be of marginal importance for healthy urban populations, may be of critical importance for farming populations. Such data should be built into future risk assessment in relation to water pollution by pesticides. A striking and encouraging feature to emerge from the farm surveys was the relatively high levels of awareness demonstrated by farm workers and employers of the health hazards associated with pesticides. Particular high-risk behaviours such as the re-use of pesticide containers were reported as virtually absent. The high awareness may be the result of training programmes run by agricultural employers over past months. Such high levels of awareness may make easier reduction in risk activities (e.g. poor hygiene in pesticide applications) and compliance with standards for pesticides in water, should the DWAF introduce such legislation.

A further issue to consider is the need for sound epidemiological studies that can begin to quantify the actual risk associated with very low levels of pesticides in drinking water. Epidemiological studies are frequently flawed by the lack of accurate data on exposures of rural populations, with the result that possible inferences may be invalidated by misclassification. Data from studies like this one should be used to provide accurate exposure estimates for aetiological studies of the health impacts of these low levels of pesticides in drinking water.

This is particularly important for a pesticide such as endosulfan, which is recognised as an endocrine disruptor.

### THE NEED FOR STANDARDS

Two approaches to setting standards for drinking water are available. The health-based approach adopted by agencies such as the World Health Organisation (WHO), and the US Environmental Protection Agency (EPA) uses a proportion of dietary intake attributable to water intake in relation to the ADI to estimate acceptable levels of a contaminant in drinking water. The derivation of the ADI or a Reference Dose (US EPA) is dependent on various risk assessment assumptions and inclusion of safety factors. In contrast, the policy-based approach adopted by the European Unions sets permissible levels of pesticides at the lowest limit of analytical capability, as a tool to drive down all exposures to pesticides. Such an approach is also predicated on the primary application of the precautionary principle and the recognition of scientific uncertainty in risk assessment.

Placing this study's results in relation to these standards, when compared to EU standards, between 22 and 57% of samples analysed yielded detects. This suggests that If judged against a policy-based standard such as the EU'S, water pollution by pesticides is a matter of concern. In contrast to the policy-based EU standards, few of the detections approached concentrations of the order of those associated with health-based standards. However, the results of the study do provide pointers for taking action on two important policy questions.

#### a) Should there be monitoring for pesticides in water in South Africa?

Given the extent of scientific uncertainty and trends in the current policy environment in South Africa, there appear to be sufficient grounds to warrant surveillance of water for pesticides on a routine basis. Future international standard setting is likely to shift thresholds for endocrine disrupting chemicals downward, and the lack of data in South Africa make rational policy decisions on pesticides difficult. Moreover, other policy commitments to international conventions will impose similar responsibilities. Data from this study suggest that even in a relatively affluent province such as the Western Cape, with a well-developed infrastructure, the levels of risk for rural residents, while low, are not inconsequential. With the growth of the informal agricultural sector and of small-scale farming, these risks are likely to be multiplied. If the precautionary principle is to be consistently acted upon by government departments, enough evidence exists from this study to warrant closer attention to pesticides in water in the form of routine or systematic monitoring, even in the absence of proven excursions above current health-based standards, such as they presently exist.

#### b) Should regulatory standards be developed for pesticides in South African waters, and if so, what kinds of standards?

At present, we are faced with the choice of health-based standards based on current risk assessment methods (e.g. EPA, WHO, etc), or policy-based standards used to drive down usage of pesticides and meet the precautionary principle (EU standards). Clearly lower thresholds may carry higher costs for

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prevention or remediation, and South Africa. may find it difficult to compete with wellresource developed countries in its environmental management practices. However, it would appear reasonable from the data that application of international healthbased standards of the EPA and the WHO would not present an overly burdensome set of thresholds for practical use in South Africa. At the very least, such standards will provide a measure of health protection not presently available to ordinary South Africans, and which the Constitution seeks to achieve. The question as to whether the much more stringent policybased standards such as the EU'S should be considered could perhaps best be left to consultative multistakeholder processes such as the National Chemicals Profile to be convened by the DEAT in 2000.

### FIELD AND LABORATORY CAPACITY

The project was reasonably successful in its capacity building approach to developing the ability at a historically disadvantaged research institution to undertake accurate and valid methods for analyses for two key pesticides. The project was also able to establish quantification limits (0.05  $\mu$ g/ℓ for chlorpyrifos and 0.1  $\mu$ g/ℓ for endosultan) lower than previous studies (about 10 times more sensitive) and more consistent with the levels of sensitivity demanded by current developments in risk assessment. Moreover, this was done whilst achieving adequate quality control and quality assurance in measurements.

Despite this, it is clear that further improvements in sensitivity would greatly assist risk assessment research. The EPA and the US Geological Services report detection limits of the order of a further 10 to 100 times lower than that achieved in this study. Achieving this level of sensitivity, which is required for protection of aquatic biota, presents significant challenges. Traditional approaches to measuring pesticides in water could well be supplemented by alternative, less costly methods, such as bioassays and immuno-assays. One important limitation in the study was the reliance on grab sampling, with the result that intermittent monitoring may give false estimates of true exposures, or inadequate characterisation of contamination patterns. Methods that integrate exposures over time would greatly assist the interpretation of data from surveillance.

Furthermore, if monitoring is to be implemented, capacity for field sampling is a key operational issue. Capacity at local government level to manage monitoring programmes needs to be developed since many technical personnel charged with key inspection and enforcement functions with regard to water quality do not have adequate training or sensitivity to the issues. Practical guidelines to facilitate monitoring in this regard would be very useful.

#### PREVENTION AND REMEDIATION

Although this study was unable to identify in sufficient detail the precise farm practices responsible for egress of pesticides to water, generic measures to control the loss of pesticides to ground water may well be appropriate. These include training of farmers and farm workers in pesticide safety, and particularly on environmental hazards, in ways that enables farmers and farm workers to take ownership of the environmental consequences of farming practices.

Other interventions of a technical nature directed at point. sources would include containment liners to mixing points used in orchards, fields and vineyards to prevent spillage at mixing sites, which should be routine farm practice. However, data in this study suggested that irrigation was a major factor driving the entry of pesticides to water bodies in the areas surveyed. This suggests that, to some extent, pollution of water sources is occurring under "normal" farming practices and not as a result of accidental or unintentional point source releases (e.g. mixing sites). The main remedial measure under such circumstances would be to encourage pesticide reduction as an overall restraint on the amount of active ingredient reaching environmental media. Integrated Pest Management should be widely encouraged to meet this objective. Further detailed research into the precise farming activities associated with these low-level exposures would also be desirable.

#### OVERVIEW AND RECOMMENDATIONS

This study suggests that although pesticide pollution of water has not previously received adequate attention in South Africa, evidence for consistent and low-level

Executive Summary

contamination by pesticides is present in rural water sources in selected regions of the Western Cape. Although the regions sampled were chosen purposively as 'worst-case' scenarios with the highest likelihood of pesticides reaching water, and are therefore not representative of all agriculture, as illustrative extreme cases, they demonstrate that pesticides can and do reach water sources in rural farming areas of South Africa in low concentrations.

There is no reason to believe that similar studies of purposively chosen sites in other Provinces would yield less severe patterns of detections. It therefore appears warranted to pay greater attention to establishing reliable mechanisms for surveillance of water sources for pesticide pollution in the future.

Furthermore, although few of the detections of endosulfan and chlorpyrifos approached concentrations of the order of those associated with health-based standards of the WHO and EPA, and therefore, did not appear to pose immediate threats to human health, South African waters cannot be assumed to be adequately protected in the absence of drinking water standards that include pesticides and their metabolites. Risk assessment methods, as discussed in Chapters 2 and 7, which take account of the multiplicity of exposure routes, of aggravating socio-environmental factors, and mixtures / metabolites should be incorporated in a specific process of standard setting for pesticides in water, taking account of different water uses.

Thirdly, although rural populations may experience diverse potential routes of exposure to pesticides other than water, awareness of the hazards of pesticides is relatively high and recognised risky practices (such as reuse of pesticide containers) are very rarely reported. Regulatory standards should therefore be able to capitalise on this relatively highly developed awareness to ensure adequate compliance and protection of human health. The positive impacts of rural health and safety training initiatives by employers and employees may be reflected in this high level of awareness and should be encouraged further.

Based on the study results, the project therefore makes the following recommendations:

#### The need for monitoring of water for pesticides

- The DWAF should actively pursue development of surveillance and monitoring methodologies to protect water supplies from pollution by pesticides. Data in this study justify the conclusion that surveillance is warranted.
- Local government capacity, particularly in rural areas, to implement monitoring of water sources for pesticide poisoning should be audited and strengthened.
- In addition, rural communities should be provided with simple, cost effective tools to undertake monitoring of their own water supplies.
- Practical guidelines for water monitoring for pesticides should be developed for all for personnel (community or governmental) charged with inspection and enforcement functions.
- v. DWAF should also seek ways to ensure that data in support of surveillance activities on farms is effectively captured. In particular, every effort should be made to ensure that toxic release inventories and use inventories for pesticides should be available and used for surveillance purposes. DWAF should liaise with other government departments to co-ordinate and maximise the impact of such measures.
- vi. This study has focused on the extreme end of a spectrum, concentrating on areas where pesticide pollution was anticipated to be most likely. By introducing routine surveillance on a broader basis, DWAF should seek to ensure that it maps a representative sample of all agricultural areas, so as to characterise the overall state of water pollution due to pesticides, both extreme and average. These data should serve as the basis for monitoring temporal trends in the country.
- 2. Standards
  - Established international health-based standards, such as those developed by the WHO and the EPA, although not without criticism, should be adopted by the DWAF as a means to offer a level of protection

consistent with the provisions of the South African Constitution.

- ii. Pursuit of more rigorous policy-based standards, such as those set down by the European Union, should be considered within the framework of an appropriate national multistakeholder process such as the National Chemicals Profile initiative to be undertaken by the DEAT in 2000.
- iii. Risk assessment in relation to pesticides should inform the setting of water standards, not only for drinking water but for other uses, and should be undertaken in recognition of the context of rural farm workers' additional exposures, and concomitant vulnerability factors. Methods used should be able to take account of cumulative risks from many sources and over time.

#### 3. Improvements in Analytical Methods

- i. Methodologies that offer the possibility of producing assessments of exposure that integrate fluctuating concentrations over time should be explored. In particular, the utility of Solid Phase Micro Extraction (SPME) fibres should be adequately assessed in vitro and under field use for possible adoption as part of a monitoring programme.
- Further research involving methods which have lower levels of detection should be explored, particularly with the view of informing risk assessment and standard setting for ecotoxicological purposes.
- Traditional GC pesticide analytical methods should be supplemented with alternative methods such as bioassays and immunoassays, subject to adequate field testing, validation and cost-effectiveness evaluation.

#### 4. Control of Exposures

- Policy measures that seek to avoid potential contamination of environmental media and reduce leaching should be encouraged: Integrated Pest Management, Containment liners at mixing sites, training, and general movement toward pesticide reduction.
- DWAF should enlist the support of key partners to encourage research directed at identifying the precise farming activities that

are amenable to intervention to reduce potential egress of pesticides to water sources.

iii. Behavioural determinants of pesticide pollution should be addressed by encouraging health, safety and environment training to employers and employees in farming communities. Any training provided on health and safety should include the hazards to the environment amongst the full spectrum of safety information and be geared to empowerment of rural residents. Particular attention should be given to empowering rural residents to protect themselves and their communities from adverse consequences of unintended pollution.

#### 5. Health Outcome Studies

- i. Studies should be done to capitalise on the careful exposure data obtained in this study. Such studies can address many of the difficulties in typical epidemiological research by improving on the quality of exposure assessment. This research can put South Africa at the cutting edge of public health / environmental health research, and can help to provide informed risk assessment for standard setting.
- ii. Studies that specifically examine the importance of spray drift in human health impacts appear warranted given the frequency with which human habitation abuts onto areas of pesticide spray. Agencies other than the Water Research Commission (such as the Medical Research Council, and the Agricultural Research Council) should be encouraged to pursue this avenue.
- iii. The benefits of high levels of awareness should be related to improved health status amongst rural farm residents. Research to evaluate the impact of safety training on the health of farm workers and employers will assist lobbying for greater resources for the control of pesticide pollution in rural farming areas.

# Chapter 1:

# INTRODUCTION

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## 1.1 BACKGROUND

Despite the undoubted short- and medium-term benefits of the use of pesticides in the control of vector borne diseases, and in boosting crop production in agriculture, the past two decades have seen a growing global realisation that widespread use of chemicals for pest control may pose serious long-term risks to human health and to the environment (Restrepo *et al*, 1990; WHO, 1990; BMA, 1992; Maroni and Fait, 1993; Repetto and Baliga, 1996; Lee *et al*, 1998; Dalvie *et al*, 1999). Much of this is particularly focused on the suspected links between xenobiotics in the environment and adverse reproductive health effects on humans and other biological systems (Danish Ministry of Environment, 1995; Editorial, 1995; Colborn *et al*, 1996; Schettler *et al*, 1996; Gray and Ostby, 1998; Porter *et al*, 1999) Increasing attention to issues of sustainable development can be seen in international conventions and agreements' that challenge national governments and transnational agencies, Non-governmental organisations (NGOs), communities, industry and ordinary citizens to promote environmentally sound development. Indeed, the 1992 World Development Report (World Bank, 1993) for the first time recognised the critical importance of environmental sustainability to future economic growth and the need for policies to ensure sound environmental management.

In relation to agriculture and public health, the widespread use of pesticides has been one of the considerations that has come under scrutiny (Leslie and Cuperus, 1993; Thrupp, 1996; Consumer Union, 1998), with particular focus on the need to reduce our dependence on chemical control of pests and disease vectors, precisely because of increasing evidence for the short-, medium- and long-term impacts on the environment of these chemicals.

For many biological systems, the most important route of exposure to pesticides is through pollution of water sources by pesticides. Moreover, contamination of groundwater is of particular concern because of the duration of impacts and the length of time taken for groundwater to recover, particular if persistent compounds are involved (Premazzi and Zigio, 1995). Furthermore, because of the propensity for many contaminants to bioaccumulate through the food chain, water is a critical medium for such long-term impacts. Thus, consideration of how to effect environmental and health policies that are able to support sustainable development requires careful attention to the prevention and monitoring of pesticide pollution of water. While concern for possible water pollution by pesticides has mobilised considerable financial, scientific and technical resources in other countries, particularly in the developed world, relatively little attention has been paid to this issue in South Africa until recently.

# 1.2 PESTICIDE USAGE IN SOUTH AFRICA: HEALTH AND ENVIRONMENTAL IMPLICATIONS

Pesticides are widely used in South Africa, predominantly in agricultural applications but also in a range of other settings, including vector control in public health, commercial pest control, domestic use and in selected industrial or food processing technologies<sup>2</sup>. However, data from the Crop and Animal Protection Association of South Africa (AVCASA) indicate that the bulk of the pesticide market in South Africa is attributable to agriculture (London, 1992). This is important because of the implications for environmental exposure in that agricultural applications in general represent potential non-point sources of pollution.

<sup>1</sup> For example, the Rio Declaration on Environment and Development (or Agenda 21) adopted at the Earth Summit, United Nations Conference on Environment and Development held in Rio de Janeiro, June 1992.

For example, the dried fruit industry makes use of pesticides in the initial preserving process. Preservatives are widely used in timber-related production activities.

Non-point source are significantly more difficult and costly to control than point sources (United States General Accounting Office, 1999).

However, although agricultural applications represent the most significant source of pesticide exposures, it is prudent to remember that a wide range of activities and occupations may bring humans into contact with pesticides, either in direct exposure, or through indirect environmental exposures (see Table 1.1).

Expenditure on pesticides in South Africa has increased markedly over the past decade (London, 1992; Rother and London, 1998) and a far greater variety of chemicals are used locally when compared to other developing countries (London and Myers, 1995c; London, 1995). Indeed, South Africa is the largest market for pesticide in sub-Saharan Africa (Dinham, 1993).

Usage patterns are extremely variable across agricultural sectors and in different regions (London and Myers, 1995a). For example, herbicide use is the largest component of the national market for pesticides associated with maize production, while in the Western Cape with its wetter winter climate, and concentration on fruit, grapes and wheat, fungicides are much more in evidence (London and Myers, 1995b).

TYPE OF ACTIVITY GENERATING EXPOSURE	EXAMPLE OF ROUTE OF EXPOSURE
Agricultural and forestry application	Drift from local orchard or plantation application
TYPE OF ACTIVITY GENERATING EXPOSURE         Agricultural and forestry application         Non-agricultural environmental applications         Domestic uses         Commercial pest control         Spraying of Public Amenities         Waste         Public Health	Drift from aerial spray
	Chemigation
	Spraying for quelea
	Baiting for predatory animals
	Locust control
Non-agricultural environmental	Aerial spray to eradicate marijuana cultivation
applications	Security applications
Domestic uses	Domestic pest control
	Gardening
Commercial pest control	Fumigation and other forms of application in
-	homes
	Spraying of public places
	Such as schools and public parks
Spraying of Public Amenities	Public parks
	Schools
Non-agricultural environmental applications Domestic uses Commercial pest control Spraying of Public Amenities Waste Public Health Residues	Golf courses
	Road verges
	Railway sleepers
Waste	Industrial waste emissions
	Residual pesticide releases
Public Health	Pesticides in endemic areas for vector control
	Airplane spraying for vector control
Residues	On treated objects (e.g. wood products)
	On foodstuffs

#### Table 1.1: Potential environmental routes exposure to pesticides

Use of protective measures by farm workers in the application of pesticides is unevenly reported (London, 1994; London, 1995; Barnes, 1997, Robins *et al*, 1998). As a result, acute poisoning by pesticides amongst farm workers is an important and under-reported public health problem (London *et al*, 1994a). Approximately 150 to 200 cases of pesticide poisoning are reported to the Department of Health each year (Department of Health, 1995). However, the real rates are probably five times as high (Emanuel, 1993; Barlin Brinck, 1991; London *et al*, 1994) with particular under-reporting of occupational poisonings and poisonings amongst women (Baille and London, 1998). If this is the case for acute poisoning, the situation in regard to chronic effects, which are more difficult to detect (Maroni and Fait, 1993), is simply unknown in the absence of any effective surveillance systems.

In addition, most South African farm workers live on the farms where they work, frequently in close proximity to the fields or orchards that are the subject of pesticide application (London, 1994a), often by aerial methods (London, 1996)<sup>3</sup>. The potential therefore exists for substantial domestic exposure arising from environmental contamination, which may be mediated through contamination of water sources, particular if surface water is used for drinking or other domestic purposes.

Furthermore, there is considerable evidence that application methods in practice take little account of the risks of environmental contamination (Myers, 1990; Barlin-Brinck, 1991; London, 1994; Yousefi, 1999). For example, mixing sites in fields and orchards in the Western Cape show little attention to industrial hygiene measures to avoid run-off (London, 1995; London, 1999). Moreover, aerial spraying, with its high degree of vulnerability to drift, continues to be widely used in settings where impacts on non-target sites may be significant<sup>4</sup> (Barlin-Brinck, 1991; London, 1994b). Most recently, the South African police services recommenced aerial spraying for the eradication of illegal cultivation of marijuana plants, without any reference to the environmental impacts of such activities (quoted in the Cape Times, 29th September 1999)<sup>5</sup>.

Notwithstanding the substantial opportunities for human exposures to pesticides, both direct and indirect, little systematic monitoring of the extent of environmental contamination by pesticides occurs in South Africa (Coetzee and Cooper, 1991). Most local authorities, constantly constrained by limited budgets see their responsibility for ensuring provision of potable water and maintenance of water quality met through the monitoring of rural water supplies for bacteriological quality and rarely test for the presence of organic contaminants (Rother and London, 1998). This emphasis on colloforms counts in drinking water has remained largely unchanged since a previous investigation in South Africa 15 years ago (Vurgarellis, 1984). The absence of monitoring for organic contaminants is largely because of the lack of availability of cheap analytical methods, and the relative sparsity of laboratories with the technical skill and equipment to conduct high-quality analyses required for measurement of pesticides in environmental media. Even in Europe, reviews of laboratory practices in support of water protection regulations have shown how difficult it is to achieve reliable and valid monitoring performance (Premazzi and Zigio, 1995).

The lack of monitoring is of concern, given the significant opportunities for human exposure and the increasing number of chronic health conditions being associated with long-term exposure to pesticides (for example, Maroni and Fait, 1993; Landrigan *et al*, 1993; London, 1995; Repetto and Baliga, 1996; Schettler *et al*, 1996; Lee *et al*, 1998; Dalvie *et al*, 1999).

<sup>&</sup>lt;sup>3</sup> Another common example is concerns expressed by rural town residents as a result of aerial spray applications of pesticides to surrounding farms.

In 1993, residents in Morreesburg were sufficiently concerned to prompt their local authority to seek advice on the impacts of aerial spray on neighbouring agricultural land (correspondence between the West Coast Regional Services Council and the Regional Director for Health, 13 August 1993).

In 1997, the Police were forced to stop aerial spraying of herbicides for the eradication of illicit rural marijuana plants after public outcry over, amongst other things, the environmental hazard - ("Expensive war the police can't win" Mail and Guardian, 25<sup>th</sup> July 1997)

#### 1.2.1 WHAT EVIDENCE EXISTS WITH RECARD TO WATER POLLUTION BY PESTICIDES IN SOUTH AFRICA AT PRESENT?

Despite international attention to pesticides in water, there is a paucity of local research to date (London and Myers, 1995b). One published study investigated rural water contamination by pesticides in two sites in South Africa (Weaver, 1993). This study found evidence of atrazine contaminating incoming waters to the Vaalharts irrigation scheme, but little evidence of locally applied pesticides reaching water sources. The investigation in the Hex River conducted as part of the same report, found no evidence of pesticide contamination in the Hex River area based on sampling 12 subsurface drains and wells in the region. However, the inferences possible from this particular study were limited by relatively coarse Quantificiation Limits (0.5  $\mu$ g/t or higher) reported by the South African Bureau of Standards laboratory for the Hex River samples (Weaver, 1993). Particularly for chronic effects of long-term exposure, the attainment of sufficiently low levels of detection is important for surveillance strategies.

A second case study involving intensive application of a range of herbicides by the South African Defence Force in the 1980s to protect a sisal fence serving as a security barrier on the Limpopo River border <sup>6</sup> Illustrates the ease with which pesticides move in water. The herbicides were applied by contractors to maintain a clear barrier in front of the sisal but because of inappropriate and too frequent use, migrated from the land into the river water, seemingly affecting the safety of irrigation water used by local farmers. Research by the Agricultural Research Council appeared to confirm this evidence for pollution of the river (Meinhardt *et al*, 1998).

Anecdotal evidence cited in Barlin-Brinck (1991) describes evidence of atrazine and selected organochlorines in surface water in the Free State in 1985 and of the impact of atrazine on fish in the former Eastern Transvaal. More recently, a farmer in the Mpumalanga province reported the presence of picloram (at concentration of  $13\mu g/0$ ) in ground water from boreholes over 100m deep that was associated with damage to tobacco seedlings and gastrointestinal disturbance amongst employees drinking this water<sup>7</sup>. However, data on environmental contamination and its health implications are relatively sparse and unsystematic in nature.

Notwithstanding the lack of systematic evidence from surveillance data, there is considerable circumstantial evidence that environmental exposures are common in rural communities (see for example, Koch, 1991, pages 26-27 and Coetzee and Cooper, 1991, page 132). Researchers investigating the impact of insecticide spraying on coffee farms in the Northern Province found lowered cholinesterase levels<sup>8</sup> suggestive of organophosphate exposure amongst rural control subjects, suggesting substantial environmental exposures were taking place (Jaga and Rama, 1993). Another study identified an environmental cluster of neurological disease in a farming area of the Northern Cape subject to high rates of aerial spray of organophosphate insecticides (London, 1994b), while other studies have shown impacts on rural women of domestically-applied pesticides for malaria control (Bouwman, 1990). Studies cited in Barlin-Brinck from the late 1970s and early 1980s identify the presence of a number of organochlorine residues in animals and fish in a number of studies. While none of these studies specifically implicated water sources as a route of exposure, the fact that there was evidence for environmental contamination by

<sup>\*</sup>Crops Poisoned by SADF herbicides' Sept 15\* 1995. Mail and Guardian.

<sup>&</sup>lt;sup>7</sup> Personal communication with Mr Brian Law, White River, April 2000.

Cholinesterase is an enzyme in the plasma and red blood cells which is inhibited by organophosphate and carbamate pesticides in humans, and is therefore used as a marker for exposure. Lowered levels indicate uptake of, and biological changes from exposure to these pesticides.

pesticides suggests that further attention should be focused on the precise contribution of water as a potential route for exposure.

# 1.3 GLOBAL TRENDS IN THE USAGE AND MONITORING OF PESTICIDES

Although pesticide sales continue to increase worldwide<sup>9</sup>, many countries, not only in the developed world (Premazzi and Zigio, 1995; Emmerman 1996; Jorgenson, 1996, Bureau of Resource Sciences, 1998) but also in developing countries (Davies, 1997) have begun to implement national policies aimed at pesticide use reduction. This has principally arisen from a recognition of the potential hazards to human health and to the environment.

Central to these pesticide reduction policies has been the implementation of Integrated Pest Management (IPM) strategies (see box below) in agriculture. IPM strategies aim to reduce reliance on chemical controls by using a diverse range of alternatives in a comprehensive toolkit of pest control options (University of California, 1992; Consumer Union, 1998). By adopting these alternatives, IPM reduces the amount and frequency of pesticide applications, while retaining economic productivity of agricultural outputs. Through widespread adoption of IPM strategies, countries have been able to significantly reduce pesticide loads and the potential for environmental contamination of water and other media. Indeed, agricultural sectors within South Africa with heavy investment in export markets have shown themselves to be most sensitive to both IPM adoption as well as to the mitigation of potential environmental impacts of pesticide applications (Rother and London, 1998). Recent World Bank reports (Schillhorn van Veen TW, 1997) have also recognised the dual economic and environmental value of IPM by including an IPM commitment to reduce reliance on chemical pesticides in future Bank-funded projects (PANUPS, 1997). Similarly, research commissioned by the Department for International Development (DFID) in the UK has focused on the potential for organic farming in sub-Saharan Africa (Harris *et al*, 1998).

Simultaneously, developed countries have maintained highly active monitoring systems for the detection of pesticides in water sources. For example, extensive monitoring has been implemented of water and groundwater in the US over past decades in response to legislative requirements to protect water quality (US Soil Conservation Service, 1988; Hogmire *et al*, 1990; EPA, 1995; USCS, 1998a; EPA, 1999). Similarly in Europe, extensive monitoring has been driven by legislative pressures to comply with EEC directives, resulting in extensive testing of water throughout the member countries of the European Union (Premazzi and Zigio, 1995).

Moreover, the World Health Organisation has provided technical guidance recommending the regular monitoring of water sources for adequate quality, including control of pesticide residues and metabolites (WHO, 1993a; WHO, 1993b). These standards are discussed in more detail in Chapter Two, but reflect a growing international consensus that the risks associated with long term exposure to pesticides through water are not insubstantial and deserve scientifically rigorous risk assessment and standard setting.

For example, pesticide sales continued to increase over the past 3 years, with 9 out of the top 10 pesticide companies in the world increasing sales in 1999 by between 0.2 and 26% -Agrow: World Crop Production News, March 26th 1999, and April 16th 1999.

#### What is Integrated Pest Management (IPM)?

IPM is a knowledge-intensive and farmer based management approach that encourages natural control of pest populations by anticipating pest problems and preventing pests from reaching economically damaging levels. Appropriate techniques are used, such as enhancing natural enemies, planting pest-resistant crops, adapting cultural management, and, as a last resort, using pesticides judiciously.

Source: US Department of Agriculture / Agricultural Research Service: USDA Programmes Related to Integrated Pest Management. USDA Programme Aid 1506, Bethesda, Maryland, cited in Schillhorn van Veen et al, 1997.

#### IPM Technical Toolbox

The main features of IPM involve the use of non-chemical methods of pest control:

- Biological controls. The use of natural enemies, often called beneficials, which include parasites, predators and insect pathogens.
- Cultural and crop or livestock management controls. Tissue culture, disease-free seed, trap crops, cross
  protection, cultivation, refuse management, mulching, field sanitation, crop rotations, grazing rotation and
  intercropping.
- Strategic controls. Planting location, timing of planting and timing of harvest.
- Genetically based controls. This includes insect- and disease resistant varieties and root stock. Environmentfriendly chemical interventions are sometimes included in biological controls such as the use of semiochemicals, including pheromones and feeding attractants, and biopesticides.

In practice, IPM often combines natural forms of control, taking advantage of (and providing training in) ecological relationships in the agricultural system, with economically derived rules for the application of pesticides. However, the pesticide use in IPM differs from the approach used in conventional pest control. When possible, IPM relies on pesticides that target specific pests, can be applied at lower rates, and are less toxic to beneficial organisms. New application methods are being developed that employ biological materials such as pheromones and feeding attractants to lure the target pest to the pesticide. Application rates, timing and frequency are chosen to minimise effects on beneficials. Pesticides that can be substituted for each other are interchanged to slow the development of pest resistance to pesticides.

Source: Schillhorn van Veen et al, 1997

## 1.4 POLICY QUESTIONS

In considering the question of pesticide pollution of water sources in South Africa, a number of policy questions emerge.

Firstly, the South African Constitution guarantees South Africans the right to an environment that is not harmful to one's health and to have the environment protected through legislative and other measures to prevent pollution. Such rights are to be seen in the context of an expectation on government to take progressive action towards their realisation. The Constitutions thus both enables and expects government to prioritise actions to support the attainment of these rights. Yet in order for government to set priorities, data is needed on what precise measures are appropriate given financial constraints and competing priorities. There is therefore a need for data to inform policy choices around environmental health priorities, particularly with regard to characterising the extent of pesticide contamination of rural water supplies and thereby helping to answer whether systematic surveillance for chemical contamination of rural water supplies should be introduced in South Africa.

Secondly, agriculture is a major employer in the country (Donaldson and Roux, 1994) and is particularly important for the Western Cape economy (WESCRO, 1992). Small-scale farming is likely to expand substantially under future government policy (ANC, 1994; Department of Agriculture, 1999). The potentially exposed rural population and the opportunities for environmental contamination is therefore large and increasing. The human health consequences are compounded by the poor living and working conditions of many farm workers, whose poor general health status and poor nutrition may make them more susceptible to the adverse effects of pesticides (London *et al*, 1998). Children are particularly vulnerable to the toxic effects of pesticides (ACOEM, 1993). Given the lack of rural child care facilities, and shortages of access to water in many parts of the country, the consequences of exposure of rural children to pesticides through water contaminated by pesticide application may be significant (Rother and London, 1998).

Moreover, it is well recognised that small-scale or emergent farmers may be particularly vulnerable to aggressive marketing of pesticides, with little technical support, thereby increasing the prospects of human exposures and environmental contamination from inappropriate and uncontrolled use (Rother and London, 1998). The expansion of agricultural activities with the framework of the Reconstruction and Development Programme, particularly related to small-scale farming, should aim to ensure practices that are safe for human health as well as environmentally sustainable. Without baseline data, such policy choices are not possible.

Thirdly, were South Africa to introduce routine monitoring for pesticides in water, what resource implications would there be in terms of capacity, skills, equipment and expertise? One of the main constraints to monitoring to date has been the lack of access to reasonable cheap analytical methods. Research should help to identify where appropriate resources are needed to address problems once identified. The need for specific and systematic monitoring systems, at a cost that is affordable and sustainable is a relatively global priority (Premazzi and Zigio, 1995).

Fourthly, environmental law in South Africa is presently undergoing fundamental revisions, with one of the principal goals being the rationalisation and/or integration of existing environmental management frameworks (Department of Environmental Affairs, 1997; Department of Environmental Affairs, 1998a; Department of Environmental Affairs, 1998b). Attempts to address water pollution by pesticides therefore need to be fully integrated into such legislative developments. Indeed, this is the best window of opportunity for such measures that South Africa has seen for many a decade.

Lastly, from a public health perspective, and from the perspective of managers responsible for planning water provision in South Africa, the relative importance of health impacts that are non-acute, often insiduous and multifactorial compared to the effects of acute poisoning are critical for policy choices. While the latter events are easy to flag, and readily interpretable to popular audiences, chronic impacts may be more difficult to understand and act upon. However, they may be of equal or even greater importance, particularly for lower middle income countries such as South Africa. Indeed, the phenomenon of the epidemiological transition (with changing patterns of preventable infectious diseases giving way to rising rates of non-communicable disease) has been well documented (Frenk *et al*, 1989). There is some evidence that South Africa has already entered such a transition in its morbidity and mortality experience (Bradshaw, 1997). Attention, therefore, to measures directed at the prevention of chronic health impacts

associated with low levels of pesticides in water, are therefore entirely appropriate for a policy agenda for South Africa at this stage of its development.

## 1.5 RATIONALE FOR THE STUDY

Given the above context, of circumstantial evidence suggesting under-awareness of environmental routes of pesticide pollution, and the many policy implications flowing from this, this study seeks to address the need for careful attention to surveillance for water pollution by pesticides.

This study was therefore motivated in order to:

#### a) CHARACTERISE THE NEED FOR SURVEILLANCE OF RURAL WATER SOURCES

A number of related research questions that arise from the previous discussion are addressed in this study. What is the extent of potential pesticide contamination of water sources in the rural areas of the country? Is it of sufficient significance to warrant regular monitoring? If survey data indicate a significant degree of chemical pollution, attention will need to be directed in future to establishing an effective chemical surveillance system for water guality in rural communities. Moreover, such systems should be able to trigger abatement and control measures to reduce exposures, as has been implemented in other countries. Therefore, data from this study should be able to be used for the development of policy guidelines and preventive strategies in future.

Such policies may address:

- whether spray activities on farms need to be curtailed.
- which spray activities are particularly hazardous for environmental contamination
- whether faulty storage of pesticides on farms is a source of environmental contamination.
- whether existing mechanisms aimed at maintaining environmental integrity are effective, or require reforming.
- which rural populations are most at risk.
- whether safety behaviours amongst rural residents require intervention.

By reporting results to appropriate forums such as the interdepartmental Advisory Committee for the Safeguarding of Man against Poisonous Substancesi INDAC, feedback will aim to maximise impact.

#### b) Address the HEALTH OF RURAL COMMUNITIES

The toxic effects of long-term pesticide pollution in water in the diet may represent a significant and unrecognised source of chronic morbidity and mortality among rural populations, who are already an impoverished community. It is precisely because of the insidious nature and multifactorial aetiology of chronic disease, that chronic disease burden may go unnoticed, barticularly in a social group with little access to power and resources to challenge the conditions under which they live. Data from this study will enable better assessment of the health risks posed to rural communities by pesticides in water.

#### C) ENSURE THAT RURAL ECONOMIC DEVELOPMENT IS CONSONANT WITH LONG-TERM ENVIRONMENTAL SUSTAINABILITY

Rural water contamination by pesticides would have major implications for rural agricultural development in general and particularly for a major expansion in small-scale farming. The control of rural water pollution by pesticides is therefore a prerequisite for the successful implementation of rural development objectives and for the attainment of the goals of the RDP in rural areas. This study therefore has the potential to contribute to development objectives consistent with current rural economic policies.

#### d) PROVIDE INFORMATION THAT CAN BE USED TO SUPPORT INSTITUTIONAL RESTRUCTURING AND GOVERNMENT SERVICES

Considerable restructuring of local government is currently ongoing, with increasing responsibilities being devolved to the lowest levels of government. At the same time, significant restructuring is taking place in many national and provincial government departments, with increasing focus on efficient, user-friendly and community-oriented service delivery. In the health field, for example, the development of district based health services, with considerable devolution of managerial responsibility and authority, is seen as the cornerstone of a shift towards Primary Health Care. Data from such a study will contribute greatly to local capacity to manage public services in ways that benefit rural communities. Given this scenario, it is likely that public health authorities will be in a position to make use of data generated by this research. A close relationship with the relevant district and regional structures in the planning and implementation of this research would ensure the best chances of the application of research findings. In addition, collaboration with other relevant government, private and NGO organisations would offer an excellent opportunity for implementing intersectoral strategies. Depending on the results obtained, it may be possible to identify which government departments (e.g. Labour, or Agriculture or Water Affairs and Forestry) and which civil society stakeholders should be most involved in developing appropriate surveillance strategies to address the problem.

#### e) IDENTIFY RESEARCH NEEDS AND CONTRIBUTE TO SCIENTIFIC KNOWLEDGE FOR OTHER RESEARCH

The generation of new knowledge creates opportunities for multiplying impacts. By characterising the nature and extent of water pollution, estimation of environmental routes of human exposure, so critical for epidemiological studies required to investigate long term impacts of low dose exposure to pesticides become possible. Furthermore, new focus areas for future research emerge from such studies, and can be used to ensure optimal application of research findings obtained in this study.

## 1.6 CAPACITY BUILDING

In addition to the value of the possible research outputs, this study also presented an opportunity for training institutions to utilise the research programme for purposes of capacity development. A research team, composed of staff from the University of Cape Town (UCT) and the Peninsula Technicon (PENTECH) undertook this study in a collaborative arrangement. The team included Associate Professor Leslie London (Project Leader), Mr Agiel Dalvie (project coordinator) and Ms Anouchka Nowicki from the Occupational and Environmental Health Research Unit in the Department of Community Health at UCT and Dr Eugene Cairncross from the Department of Chemical Engineering and Mr Abdullah Solomons and Mr Rashied Isaacs from the Department of Analytical Chemistry at PENTECH.

Through the project, one of the project team (AS) was able to undertake a three week study tour of laboratories at the University of Michigan (Ann Arbor) and the University of Michigan State (Lansing) for training in analytical techniques for organic pesticides. This was made possible by collaborative links established between the University of Cape Town (Department of Community Health) and the University of Michigan (School of Public Health) through a Fogarty Centre award for capacity development in occupational and environmental health in South Africa. The same team member was able to utilise the research towards an M.Tech degree at the Peninsula Technicon. Moreover, the research programme has been used for teaching under-graduate and post-graduate health professionals at both collaborating institutions (UCT and PENTECH) in relevant skills and in exposing them to relevant rural health projects. Students in public health, occupational health, geographical sciences and epidemiology have been involved in various related projects through the main study. For example, students in Public Health at PENTECH undertook the field surveys for the water use and knowledge, attitude and practice questionnaire component of the study. Such multidisciplinary training opportunities are well suited to attempts to reorientate training of a range of health professionals to a primary health care approach and to provide rural exposure for other disciplines. In general, this research project has played an important role in building links between UCT and PENTECH at institutional level that may have long-term benefits for both institutions.

Lastly, opportunities for collaboration with other institutions have also been utilised. Thus, the University of Stellenbosch Zoology Department who are currently undertaking a WRC-funded project investigating endocrine disruption have made use of the project sampling points and access routes.

## 1.7 AIMS AND OBJECTIVES

Based on the preceding discussions, the project therefore aimed to assess the extent of possible rural pesticide pollution of water sources in the Western Cape.

The study objectives were:

- a) To identify rural water sources in the Western Cape at high risk of contamination by means of:
  - review of secondary data
  - field observation
  - interviews with rural health care providers, farmers and environmental officer, technical officers and other agricultural personnel.
- b) To ascertain the presence of, and to quantify chemical pollution at "high-risk" sites, relating the presence of these chemicals to different routes of contamination, and to spraying patterns on farms.
- ci To establish the reliability and validity of methodologies for accurate determination of pesticides in rural water and the practicability of detection levels for determining low levels of pesticides in water.
- d) To characterise more broadly the extent to which farm pesticides contaminate rural water supplies on farms and In rural towns in the Western Cape, taking account of seasonal variations related to spraying patterns and other confounding factors.
- e) To identify additional sources of individual exposure, particularly non-occupational routes such as the re-use of pesticide containers, spray drift into and onto dwellings, and the unsafe domestic use of pesticides.
- f) To describe the water sources available to farm workers, farmers and their families for drinking and ablution.
- g) To estimate total dietary intake of pesticides of rural residents from water pollution, and to compare this to international standards.

# 1.8 AN OVERVIEW OF RESEARCH METHODS AND AN OUTLINE OF THIS REPORT

The project was undertaken in a phased approach.

Phase I was concerned with:

- a) the identification of sites in the rural Western Cape thought to be of concern from the perspective of potential contamination of water sources, and the identification of appropriate sampling points within the study sites
- b) the choice of specific pesticides and metabolites for analysis
- c) soliciting local stakeholder cooperation
- d) establishing reliable and accurate analytical methods for pesticide analyses, including establishment of quality control and quality assurance protocols
- e) formalising protocols for field sample collection
- f) piloting of farm-based questionnaires, and
- g) review of the literature, an activity that continued throughout the project.

Phase II involved the regular sampling of the selected sites, implementation of quality assurance protocols, and ongoing liaison with stakeholder groups. Phase III involved the completion of farm-based user surveys, as well as the analysis and write up of the findings.

This first chapter of the report therefore sets out the background to the study, charting the important policy questions that motivate the study, as well as outlining the aims and objectives. Chapter Two of this report provides a comprehensive literature review addressing the behaviour of pesticides in the environment, methods for the measurement of pesticides in water, a summary of the empirical evidence relating to the contamination of water sources by pesticides, a review of epidemiological studies addressing the health impacts of pesticide contamination of water, and a review of policy and legislation with regard to pesticide in water. The latter section includes specific attention to methods used to set legal limits for water contamination, as well as comparisons of international guidelines and standards.

Chapter Three outlines in detail the study methods, providing an account of the method of site selection, of field sampling, and of analytical techniques used. Strategies applied in pursuit of support quality assurance and quality control are outlined. This chapter also elaborates on the methods used for the farmbased user surveys and the methods used to estimate daily dietary consumptions. The ethical issues, particularly relating to stakeholder involvement are explored.

Chapter Four presents the main results of the study, outlined by study site, and over the period of the study. Interpretation of the results, in relation to exposure data, temporal patterns and other predictive factors is included in this section.

Chapter Five addresses the health and environmental implications of the study, with particular reference to the findings of the farm-based surveys, workers' knowledge, attitudes and practices and the implications of anticipated human exposures to pesticides.

The final chapter (Chapter Six) reflects on the role of surveillance, and on implications for future policy, providing general recommendations as well as recommendations for future research.

# Chapter 2:

# LITERATURE REVIEW

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A literature review was undertaken to address a wide range of key issues:

- a) the behaviour of pesticides in the environment,
- b) methods for monitoring for pesticides in water,
- c) empirical evidence of pesticide contamination of water sources and the relevance of this research to South Africa,
- d) epidemiological studies on the health impacts of pesticide contamination, and
- e) a review of policy and legislation with a comparative analysis of standards, regulations and interventions.

The review was undertaken by tapping a number of sources, including Waterlit, MEDLINE searches and email list server discussion groups. Key informants were consulted for access to literature. The World Wide Web was also used to access relevant information.

# 2.1 BEHAVIOUR OF PESTICIDES IN THE ENVIRONMENT -FACTORS INFLUENCING POLLUTION OF WATER BY PESTICIDES

Factors which determine contamination of water by pesticides' include the pesticides physicochemical properties, pesticide formulation, site of application, soil type, climate and irrigation practices and amounts of pesticides applied (California Environmental Protection Agency, 1996, Beach 1995).

Pollution of surface water usually occurs from runoffs which is the lateral movement of pesticides into nearby water systems such as drains and rivers, but can also occur by volatilisation which is the dispersion of pesticides from plant and soil surface into the atmosphere (McCregor, 1999). Groundwater contamination usually occurs from leaching, which is the downward movement of pesticides into soils, but can also occur from direct streaming which is the movement of pesticides through conduits. The factors which determine runoff and leaching are the physiochemical properties of pesticides and soil characteristics.

The physicochemical properties of pesticides which make them vulnerable to leaching and runoff include,

- a) Water solubility. Pesticides that are highly soluble in water will tend not to remain in soil and will be vulnerable to both leaching and runoffs.
- b) Soil mobility which is determined by the affinity of pesticides to soil and is in turn usually measured by its sorption to soil (Koc) value. Pesticides with a small Koc will be more mobile in soil and more prone to runoff and leaching.
- c) Persistence is the tendency of pesticides to remain in soil and is often measured by its half-life: the time required for 50% of the pesticide to degrade (T<sub>12</sub>). A pesticide with a high persistence will be more prone to leaching into groundwater. For example, Hogmire *et al* (1990) found evidence for endrin contamination of wells in orchards in West Virginia that appeared to be associated with pesticide mixing operations. The fact that registration for endrin had long previously been withdrawn yet the agent still appeared in groundwater, reflects its persistence in the environment. Similar findings of atrazine in groundwater have been reported in Europe, despite discontinued use in the countries where atrazine has been detected (WWF, 1996).

<sup>&</sup>lt;sup>1</sup> For a more detailed description of the different types and classification of pesticides, readers are referred to CODEX (1984), FAO (1986) and the International Programme on Chemical Safety (1998).

Several screening methods have been proposed to quantify leachibility of pesticides including the Groundwater Ubiquity Score, GUS (Gustafson, 1989), which is an index based on the mobility and persistence of pesticides. A GUS score for a particular pesticide is derived by plotting the organic carbon sorption coefficient (mobility) and half-life in soil (persistence). Leachers have GUS scores of above 2.8, transition pesticides have a GUS between 1.8 and 2.8, and improbable leachers have GUS scores < 1.8.

Soil characteristics which determine leaching and runoff events are,

- a) Soil textures. Sandy and porous soil will promote leaching.
- b) Organic matter content of soll. Soils with high organic content will enhance adherence of pesticides to soil.
- c) The depth of the soil horizon. Shallow soil upperlayers will promote water reaching the watertable.
- d) Soil erosion which are determined by soil erosion potential and hydrological factors. Soils with a high degree of soil erosion are more prone to runoffs of pesticides.
- e) Soil pH.
- f) Microbials present in soil (WWF, 1996).

Run-off events (precipitation, rains, etc) important for moving pesticides into water via drains, streams, etc, especially when immediately after application. For atrazine, up to 2% of applied dose may be lost to water in this way, mainly in the first two weeks (Jayachandran *et al*, 1994) but detectable levels may be found up to a year later in experimental situations (German Environmental Protection Agency, 1994).

For atrazine, aged residues desorb more slowly from organic matter than recently applied atrazine, and hence, may continuously leach to groundwater (Montiel and Welte, 1992). Simultaneous application of ammonia (contained in fertilisers) appears to increase the risk of contamination of shallow aquifers (Liu *et al*, 1995). Because of the many factors that influence desorbtion, leaching of atrazine to groundwater may occur at rates of surface application compatible with currently company and regulatory recommendations (WWF, 1996).

Atmospheric deposition via precipitation is also important to consider. During application, pesticides may enter the atmosphere as fine droplets, or bound to fine soil particles during winds. Evaporation may also occur after field application. Once atmospheric, air currents may move particles over long distances. When precipitated, or washed out by rain, this may result in deposition at great distances from their original source, and possibilities of entry to water sources, either directly or through the soil. Thus, background contamination of areas remote from agricultural activities or other primary sources is likely although at low levels (WWF, 1996). For example, low concentrations of atrazine (0.02 to 0.08  $\mu$ g/t) were found in precipitation in Norway in 1992/93 despite the banning of atrazine use in the country 4 years previously, suggesting long-distance transport as the likely reason for contamination in Norwegian rain (Lode *et al*, 1995).

Typically a mix of pesticides are detected in water sources at low levels with seasonal pulses of higher concentrations (EPA, 1999). For example, more than 50% of all stream samples monitored by the US Geological Services programme from 65 sites between 1992 and 1996 had 5 or more pesticides detected (Gilliom et al, 1999). Although grab sampling is commonly used for water monitoring, such methods have severe limitations. Grab samples simply reflect an instantaneous cross-section whereas contamination is often random and intermittent and may be missed by occasional sampling (WHO, 1984). Another constraint is the problem of pesticides or their metabolites absorbed to sediments. By taking unfiltered 'whole-water' samples, monitoring misses the pesticides and residues absorbed in sediments (Rae, 1998). These pesticides may easily be mobilised with heavy rains or changes in the pH and may have substantial health and ecotoxicological impacts.

## 2.2 ANALYTICAL METHODS

For routine screening of water, existing analytical techniques able to detect more than one compound (for example, using multiresidue methods) tend to be expensive, time-consuming, limited to certain pesticide classes and lacking in sensitivity (Holden, 1986, cited in Premazzi and Zigio, 1995). Moreover, much of the regulatory frameworks are dependent on analytical methods capable of detecting low concentrations of pesticides with good sensitivity and precision. However, achieving such analytical standards is often difficult. Indeed, review of pesticide monitoring practices in the European Community (EC) in the early 1990s showed a number of problems in surveillance practices (Table 2.1).

#### Table 2.1: Problems in pesticide monitoring practices in European Community countries, 1991

Equity in practices	<ul> <li>Large disparities in the degree to which monitoring occurs.</li> <li>Differences appears to be due to country size and location, culture, economic status, agricultural practices and main source of drinking water.</li> </ul>
Different emphases on different pesticides	<ul> <li>Different rationales between states.</li> <li>Some pesticides are commonly monitored.</li> <li>Ease of monitoring major determinant for monitoring.</li> </ul>
Disparities in sampling procedures	<ul> <li>Lack of standardisation for cleaning of vessels, measures to avoid cross-contamination, storage time, storage procedures.</li> </ul>
Disparities in analytical procedures	<ul> <li>Lack of standardisation on extraction techniques (liquid/liquid versus solid/liquid) and clean-up methods.</li> <li>Different instrumentation (GC-NPD, GC-ECD, GC-MS AND HPLC).</li> <li>Sometimes historical, reflecting past practices, abilities to raise funds, expertise.</li> </ul>
Disparities in Quality Control	<ul> <li>Variations in external certification and audits.</li> <li>Variations in interlaboratory comparisons.</li> <li>Variations in interlaboratory procedures and good practice.</li> </ul>
Disparities in interpretation of results	Gaps in knowledge.     Omission of key environmental factors.

Adapted from Premazzi and Zigio, 1995.

## 2.3 CONTAMINATION OF WATER BY PESTICIDES

Contamination by pesticides of both ground and surface water have been reported widely Uabbar *et al*, 1993, Johnson, 1994, Bouguerra, 1994, Loaiciga and Robinson, 1995, Vighi and Funari 1995, California Environmental Protection Agency, 1996, Pesticides News, 1997, Domagalski, 1997, Espigares, 1997, Texas Center for Policy Studies, 1999, Gilliom *et al*, 1999; Abassy, 1999, Barlas, 1999). There is extensive data in North America and Europe but data in other parts of the World is lacking. Of the over 293 pesticides that have already been tested in water, 94 have been positively detected. The pesticides that have been detected are usually in high usage or are persistent in the environment. The frequency of detection for some pesticides are high, for instance for atrazine (WWF, 1996), which is the pesticide detected most frequently in both groundwater and surface water. Atrazine has been found in 53% of surface water samples in Texas monitoring programmes (Texas Center for Policy Studies, 1999) and 38% in European groundwater samples (Vighi and Funari, 1995). Other pesticides such as 2.4 D (17%) and silvex (16%) has been
found regularly in surface waters (Texas Center for Policy Studies, 1999) and molinate (20%) alachor (10%) in groundwater. The US Geological Services identified atrazine, simazine, diazinon and prometon at concentrations in excess of 0.01 µg/c in over 60% of streams and groundwater sources sampled in urban areas between 1992 and 1996 and at slightly lower frequencies in rural areas (Cilliom et al, 1999).

The class of pesticides found frequently are organochlorines, organophosphate, trazines and phenoxy derivatives (Vighi and Funari, 1995, California Environmental Protection Agency, 1996, Texas Center for Policy Studies, 1999, Espigares *et al*, 1997, Abassy *et al* 1999; Gilliom *et al*, 1999). In a review of groundwater pollution by pesticides in Europe (Vighi, 1995), herbicides have been identified as the group of pesticides found most in groundwater because of being directed into the ground when applied. Thirty-two herbicides, of which 29 exceeded the European water standard, were identified in this review. Nineteen insecticides including aidicarb and carbofuran has also been detected in groundwater (Vighi and Fuanri, 1995). Nematocides have also been found frequently in groundwater, whereas fungicides have not been detected frequently. Nematocides have been found most frequently in Dutch waters (Pesticide News, 1997).

Many banned or restricted pesticides such as the persistent organochlorines DDT and Dieldrin as well as ethylene dibromide, 1,2 dibromo-3-chloropropane (DBCP) are still detected in water (Beach et al, 1995, Weaver 1993, Vighi and Funari, 1995).

The levels at which pesticides have been detected usually vary between 0-100  $\mu g/l$ , but levels as high as 1000  $\mu g/l$  has been reported (Vighi and Funari, 1995). This include drinking water, mostly in wells and at depths of up to 60m (Vighi and Funari, 1995). There have been many exceedences of the European drinking water standard, as well as other less stringent water standards such as the United States Drinking water standards and those of the World Health Organisation. Twenty nine pesticides have already exceeded the European standard in UK waters (Pesticide News, 1997).

For surface water, pesticide water pollution appears to occur during high rains or during irrigation periods Uphnson et al, 1994, Domagalski, 1997). Most of the surface water contamination was detected in rivers at the outlet of irrigation drainage (Barlas, 1999, Domagalski, 1997).

In the USA, EPA (1999) estimates that up to 95% of streams and about 50% of wells near agricultural and urban areas contain detectable levels of at least one, and often two or more pesticides. Most aquifers and half of the streams investigated by these programmes are direct sources of drinking water. Precisely because groundwater supplies drinking water to over 97% of US rural population (Office of Technology Assessment, 1984) and provides drinking water to 40% of population served by public water supplies in the US (Nielsen and Lee, 1987), groundwater contamination by pesticides is of particular concern in the US. In 1988, the presence of pesticides in groundwater had been confirmed in 37 States and suspected in 8 others (Soll Conservation Service, 1988). Once groundwater is contaminated, the difficulties of managing such contamination are substantial. Besides the ongoing health consequences, water contamination may reduce the value of property as has been reported in North Carolina (Quillin, 1999).

In Germany, atrazine has been found in 33% of wells in Bavaria and 6% of wells in Baden-Wurttemberg at levels in excess of the EC Maximum Allowable Concentration (MAC). Overall 11% (22/206) wells in Germany tested during 1984-86 had detects > EC limit (Premazzi and Zigio, 1995). Subsequent testing by the German Environmental Protection Agency between 1986 and 1990 found that the percentage of detects with atrazine levels above 0.1 µg/c has risen to close to 20% (data cited in WWF, 1996).

In Italy, 94% of samples carried out in 1986/87 found evidence of at least one pesticide contaminant in 318 sites examined, and over 50% exceeded the EEC MAC. Most detects were atrazine (Premazzi and Zigio, 1995). In the UK, triazines are commonly found in groundwater, particularly atrazine, and phenoxyacetic

acids in surface water. Between 1989 and 1990, 2/3 of 170 samples of London drinking water had detects > EC limit, but for the whole of England and Wales the figure was only 2% (Premazzi and Zigio, 1995) suggesting that contamination is very unevenly distributed.

With reference to South Africa, atrazine is presently declining in use, but has previously been detected in irrigation water entering the Vaalharts area as a product of run-off from surrounding maize farming areas (Weaver, 1993). Other triazines (particularly simazine) are in use in the Western Cape but have not been widely monitored.

A study of 29 farm dams in the Eigin area in the Western Cape (Davies, 1997) found that endosulfan isomers and metabolites were commonly detected (in 28 out of 29 dams) at levels above the Target Water Quality Range<sup>2</sup> of < 0.01  $\mu$ g/t and almost half of the dams had levels above the Acute Effect Level<sup>3</sup> of 0.2  $\mu$ g/t (DWAF, 1995). These are levels associated with substantial impacts on aquatic ecosystems. In addition to endosulfan, the study found detects of other pesticides, including chlorpyrifos, azinphos methyl, penconazole and parathion, with less frequency than endosulfan, but still above EEC standards for drinking water.

## 2.4 EPIDEMIOLOGICAL STUDIES ON THE HEALTH IMPACTS OF PESTICIDE CONTAMINATION OF WATER

Acute effects of water contamination may arise through ingestion or skin or mucosal contact. For example, Koo et al (1995) report on an outbreak of dermatitis arising in workers cleaning up a pesticide spill in California in 1991. However, it is well-recognised that acute toxic effects from pesticides in water are unlikely unless there has been some unusual accidental spillage (WHO, 1993). Most concerns related to pesticides have focused on the capacity of lower levels of pesticides in water to cause chronic effects (Bedding et al, 1983).

However, many factors complicate the design of an epidemiological study investigating the chronic health effects of pesticide drinking water contamination. These problems are typical of environmental epidemiology, and principally relate to:

- difficulties in characterising the exposure of subjects to environmental hazards because of a lack of biomarkers, or the presence of multiple interactions,
- difficulties in identifying specific outcomes, particularly where latent phases (for example, for cancer) are long, and where competing causes are multiple,
- levels of increased risk are often small excesses necessitating large studies to achieve sufficient power,
- confounding of study results may be common.

One important type of confounding is occupational exposures, which will correlate highly with exposures in drinking water in an agricultural setting. This could be overcome by identifying non-agricultural areas where water contamination occurs and comparing them to areas where no water pollution occurs. For certain pesticides, pollution of water might be more important than in an occupational setting. Other problems are confounding due to other risks factors and the absence of water monitoring and health outcome data in developing countries.

<sup>&</sup>lt;sup>2</sup> The Target Water Quality Range is that range for which no measurable adverse effects are expected on the integrity of aquatic ecosystems. (DWAF, 1995b).

<sup>&</sup>lt;sup>3</sup> The Acute Effect Level is the concentration above which there is a significant risk of acute toxic effects on sensitive organisms in the aquatic environment (DWAF, 1995b).

Much of the epidemiological evidence for chronic health effects of pesticides arises from studies of occupationally-exposed workforces. These groups are different from subjects exposed to pesticides in drinking water in a number of ways:

- Workplace exposures are generally higher than environmental exposures and may have different characteristics (peaks, etc.)
- Different types of factors influence breakdown and egress more predictable than environmental media
- Because contained environment, monitoring is relatively easier both of air and surfaces, and biological measurements in exposed subjects
- From an epidemiological perspective follow up of groups and allocation of exposure categories may be more accurate. Often in environmental epidemiological studies, exposure characterisation is ecological, i.e. unlinked to the individual.

As a result of these difficulties, considerable debate exists in the epidemiological literature as to the relative contribution of environmental hazards to the causation of chronic disease, particularly cancer.

Given the difficulties of establishing causative relationships between environmental exposures and adverse health outcomes, let us turn to the exact literature.

A number of studies have found health effects including reproductive, cancer and other adverse health outcomes (Swan et al, 1998; Cantor et al, 1998; Hildesheim et al, 1998, Zhang 1997, Vojdani 1997, Lewis 1999) resulting from chemical pollution from non-agricultural sources of drinking water at concentrations in the order of magnitude detected in ground and surface water. For example, the association between chlorine and chlorine products in drinking water and birth defects has long been controversial (Williams and Weiss, 1998). Another study of drinking water from rural China found evidence for an association between the use of pond water and spontaneous abortion, one cause of which may have been run-off from surrounding cotton plantings (Cho et al, 1999). However, this linkage was only hypothetical and relatively few epidemiological studies have implicated pesticides other than arsenic, whose use as an insecticide in agriculture has declined substantially, at least in South Africa.

Only two epidemiological studies investigating the human health effects of pesticide contamination of water could be found in the literature. One study had an ecological design and found no relationship between DBCP contamination in drinking water and birth rates in Fresno County, California (Wong et al, 1988). The other showed altered numbers of T-cells but no alteration in disease status in women who ingested low levels of aldicarb (Thomas, 1991). In both studies it is unclear how occupational exposure was controlled for. Research seems to have concentrated on health effects due to occupational exposures to pesticides.

Despite the absence of relevant epidemiological studies, contamination of water by pesticides is potentially an important health problem. There have been reports of acute ill-health due to improper disposal of pesticides in water (editorial Lancet, 1992, Amstrong 1984). A growing number of chronic health conditions including cancer, neurological diseases, respiratory diseases are increasingly being associated with long-term occupational exposure to pesticides (Maroni, 1993, Gray and Ostby, 1998, Porter 1999, Dalvie *et al* 1999). Interactive mixtures of aldicarb, atrazine and nitrates have been shown to have chronic effects on the immune, endocrine and nervous system of laboratory animals at maximum contaminant levels (MCLs) (Porter, 1999). Additionally contamination of water by pesticides have been found in fish (Jeffery, 1992) and has been shown to alter reproductive abilities in amphibians (Ouellet *et al* 1998).

An additional concern has been that the focus of epidemiological research may be placed on the incorrect agents in that breakdown products of pesticides may be more acutely toxic or of greater concern from the perspective of chronic health effects. For example, dealkylation of triazines produce metabolites Desethyl-atrazine (DEA) and Desisopropyl-atrazine (DIA) which are reported to have endocrine disrupting properties (WWF, 1996).

## 2.5 LEGISLATION AND THE CONTROL OF PESTICIDES IN WATER

#### 2.5.1 HISTORICAL OVERVIEW

The traditional approach to water quality has been historically dominated by a public health focus on microbiological contamination (Packham, 1990). For example, the World Health Organisation views the control of microbial contamination as paramount, and acknowledges that chemical standards could be considered of secondary importance (WHO, 1993a).

This policy bias has been reflected in the type of legislation covering water quality concentrating on control of bacteriological, parasitic and virological threats, it was only when evidence emerged that potentially hazardous organics could be generated from water treatment processes that regulatory emphasis shifted to include standards for organics such as pesticides (Toft, 1985). The first US legislation to address specific contamination by organics was the 1974 Safe Water Drinking Act (SWDA) which enabled a set of regulations to set Maximum Contaminant levels that assured "no known or anticipated adverse effects of the health of persons...". By 1979, US regulators, pesticide companies and researchers began to focus increasingly on pesticides in groundwater as a result of frequent detections of DBCP and aldicarb in groundwater in the Eastern US (Cohen, 1996). The SWDA has subsequently been amended in 1986 and 1996 so as to ensure that "the food they (the US population) eat and the water they drink are safe" (Bill Clinton, cited in USEPA, 1999). Similarly, Canada promulgated its first legislation specifically addressing pesticides in water as Federal regulations in 1978, which included health-based limits for 16 pesticides in water (Toft, 1985). Since then, there has been much development of legislative standards with the recognition of important long-term hazards associated with organic pesticides and other chemicals in water sources, particularly those used for drinking.

European legislation has also seen a proliferation of legally binding standards over the past decade, with a move from away from legal flexibility to one that seeks to put explicit measure to public judgements about the acceptability of the impacts of human activities on the environment. Between 1970 and 1991, over 30 directives and other regulations to address water quality were passed by the EEC (Premazzi and Zigio, 1995). In the United Kingdom, for many years the legal standard for drinking water was simply expressed as "wholesome water" for which the law offered no precise definition. Today, however, standards for drinking water are subject to an array of standards, requiring the support of a complex institutional machinery for development, implementation and monitoring (Macrory, 1999). Much of this has been driven by the adoption of the European Economic Community (EEC) Directive on the quality of water intended for human consumption (80/778/EEC) (Premazzi and Zigio, 1995).

The rationales for these shifts and differences in approaches is outlined below. Given the high costs of analyses for the presence of organic contaminants in water, it is critical for regulators to ensure sound science in the judgement of how to implement water quality monitoring.

#### 2.5.2 BASIS FOR STANDARD SETTING

The underlying premise for the setting of standards for water is to safeguard human health particularly with regard to drinking water (Toft, 1985; WHO, 1993a) although more recent developments recognise the importance of maintaining ecological integrity and mitigating or avoiding impacts on aquatic ecosystems (Premazzi and Zigio, 1995). Standards to attain these two objectives may differ significantly, with requirements for ecotoxicological safety higher than for human health, and management interventions required may also differ (Bedding *et al.*, 1983). For example, the WHO guideline value for atrazine based on human health considerations is 2  $\mu g/l$  (WHO, 1993a) while thresholds for aquatic toxicity are of the order of 0.008 to 0.23 (cited in Dallas and Day, 1993). Safeguarding health can include both primary standards which seek to avoid risk of disease or death, and secondary standards of aesthetic satisfaction<sup>4</sup> (Toft, 1985). Water that is of an aesthetically unacceptable quality may lead to rejection of an otherwise safe water supply for one that is less safe (Packham, 1990; WHO, 1993a).

Approaches to standard setting with regard to pesticides in water have differed across the world. Approaches based on modelling health risk using experimental data (such as adopted by the USEPA and the WHO) differ substantially from approaches adopted by the European Union, whose standards have been set rather as policy tools. These approaches are outlined in more detail below.

#### 2.5.2.1 US EPA approach

Not unlike many other countries<sup>5</sup>, there are a number of different laws in the US<sup>6</sup> that address the control of pesticide contamination of the environment. However, despite the potential for legal duplication and overlap (Rother and London, 1998), institutional responsibility in the USA for monitoring, enforcement and remediation is at least co-ordinated through the US Environmental Protection Agency and its policies.

The principal legislation governing water quality is the Safe Drinking Water Act (SDWA) which places the responsibility for protection of national water resources on the United States Environmental Protection Agency (EPA). In meeting this obligation, the EPA has chosen to focus on prioritising the protection of water sources currently used to supply drinking water, those with potential to supply drinking water in future, and those water sources that represent particularly vulnerable ecosystems. Standards for water quality form part of a comprehensive set of measures for water protection, including adequate treatment of water sources, ensuring the integrity of distribution systems and providing information to the public (EPA, 1999).

EPA's general approach has been to develop standards that are health-based with some account taken of technical feasibility, availability of methods of detection, and the impacts of regulation on water systems, the economy and public health (EPA, 1999). Where no reliable method exists that is economically and technically feasible to measure a contaminant at particularly low concentrations, a Treatment Technique (TT) is set rather than an MCL. A TT is an enforceable

In the USA, these primary health based standards fall in the category of National Primary Drinking Water Regulations (NPDWR) and the secondary cosmetic or aesthetic standards fall in the category of National Secondary Drinking Water Regulations (NSDWR). Compliance with secondary standards is optional for State Regulators.

<sup>&</sup>lt;sup>5</sup> For example, South Africa had at last count 14 pieces of legislation administered by 7 different government departments pertaining to pesticides in 1998 (Rother and London, 1998). Legislation governing water resource management included 5 Acts and 2 Bills involving at least four government departments (DEAT, 1998c).

<sup>&</sup>lt;sup>6</sup> These include the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), the Safe Water Drinking Act (SDWA), the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or "Superfund").

procedure or level of technological performance which public water suppliers must follow to avoid contamination (EPA, 1999). Although there is some attempt to develop standards that encompass environmental impacts using ecologically based protection criteria (Premazzi and Zigio, 1995), EPA standards presently remain essentially focused on human health. However, a number of workgroups were established by EPA in 1998 to improve methods used to evaluate potential threats to ecosystems (BNA, 1998).

It should be noted, however, that the EPA is also subject to the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) which allows for the tolerance of a non-negligible risk if important socioeconomic concerns warrant deviations from strict adherence to health based limits. EPA thus has to try to balance potentially conflicting legal imperatives in this regard.

For purposes of dietary risk assessment mandated by the Food Quality Protection Act (FOPA), EPA has sought to take into account sources of pesticides in drinking water to inform its regulatory decisions. Prior to 1996, EPA assumed that 10% of dietary intake of residues was acquired through consumption of water. However, after the passing of the Food FOPA in August 1996, the Office of Pesticide Programmes (OPP) has adopted a more complex risk assessment approach that makes use of pesticide-specific data on movement to groundwater, degradation potential, persistence and toxicity breakdown products in mathematical modelling to estimate pesticide concentrations in water in pesticide use areas (EPA, 1999). This screening data is then compared to health-based "Drinking Water Levels of Comparison" (DWLOC) which take account of food-based and residential exposures for which data exist. A DWLOC will be low if competing exposures are substantial, but if there are few competing exposures, the DWLOC will be higher. If the screening data exceed the DWLOC, the OPP will seek empirical data to clarify the finding, and may then implement monitoring or mitigation actions (EPA, 1999).

Key to this approach is the use of screening models, a number of which have been shown to be useful for risk assessment (Cohen, 1996). In general, these models tend to give conservative estimates and that can be used to rapidly identify pesticides unlikely to be a water problem (EPA, 1999). However, the models need verification against empirical data.

Mitigation actions (including revocations or denials of a tolerance) are generally based on more than just a screening estimate. Monitoring data are applied to known human health risk models that address both acute and chronic effects (cancer) using levels in the high range of the reported monitoring results (not the highest), in conjunction with estimates of food and residential exposure to complete an aggregate risk assessment, and characterise human health risk. In theory such data can also be used to produce a regional-based picture of the distribution of measurements. In future, the OPP has been reported as wanting to move towards probabilistic drinking water exposure assessments (EPA, 1999). However, such developments will demand much more accurate scientific data than currently available, since most existing monitoring data provide little more than a piece of a complex puzzle. Residues or metabolites in water are static indices of dynamic processes (Kerr and Vas, 1973 cited in Dallas and Day, 1993).

A useful observation to be made about the US framework is its model of governance for the control of pesticide pollution of water sources. Under the US federal system, the EPA takes national responsibility for uniform action for particular pesticides of high concern, while leaving substantial responsibilities to States at regional and local level for ensuring adequate regulations and monitoring to protect water quality. EPA sees its role as critical in providing support for States and for users, that hold responsibilities to change practices through education and training, and adoption of alternatives (Premazzl and Ziglo, 1995). Given South Africa's complex system of often-competing national and provincial competencies, such frameworks might be useful for addressing the institutional governance needed in South Africa to manage water quality standards.

#### 2.5.2.2 EEC approach

Underlying European standard setting for pesticides is an environmental management policy stemming from the 1972 Stockholm Conference on the Environment and subsequent action programmes (Premazzi and Zigio, 1995). Key elements to this approach include recognition of the primacy of prevention, adoption of the "polluter pays" principle, the optimal use of scientific information to inform standard-setting, and application of the precautionary principle where data are insufficient, and the recognition of the transboundary nature of many pollution problems (Commission of the European Communities, 1996).

Although the EC directives seek to harmonise standards across EC member states, there is still some discretion left to individual countries to treat EC standards as a minimum, or to justify differing standards on the basis of differing social and cultural contexts (Commission of the European Communities, 1996; Macrory, 1999). For example, Dutch standards effectively set at 0  $\mu$ g/r the MACs for 12 pesticides, and indications are that this list will be extended in future. The 1991 directive places groundwater management in the context of an integrated approach to address both surface and groundwater. The Fifth Environmental Action Programme of the EEC (1993 to 2000) highlights a move away from "command and control" approaches to using a range of policy instruments, including co-regulation and self-regulation (Premazzi and Zigio, 1995).

In terms of water quality, three groups of EEC directives apply, the first geared towards protection of public health, the second to eliminate pollution by nitrates from agricultural activities, and the third to control discharges to groundwater and surface waters. The directives list various schedules of hazardous chemicals with different levels of responsibility on governments to prevent egress to groundwater. EEC directives establish both Maximum Admissible Concentrations (MACs) and Guide Levels (GLs). MACs were originally calculated assuming a 85% compliance rather than 100%. For pesticides, the MAC is set at 0.1µg/( for any pesticide and 0.5 µg/l for all pesticides. Unlike other contaminant MACs, the MAC for pesticides not based on toxicological data, but was set at the limit for the detection of chlorinated pesticides, presumably as a surrogate for a zero standard (Premazzi and Zigio, 1995). Indeed, as indicated above, Dutch standards explicitly list a zero standard for 12 pesticides. By placing such low limits on acceptable limits, the Dutch authorities are essentially signalling that their limits are to be led by analytical capabilities. In doing so, they are merely extending current EEC approaches where maximum acceptable levels have been set at the current detection capabilities of existing technologies. EEC policy is to pursue high levels of water protection, for reasons of human health as well as protection of natural ecosystems (Commission of the European Communities, 1996). Not surprisingly, the pesticide industry has been amongst the most vociferous critics of this approach (GIFAP, 1990).

One of the criticisms of the approach that relies on rigorous standards expressed in quantifiable form is that there is inherent to science a degree of uncertainty the complexity of which is lost in the regulatory urge for clarity (Macrory, 1999). For example, the difficulties of establishing causation for chronic health outcomes from low dose exposure, and of characterising the doseresponse relationship are substantial, particularly when dealing with extremely low exposure levels typical of environmental exposures.

However, the EEC makes use of other regulatory mechanisms to protect groundwater. For example, EEC directives link pesticide registration to requirements to demonstrate environmental safety with respect to water sources. Pesticides should not be registered if they have 'unacceptable' impacts on drinking water, or if no methods for analysis exist which can meet the levels of detection demanded by EEC standards (Premazzi and Zigio, 1995). Thus, for example, the Netherlands has cancelled registration of any pesticide found to leach at concentrations exceeding 0.1 µg/l after a transport time of four years at a depth of 10m below the ground (Organisation for Economic Co-operation and Development, 1996). EEC directs countries to consider both health and environmental consequences under anticipated conditions of use and taking into account scientific uncertainty, and consideration of all routes of exposure (Premazzi and Zigio, 1995).

#### 2.5.2.3 The approach of the WHO

In pursuit of its public health agenda, the World Health Organisation has focused on the quality of drinking water and provides guidelines for action by member states. The guidelines are not intended to be mandatory limits. WHO recognise that national regulatory standards should take into account local and national environmental, social, economic and cultural considerations using a risk benefit approach (WHO, 1993a). For example, in situations of relative water scarcity, adoption of drinking water standards of overly rigorous stringency may compromise water availability for communities with marginal access to water, with adverse health consequences. WHO emphasises that the trade-off in risk-benefit needs to aim for maximal protection of human health, and should be based on informed societal decision-making.

As with the EPA, the WHO has adopted a health based toxicological approach to guideline setting, and guideline values represent concentrations that are regarded as not resulting in any significant risk to the health of a consumer over a lifetime. WHO cautions against treating the guideline values as sufficient for minimalist regulation by countries and encourages standard-setting to aim for the highest water quality (WHO, 1993a). The WHO Guidelines also recommend flexibility in application to take account of the purpose of the water use. In practice, many countries adopt the WHO approach if not their Guideline Values in their regulatory frameworks.

Two difficulties exist in relation to health hazards at low concentrations of contaminants. Methods to measure particular pesticides might not be available at the very low concentrations in the range where long-term health impacts might be expected. Furthermore, methods to remediate or control exposures at these levels may not be practical or available. WHO takes these problems into account by setting provisional guideline values.

While the WHO Guidelines apply to bottled water, and to ice intended for human consumption, natural mineral waters are covered by standards developed by the Codex Alimentarius Commission.

#### 2.5.2.4 New Directions

Recent empirical evidence suggest that the use of animal populations as sentinel populations would be useful in risk assessment to inform regulatory standards (van der Schalie *et al*, 1999). Indeed, Casey and Meyer (1996) cite evidence that in Canada drinking water standards for humans are partly based on possible bioaccumulation of pesticides in livestock with secondary impacts on human consumers. Proposed South African standards for pesticides for livestock watering (Casey and Meyer, 1996) are of the same order as levels summarised for human drinking water standards in Appendix A. Future research will focus on developing bioassays and sampling procedures for histopathological examination of animal tissues to assess risk from pesticides in groundwater (personal communication, Mr K Pietersen, Water Research Commission, November 1999).

#### 2.5.3 STANDARDS

Published standards for maximum levels of pesticides permitted in water are summarised in Appendix A.

#### 2.5.3.1 EPA Standards

EPA's general approach has been to develop standards that are health-based (generating Maximum Contaminant Level Goals, MCLGs) but which take into account, to some extent, the practical and scientific feasibility of achieving the health based standards (generating Maximum Contaminant Levels, MCLS). The process of developing health based standards differs for carcinogens and non-carcinogens. Because carcinogens are thought to have no threshold of risk, the MCLG is set at 0, while for non-carcinogens, the goal is based on a percentage of an Acceptable Daily Intake (ADI) derivable through water intake (see below). The MCLs are, in general, set as close as possible to the MCLGs.

However, for carcinogens, the goal of zero exposure is not practicable, both in terms of eradicating all exposures, and in terms of having the technical capacities to measure exposures at extremely low levels. Thus, for carcinogenic effects, EPA relies on the notion of negligible risk, based on a probability of anything less than 1 in 10<sup>6</sup> excess risk in a lifetime being negligible. This means that for carcinogenic effects, a probabilistic model is used. Because this model makes assumptions (usually assumptions involving linearity) about risk at low levels, for which empirical data are not available, there have been many criticisms of this approach, both from the point of view of overestimating and underestimating risk.

Where there are deviations from MCLGs in setting MCLs, the concerns are usually for whether the health-based limits are at all achievable. Unlike Health Advisories (see below) MCLs are legally enforceable standards. MCLs are said to take account of vulnerable sub-populations. However, to estimate MCLs for non-carcinogenic pesticides in drinking water, EPA does not take account of total dietary intake of pesticides through all media.

Health Advisories (HAs) are prepared by the Criteria and Standards Division of the Office of Drinking Water (ODW) of the EPA to provide technical guidance to public health officials on health effects, analytical methodologies and treatment technologies associated with drinking water contamination (Anonymous, 1988). They are primarily aimed at addressing public need for guidance in response to emergency situations involving contamination of drinking water. The HAs summarise data on the occurrence, pharmacokinetics and health effects to estimate concentrations of a contaminant in drinking water that are thought to have no adverse health effects. Unlike MCLs, HAs are not enforceable and are only used to provide guidance.

Because no threshold is understood to exist for cancer, HAs only apply to non-carcinogenic effects. HA's are calculated for varying durations, including 1-day, 10-day, long-term (approximately 10% of a lifetime or 7 years) and lifetime HAs.

HAs make use of No Observed Adverse Effect Levels (NOAELs) and Lowest Observed Adverse Effect Levels (LOAELs) from studies specific to the duration of exposure for that HA. Generally, studies with the highest NOAELs or LOAELs are used, and the degree of confidence of the study and the degree to which its findings are supported by other dose-response data also influence the final choice of parameter. The calculations used to derive a HA from a NOAEL or LOAEL take into account body mass, assumed daily water consumption and make use of an Uncertainty Factor which is 10 where data is most reliable and 1000 where data is least reliable. Short-term HAs are calculated for a 10 kg child, while lifetime HA is calculated for a 70kg adult. Lifetime HAs also take into account other sources of exposure other than water (which is modelled as being the source of 10 or 20% of exposure, depending on whether it is an organic or inorganic contaminant).

For chemicals that are classified as possible human carcinogens, an additional 10-fold uncertainty factor is added. For chemicals classified as probable or definite human carcinogens, an entirely different approach is used involving multistage mathematical modelling, which determines theoretical upper-bound cancer lifetime risks based on existing epidemiological and toxicological data. (EPA, 1999). This latter approach has been criticised for assuming uniform susceptibility amongst the population and the absence of interactions between chemicals and other susceptibility factors, when much empirical data exists to the contrary (Perera and Boffetta, 1988).

However, although the short-term HAs use child parameters for mass in the calculations, they do not use child or immature (in animal studies) subject toxicological data for the estimation of the HA. Given that the toxicity per kg is recognised to be greater in children, the uncertainty factor may not be sufficient to compensate.

#### 2.5.3.2 EEC Standards

As indicated above, the EEC standards  $10.1 \,\mu g/t$  for any one pesticide and  $0.5 \,\mu g/t$  for all pesticides are not based on toxicological information but on technical feasibility and policy considerations, intended as a proxy for a zero standard. As a result, it is clear that the EEC standards will result in some cases, in levels of control in excess of what would be needed for the protection of human health, while in other cases, EEC standards may still be compatible with contaminant levels of concern from a public health perspective. One of the other problems with the EEC standard is that, notwithstanding  $0.1 \,\mu g/t$  being at around the Quantification Limit for organochlorine pesticides, many other pesticides (for example, DNOC, oxamyl, tebuthion, etc) are not detectable at these levels. Thus real presences of pesticides at very low levels may be recorded as nondetects and thus underestimate exposure scenarios.

Premazzi and Zigio (1995) report that the UK has indicated that it intends to push for groundwater limits based on toxicological data because of the limitations of analytical methods to achieve levels of detection low enough to support the EC standards, and because of a preference for methods that take account of toxicity. However, it appears that the EEC standards are likely to remain in force, primarily as a policy tool to drive down pesticide use.

In general, European countries tend to follow the EEC standards, although France has been reported to include toxicological-based standards for some pesticides, while the US, Canada and Australia use approaches to standard setting that use toxicological data (Premazzi and Zigio, 1995).

#### 2.5.3.3 WHO Guidelines

As indicated above, the World Health Organisation essentially uses the framework of health-based toxicological assessments to inform its standards for pesticides similar to the EPA approach. Its 1993 standards (WHO, 1993a) identify 7 categories of water pollutants for which risk assessments are developed, of which one category is pesticides. Data for these assessments are derived from data provided by the International Programme on Chemical Safety (IPCS), the International Agency for Research on Cancer (IARC), the Joint FAO/WHO meetings on Pesticide Residues (JMPR) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA). In estimating risk, WHO generally assumes an average daily consumption of 2 I water for a 60kg adult.

Central to the risk estimate is the calculation of an Acceptable Daily Intake (ADI) or, in the case of xenobiotics, a Tolerable Daily Intake (TDI). TDIs, expressed as a mass unit of contaminant per mass unit of organism, are usually reliant on animal studies to provide No-Observed-Adverse-Effect-Levels (NOAELS) or Lowest-Observed-Adverse-Effect-Levels (LOAELS). The NOAELs/LOAELs are adjusted by a series of uncertainty factors that take account of inter-species variation for extrapolation from animals to humans, inter-individual variability, adequacy of the studies, and the nature and severity of the effect. Use of a LOAEL (in the absence of a NOAEL) also necessitates an additional uncertainty factor. The total weighting from the sources of uncertainty is not allowed to exceed a factor of 10 000. The TDI, thus adjusted, is then modelled on daily drinking water consumption, average body weight, and the fraction of the TDI allocated to intake through dietary water (WHO's default assumption in the absence of empirical data is 10%) to generate a Guideline Value (GV) see box). Where the uncertainty factors used in calculating a TDI are greater than a 1000, WHO cites these Guideline Values as provisional to emphasise the high level of scientific uncertainty.

For carcinogens, WHO distinguishes between compounds thought to be genotoxic, for which no threshold exists and mathematical low-dose extrapolations are applied, and carcinogens acting through other mechanisms for which thresholds and believed to exist. For the latter group, the CV is derived using the TDI approach outlined above. For the former group, an excess lifetime risk of 1 in 10<sup>5</sup> is used as representing significant increased risk. Generally, a linear multistage model is used.

The WHO guidelines have been criticised on a number of grounds:

- Because they are averages for adults, they may not take into account the higher consumption of water per kg for children, for people in hot climates.
- b) Sub-groups of the population (women, children, undernourished, etc) may have higher risks due to biological and behavioural factors that increase vulnerability.
- c) Interactions between multiple chemicals may result in risk profiles that are more than simply additive, as assumed by the WHO approach.
- d) The linear assumption for risk associated with low-level extrapolation may not be valid.

WHO argues that the addition of safety factors with wide margins addresses these concerns (WHO, 1993a). Furthermore, for some agents indicated by social and public health significance, WHO has reportedly based its estimates on children or infants consuming proportionately more water per kg body weight than adults. The derivation of GVs for some carcinogens is said to take account of empirical evidence where alternative extrapolations appear suited for specific pesticides.



However, of the 33 pesticides for which WHO has established GVs (see Appendix A), only one (DDT) makes use of an estimation including the intake of an infant, and none of the 4 pesticides for which estimates were based on carcinogenicity used non-linear extrapolations to estimate excess risk. For most pesticides for which GVs exist, the default assumption of 10% of dietary intake through water has been used except in 6 cases where the assumption was 1%. These include 5 organochlorine pesticides assumed to have greater presence in diet due to persistence and permethrin, thought to have greater environmental routes of exposure (WHO, 1993b).

WHO standards are supposedly based on toxicological criteria and intended to represent 'safe' levels for human consumption as an average daily intake over a lifetime. But criticisms levelled against the standards stress that they only address a small proportion of the 1000s of active ingredients, do not address problem of mixtures; and do not take ecotoxicity into account (Anonymous, 1996).

#### 2.5.3.4 Standards in other countries

In practice, the WHO guidelines are the main source of standards used by many countries (Packham, 1990; Macrory, 1999). Australia, for example, uses a similar approach in setting standards for pesticides, that include Health Values based on 10% of an ADI to be derived from drinking water, whilst also including Guideline Values, which are based on the analytical limit of determination, in order to prompt investigations and remedial actions (National Health and Medical Research Council, and Agriculture and Resource Management Council of Australia and New Zealand, 1996). The USSR established explicit standards for organic substances in drinking water in 1973 that included toxicological standards for only two pesticides, DDT (limit of 100  $\mu$ g/t) and heptochlor (limit of 50  $\mu$ g/t) but organoleptic standards for at least 19 others. These regulations were regarded at the time as modern and explicit (Bedding *et al*, 1983) but were not necessarily supported by any enforcement or monitoring, as was typical of much of Soviet standard-setting.

In the rest of Africa, legislation is extremely underdeveloped, and what little regulations exist focus mainly on the registration process and on occupational standards, with little reference to environmental impacts (Akhabuhaya, 1991; Mbiapo and Youovop, 1993; Lekei and Mndeme, 1999).

#### 2.5.4 HUMAN STANDARDS IN RELATION TO ENVIRONMENTAL STANDARDS

Dallas and Day (1993) summarise water quality criteria related to biocides for the protection of aquatic life from different countries. When compared to human health standards, it is clear that levels needed for ecolotoxicological integrity are far stricter. It is perhaps not surprising that much early environmental standard setting to protect water quality sought to promote human health and welfare above ecotoxicological integrity (Bedding *et al*, 1983).

Aquatic life criteria established by the EPA, Canada or International Joint Commission for the Great Lakes were exceeded by at least one compound for two-thirds of streams sampled for routine monitoring by the US Geological Services between 1992 and 1996 (Gilliom *et al*, 1999). Diazinon, chlorpyrifos and malathion were the agents most frequently found to exceed aquatic limits.

SUBSTANCE	SOUTH AFRICA	UNITED KINCDOM	US EPA	AUSTRALIA	CANADA
Aldrin	0.01	0.01		0.01	0.004
Chlordane	0.025			0.004	6.0
DDT	0.0015	0.025		0.0005	0.001
Dieldrin	0.005	0.01		0.002	
Chlorpyrifos				0.001	
Endosulfan	0.003			0.001	
Endrin	0.002		0.05	0.003	0.0023
Azinphos-methyl				0.01	
Heptochlor	0.005			0.0003	
Lindane	0.015			0.003	
Malathion	0.1			0.07	
Methoxychlor	0.02			0.04	
Mirex	0.001			0.001	
Parathion	0.008			0.004	
Toxaphene				0.002	
2,4 Dichlorophenol	4.0				4.0

### Table 2.2: Water standards to protect aquatic ecosystems ( $\mu g/t$ )

From: Dallas and Day, 1993.

#### 2.5.5 SOUTH AFRICAN EXPERIENCE

The history of environmental legislation in South Africa has been one of weak and fragmented regulatory systems, lacking in monitoring and enforcement capacity that have inspired little confidence in the ability of government to control major environmental hazards (White, 1991; Lazarus *et al*, 1997; Asmal, 1998). Under the previous government, legal standards for drinking water were underdeveloped. Indeed, some critics argued that guidelines had actually been relaxed in the course of the last decade (Coetzee and Cooper, 1991). To some extent, sanctions imposed on South Africa under its apartheid government ensured that South Africa was relatively isolated from international developments in environmental management that applied to markets in other countries (Morris, 1996).

However, since the 1994 elections, considerable changes in the legislative and policy framework have taken place, with far greater emphasis placed on modern approaches to environmental management that recognise firmly the importance of environmental sustainability as a pre-requisite for economic development. Indeed, the post 1994 period has seen stricter implementation of existing regulations by the Department of Water Affairs and Forestry (Morris, 1996). Principal amongst these developments, has been the adoption of far-reaching clauses under the Bill of Rights under the Constitution. The current South African constitution guarantees all South Africans the rights to "an environment that is not harmful to their health or well-being" and to have the environment protected through legislative and other measures "that prevent pollution and ecological degradation ..." (Chapter 2, Clause 24 of the South African Constitution). The presence of this clause will ensure that future legislation will be held to this standard, and will also influence judicial decision-making by requiring greater weight to environmental considerations in legal matters (Lazarus *et al*, 1997).

In terms of water pollution control, South African legislation has undergone substantial revision over the past 5 years. Following a consultative process involving the publication of a White paper on a National Water Policy for South Africa (Department of Water Affairs and Forestry, 1997), and a Draft White Paper on Integrated Pollution and Waste Management for South Africa (Department of Environmental Affairs and Tourism, 1998b) parliament enacted the National Water Act in 1998 (Department of Water Affairs and Forestry, 1998). Principal in the changes contained in the Act is the move toward management of water resources on a catchment basis, based on "demand" rather than supply, and emphasising greater conservation of water resources, through measures such as an appropriate pricing system. The Act also emphasises public participation and provides for greater community involvement in water management structures.

The Act also adopts the concept of "fitness for use" in relation to water quality. Thus, different users requiring different qualities of water will be accommodated in the legislative framework, which will move away from sole reliance on uniform effluent emission standards, to an approach based on receiving water quality objectives, a shift in approach which has been ongoing since 1991 (Lazarus *et al*, 1997). Uniform emission standards, which were in practice often subject to widespread exemptions, were unable to prevent the deterioration in South Africa's water quality, and the application of an approach based on receiving water objectives aims to ensure that downstream users receive adequate quality water.

The current approach framed by the Act also contrasts with the traditional reliance on management of pesticides pollution on a voluntarist basis, relying on SABS codes to guide decision-makers without standards. Despite this, the most recent DWAF water Quality Guidelines (1996) refer only in a very limited manner to pesticides, and set specific standards only for aquatic ecosystems and for aquaculture use but not for human consumption?.

Another key piece of environmental legislation to undergo revision in recent years has been the Environmental Conservation Act, now replaced by the National Environmental Management Act, NEMA (Department of Environmental Affairs and Tourism, 1998d). The NEMA is a framework act that places on record a set of principles and approaches for all aspects of environmental management, and to which all other government legislation and practice, at all levels of government, must conform. It seeks to translate constitutional provisions to the right to a safe environment into policies, practices and laws of all key players. The Department of Environmental Affairs and Tourism (DEAT) also has responsibility as lead agent for managing a number of key international conventions, such as the Convention on Prior Informed Consent (PIC), and the United Nations Environment Programme (UNEP) Convention on Persistent Organic Pollutants (POPs) (UNEP, 1999). Moreover, DEAT has indicated its intention to pursue a national audit of management of chemicals within the framework of a United Nations sponsored National Chemicals Profile format (personal communication, Mr Mashaba, DEAT, November 1999). Such an audit would address all aspects of chemical management and policy at a national level.

The main piece of legislation specifically regulating pesticide usage and registration in South Africa, Act 36/47 (Department of Agriculture, 1947) does not address environmental consequences of pesticide usage. While the Act provides for the establishment of a Registrar's Office to deal with registration of pesticides and regulates their toxicity classification, requirements for labeling, advertising, disposal, sale, importation and use of pesticides, it does not specifically address issues of pollution of water. Users may be guilty of an offence if they apply a pesticide contrary to the label and thus, in theory, control might be exercised over inappropriate use. However, lack of enforcement characterises much of South Africa's pesticide regulation (Rother and London, 1998). The act is currently under revision, and appropriate changes could substantially improve on the Act's capacity to obviate adverse environmental impacts on water sources, through for example, including as a registration requirement, data on anticipated environmental impacts on water, under usual use conditions in South Africa.

## 2.6 INTERVENTION MEASURES

In countries where large numbers of people are dependent on surface and groundwater sources that are potentially contaminated (for example, the USA), interventions to restore water quality are critical. Many rural communities in South Africa depend on both surface and ground water and the potential hazard to their health may need similar interventions.

However, approaches to the management of polluted water are complex. The bulk of water treatment methods focus on removing turbidity and bacteriological contamination and are not set up to address organic pesticide contamination (Toft, 1985). Even though they will remove up to 80% of natural organic matter in water, inorganic coagulants have little effect on synthetic organics dissolved in water. Other methods of removal (activated carbon filters, aeration facilities) have been used to remove volatile organics from contaminated groundwater providing communal water supplies (Toft, 1985) but these are resource-intensive. Given the high costs associated with remediation (United States General Accounting Office, 1999), it is prudent to remember that regulation should be shown to have a beneficial impact on improved health status (Premazzi and Zigio, 1995). Moreover, prevention of contamination is always a better option.

<sup>&</sup>lt;sup>7</sup> The herbicide atrazine is the only pesticide for which guideline levels for drinking water are described in the DWAF Water Quality Guidelines.

Under the US EPA framework, interventions aimed at remediating contaminated groundwater will be triggered by the number of sampling sites with detections and the frequency of detections made (Premazzi and Zigio, 1995). Management measures proposed by EPA are listed in Table 2.3.

### Table 2.3: Pesticide Management Measures proposed by EPA

- Moratorium areas
- Wellhead protection areas
- Buffer zones: location, depth and construction only for new wells
- Change in practice of applications (time, rate and method)
- Restrict area or form of application, or no application permitted at all
- Advance notice of application
- Best management practices
- Integrated pest management
- Training and certification

From "Agricultural Chemicals in Groundwater - Proposed Pesticide Strategy" US EPA. Office of Pesticides and Toxic Substances, 1987, cited in Premazzi and Zigio, 1995, and adapted from Premazzi and Zigio, 1995.

To protect groundwater geographic restrictions on pesticide use, and buffer zones near water bodies where pesticide use is prohibited may be useful to protect surface water IEPA, 1999). Restrictions have played an important role in responses to evidence of groundwater contamination throughout OECD countries (Organisation for Economic Co-operation and Development, 1996). In the case of atrazine, the first action was withdrawal of registration in Finland and its cancellation in Sweden in 1989. Over the next decade, findings of the persistent presence of triazines, particularly atrazine, in groundwater, led to various restrictions of its use in 13 countries. These restrictions ranged from regulations reducing use rates or settings conditions for application, through to outright bans (WWF, 1986). Such restrictions have sought to reverse the trend of contamination by atrazine found in many studies.

Other measures such as buffering have played an important role. For example, more than 2200 km of border strips are legislated in Germany to separate waterways from crop lands (Organisation for Economic Co-operation and Development, 1996). Preventive measures such as tightening of restrictions on filling and cleaning of spray equipment have also been successfully pursued.

One of the many options at a policy level for addressing pesticide pollution is to levy a tax that aims to reduce usage and therefore the potential for exposure. Huang and Uri (1989) have modeled the level at which such a tax might be set in order to reach the optimal trade-off between achieve adequate agricultural production and limiting adverse environmental impacts on water sources. Although such measures are relatively blunt tools for controlling water pollution, they should still be considered in the scope of regulatory and policy interventions to be considered for protecting South Africa's water quality. Taxation as a tool for discouraging unnecessary use has not been widely applied in OECD countries, where economic instruments such as green labeling and environmentally-linked subsidies have found wider implementation (Organisation for Economic Co-operation and Development, 1996).

## 2.7 CONCLUSION

A wide variety of factors will determine the movement of a pesticide into water and all these factors will need to be taken into account when conducting monitoring, or setting standards for pesticide contamination of water. Analytical methods for measurement of many pesticides in water are available but the effective implementation of monitoring requires careful attention to standardisation of sampling and analytical procedures, quality control in laboratory performance and accounting for key environmental variables.

Empirical evidence, largely driven by regulatory requirements for surveillance in the US and the EC, have vielded extensive databases of testing reports, indicating fairly widespread detection of pesticides in ground and surface waters at relatively low concentrations in Europe and the USA. It appears that certain pesticides, such as atrazine, are more commonly detected in water and that these patterns are fairly ubiquitous across different continents. However, the health implications of these low levels in water is less than clear, with very sparse epidemiological research available, and equivocal findings emerging from these studies.

In the face of uncertainty, regulators have to make decisions as to how to set permissible standards for pesticides in water. In this regard, two approaches that differ fundamentally in their outlook, are available. The US EPA and the WHO adopt a health-based approach to standard setting, using existing scientific data, albiet known to be imperfect in its depth and coverage, to derive levels thought to be protective for human health. Use of multiple protection factors is thought to compensate for the uncertainty in the data. Where standards are set for pesticides in water in countries outside of Europe and the USA, these generally tend to follow the WHO guidelines. Differences between the WHO approach and the US EPA are not fundamental, but relate to the type of data fed into the modeling.

In contrast, the European Union has adopted regulation as a policy tool to drive down pesticide usage, rather than seeking to use science to establish supposedly safe levels. The underlying philosophy is that where uncertainty exists (as it does for much of the toxicology with regard to pesticides, particularly for chronic effects), a precautionary approach is used. The EEC thus set their standards effectively at the lower limit of analytical capabilities to detect pesticides. In general, EEC standards are lower than WHO or US EPA standards, but because they are not health-based, are not in themselves, guarantees of absolutely safe limits.

Moreover, standards for human health are generally much higher than standards needed to maintain ecosystem integrity. Attempts to incorporate aquatic ecosystem impacts into regulatory frameworks will therefore impose even greater requirements for lowering of levels and increasing sensitivity of Quantification Limits.

# Chapter 3:

# MATERIALS AND METHODS

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# 3.1 IDENTIFICATION OF STUDY AREAS ("AREAS OF CONCERN") AND SAMPLING POINTS

The choice of study areas and sampling points was primarily motivated to identify settings with the worstcase potential for pesticide pollution of water. This was largely intended to address the fact of previous negative studies by locating sites with the best opportunity to identify pesticide pollution, should it be present.

## Table 3.1: Criteria used for choice of study areas - factors associated with highest likelihood of pesticide pollution of water

CRITERION	KEY FACTORS	SOURCE
Annual rainfall	Run-off to surface water and leaching into ground water are initiated by rainfall triggers	Department of Water Affairs rainfall maps and 1997-1998 rainfall data from the SA Weather bureau
Watertable	A shallow watertable (< 5 m) favours groundwater pollution	Consultation with geohydrologist
Soil Characteristics	Upper soil characteristics governing run-off and leaching, includes permeability (soil structure and texture), organic matter content, moisture, pH and cation exchange capacity.	Direct measurements absent. Soil mapping data, ARC Institute for Soil, Water and Climate (Stellenbosch), interpreted by soil scientists from Elsenburg Agricultural College
intensity of agriculture	Intensity and duration of pesticide spraying	Sales data costly. Consultations with persons in industry
Accessibility of areas.	Areas where accessibility could be arranged.	Farming unions, environmental officers and co-ops.
Boreholes	Groundwater usage	Borehole data from the Department of Water Affairs

#### 3.1.1 STUDY AREAS

Identification of study areas was conducted through an iterative process of review of secondary data, field observation of potential sites and interviews with rural health care providers, farmers, environmental officers, technical officers and other agricultural personnel. Study areas were regarded as areas of concern where there was greatest potential for water contamination by pesticides. Access to sites was negotiated with local farmer associations or producer organisations<sup>1</sup>. Specific assistance was sought from geohydrologists outside the project team<sup>2</sup> both to identify areas which might be most vulnerable to pesticides reaching water and to locate sampling points within these areas. Criteria considered in determining study areas are summarised in Table 3.1. Based on these criteria, three districts (Piketberg, Grabouw and the Hex River Valley) were selected as study areas (Figure 1). Table 3.2 lists a summary of hydrogeological data for the three regions. Full data are contained in Appendix B. Sampling points were selected in each area to capture a spectrum of ground and surface water points and in configurations that could assist in explaining potential routes and sources of contamination.

See discussion on Ethics and Stakeholder involvement, as well as Appendix 2.

<sup>&</sup>lt;sup>2</sup> Assistance from John Weaver, Gideon Tredoux and Kevin Pietersen are acknowledged in this regard.



Figure 3.1: Location of study areas for pesticide sampling in the Western Cape, South Africa



Figure 3.2a: Location of sampling points for pesticides in the Hex River Valley



Figure 3.2b: Location of sampling sites for pesticides in the Grabouw/Vyeboom Area



Figure 3.2c: Location of sampling points for pesticides in the Piketberg Area.

The **Hex River** district (Figure 2a) is an intensive grape-farming area with high pesticide usage. Water drawn from a nearby dam high up in the mountains is the most important source for drinking as well as for irrigation. Soil conditions are conducive to pesticides reaching the water table and contaminate groundwater (shallow water table, unconfined aquifer, coarse soils with low clay content). The soil is also advantageous for surface water pollution (table 3.2). The Hex River, which runs through the middle of the farming area is vulnerable to pollution. The climate is Mediterranean to semi-arid, with moderate winter rainfall.

The **Grabouw** district (see Figure 2b) included two areas (Grabouw and Vyeboom) which are intensive pome-fruit farming areas, with high pesticide inputs (London and Myers, 1995a). In both areas, the soil is complex (Table 3.2) but is generally advantageous for run-offs to surface water sites. The high annual rainfall is also advantageous for water contamination. Climatic conditions are typically Mediterranean.

AREA	SOIL	ANNUAL RAIN (MM)	NUMBER OF BOREHOLES
Hex River	Sandy and moderately deep, with rapid infiltration and permeability, but rock layer will send water sideways to nearest river. Low probability of groundwater contamination	100 - 700	< 20
Grabouw, Highlands Vyeboom	Medium textured, moderately permeable. Sideway run-offs probable. Medium textured, and slowly permeable. Lateral movement probable.	>1000	< 20
Piketberg/ Mooreesberg Mountains Plain	Sandy, moderately deep soil on rock Run-offs to rivers and leaching into groundwater through rock cracks possible Sandy soils on clay and medium-textured soils. Leaching and surface run-offs probable.	> 100 - 400	> 20

### Table 3.2: Soil, climate and hydrological characteristics of the three study areas

Source: Institute for Soil, Water and Climate, Agricultural Research Council, Stellenbosch, 1998.

**Piketberg** (Figure 2c) is an important farming region covering a vast area. Climatic conditions are Mediterranean to semi-arid. Fruit farming is practiced on the Piketberg mountains and wheat farming on the non-mountainous areas. The soil in both areas is multi textured, but generally leachable and prone to run-offs (Table 3.2). The water table is moderately shallow and annual rainfall low. There are numerous boreholes in the area. The Berg is the major river running through the area and water is purified for domestic consumption at a number of places along its course. The purification scheme at Wittewaters is a major source of drinking water in the rural Western Cape and is fed by the Misverstand Dam, situated amidst extensive wheat farms, where aerial spraving of pesticides is commonly practiced. The Bergriver, flowing through fruit farming areas also flows into the Misverstand Dam.

#### 3.1.2 SAMPLING POINTS

Table 3.3 summarises the different sampling points used in the study.

#### HEX RIVER

Sampling points in Hex River region included three points along the course of the Hex River (E, F and G), representing a sequential flow downstream. Point G was of river water after the Hex River had been joined by a tributary draining pristine mountain water from a northerly direction (see Figure 2a). Other river points (M and D were added in the course of the study based on preliminary findings, as well as a point (K) on another river. Other points included two water reservoirs situated alongside vineyards (Ar and Bdr). Both are open tanks receiving water from a protected mountain spring. One reservoir (Ar) was situated in close proximity to a labourer's house.

Two drains in the vineyards (Bdr and Cdr) that collect water from soil surface run-off and seepage were also included. Cdr is a collection point for an open drain that drains both direct surface run-off (during heavy rain and irrigation), similar to a stormwater drain, as well as water moving through soil under the surface. Bdr is a collection point for a set of underground pipes that act as a sub-surface drain collecting seepage through the soil in the vineyards at a depth of approximately 1 m. Both drains eventually feed into the Hex River. The drain Bdr is enclosed and flow was maintained throughout the year. Drain Cdr is open, and flow in this drain ceased during the dry summer months.

Also included was one of the many large open dams situated near vineyards and accessible to farm workers (Dd). This dam is made of earth and receives water from the Hex River. It was subject to considerable fluctuations during the year as water was pumped in and out of the dam.

During the course of the study a further point (H) being a shallow well used for domestic water consumption was included. The depth of this well was 2 m. However, the well also received some surface water carried by a shallow open surface canal and the contents therefore represented a mixture of ground and surface water. The only other site for sampling for drinking water in the area was a tap (J) at the Hex River Irrigation board receiving piped reservoir water from a dam outside the valley.

#### GRABOUW

Sites in Grabouw were selected on farms belonging to one of two major apple-packing Cooperatives in the region. One borehole site (G6b) in the Vyeboom area was included for sampling. The borehole is 30m deep and is pumped throughout the year. On both farms, water from the boreholes is used for domestic purposes by the owners.

Two sites were selected on the Palmiet River which runs through the main agricultural area of the valley. One site (G3) is situated in the middle of intensive agricultural production and the other (G4) towards the end of the river before it leaves the agricultural area.

Four dams were selected, three in the Grabouw area (G1d, G2d and G5d) and the other in the Vyeboom area. The one dam (G1d) receives irrigation drainage water from the farm and then flows out to the Palmiet River. The other dam (G5d) receives water from a number of sources including other dams, irrigation and the Palmiet River. This water is pumped to another reservoir

for purification through sand, charcoal and UV light for domestic use, including for drinking purposes. The water output from this scheme was sampled from a tap in a farm office (G8t).

Hex River		
Valley	E	River point - high up the valley, towards the top of the production area
	F	River point - in the middle of the river's course through the valley, at
		densely agricultural area
1	G	River point - at lowest end of the valley, after confluence with a fresh river
		from pristine area
	L	River point-between F and G
	M	River point – between E and F, before discharge of Bdr
	Ar	Reservoir on farm: Spring water and mountain is source, but reservoir is
		open
	Br	Reservoir on farm: Mountain is source, but reservoir is open
	Cdr	Surface drain; Drains superficial vineyard run-off; Open drain
	Bdr	Surface drain; Drains vineyard run-off and run-off from neighbouring farms; Closed drain.
	Dd	Open farm dam
	н	Shallow well: water level about 5m deep. used for domestic consumption
	J	Tap at Irrigation Board Offices: representative of potable water supply to
		the valley. Source = distant mountain dam close to Ceres
	К	Point on another river near F
Grabouw /	G1d	Dam, receives irrigation drainage, flows into river
Vyeboom	G2d	Farm dam, water pumped from Palmiet.
	G3	River point in midst of an intensive agricultural production area
	G4	River point lower in the course of the river
	G5d	Dam receiving a wide range of source, including river, irrigation run-off,
		other dams; Purified for domestic use.
	G6br	Borehole used by farmers for domestic use, 30 m in depth
	G7	A stream flowing from agricultural area into the Theewaterskloof Dam . The
		stream is part of the dam when the dam is full.
	G8t	Tap water using output of C5d
	C9	River point on Palmiet after joining Krom
Piketberg	P1b	Borehole (depth = 100m) on farm in intensive farming area; used for
		domestic water supply
	P2d	Dam receiving borehole and surface water but near the top of the
		mountain
	P3b	Borehole (depth = 70m) on farm in intensive farming area; used for
		domestic water supply
	P4r	River site just after stream running through Moravian Mission
	P5r	River site mid-way further on
	P6r	River site at pumping station providing municipal water
	P7b	Borehole on wheat farm on the plain below the mountain, depth
	P8r	Tap at water purification scheme (river)

## Table 3.3: Sampling points in the three study areas

The 8<sup>th</sup> sampling site (G7) was taken from a stream entering the Theewaterskloof dam supplying just over 50% of Cape Town's drinking water, which is surrounded by intensive farming activities in the Vyeboom area, some 15-30 km from Grabouw. The stream is filled with water from the upper reaches of the dam when dam levels are high. Another site (G9), situated on the Palmiet River after the Kromrivier has joined it, was sampled at a late stage in the project.

#### PIKETBERG

Unlike the other two areas, access to farms for sampling was arranged in Piketberg by the local environmental officer, a municipal official responsible for public health functions in rural areas.

Two boreholes (P1b and P3b) which are 100m and 70 m in depth, respectively, and pumped throughout the year, were chosen on a large farm in the Piketberg mountains serving a community of over 250 people and situated in an intensive fruit farming area. Water from the first borehole (P1b) was collected from a domestic tap and the other (P3b) from a pipe feeding a local farm dam. A third borehole (borehole depth, pumped throughout the year) (P7b) was selected on a wheat farm at the foot of the Piketberg mountain and water samples collected from a tap.

The only dam site (P2d) is located on the same farm on which the two first boreholes are located, at the top of the Piketberg mountain, and receives irrigation drainage from surrounding farming activity as well as the one borehole (P3b). Water from this dam passes through a Moravian Mission Station community of about 400 residents where it is purified for domestic consumption. The stream serving this community was also chosen as a sampling site (P4r). Further from this point, the stream discharges into the Berg River and sampling points were selected further along the Berg, one at a nearby farm (P5r) that purifies water from the Berg for domestic consumption, and one at a municipal pumping station (P6r) just below the Piketberg.

In addition, sampling was also conducted from the tap at the water purification scheme at Wittewaters (P8r).

## 3.2 FIELD SAMPLING

The analyses were based on regular grab sampling conducted on average monthly in the study areas over a 12 to 15 month period. Sampling commenced in the Hex River in February 1998, in Grabouw in April 1998 and in Piketberg in May 1998, and was completed for all 3 areas in May 1999. Samples were collected by the project research co-ordinator once monthly in each area, on a rotating cycle, and twice in the week after the first rainfall trigger (> 10 mm over 24 hours or > 15 mm over 48 hours), using a standardised collection procedure.

Samples were collected in 2.5 and 1L amber bottles fitted with a screw cap lined with clean aluminium foil. The samples were collected directly into the bottles which had been prepared by cleaning with water, rinsing with methanol and air drying. Samples were kept at ambient temperature in a holding box for transport to the laboratory where it was stored in a refrigerator until extraction. The researcher recorded sample pH, water temperature river flow (low, medium or high) and the occurrence of spraying within 1km of the sampling point with every sample. Approximately 7 to 10 sites were sampled with every field visit.

A more detailed description of Sampling Protocol, including collection, preservation, handling, and equipment are contained in Appendix C.

## 3.3 CHOICE OF PESTICIDES FOR ANALYSES

Because of the prohibitive costs of multi-residue screening methods, and the concern of the project to develop in-house capacity for analytical techniques, attention was paid to focusing on only the most critical pesticide agents for analysis rather than attempting to measure all organic contaminants arising from pesticide applications. Thus, expert industry opinion and recommended cooperative spray programme data were used to draw up a comprehensive list of pesticides in use in the respective areas. From this list, pesticides were selected on the basis of:

- Their potential to cause adverse health impacts. This was assessed from their presence on the EPA list
  of endocrine disruptors (World Wild Life Fund, 1997), a German list of endocrine disruptors (Bruhn et
  al, 1998) and from Schettler et al, 1996 (Summarised in Appendix D). We also took account of the WHO
  list of drinking water standards (WHO, 1993) and the EPA list of drinking water regulations and health
  advisories to select pesticides for analysis (USEPA, 1992).
- Significant usage in the specific study area as determined from expert industry opinion and from
  published literature (London and Myers, 1995a; London and Myers, 1995b). Data were also collected on
  local spray application from farmers, commercial spray operators and cooperatives regarding
  chemicals used (types, concentrations, methods of application) and on weather conditions at the time
  of water sampling.
- Likelihood of contamination based on a combination of industry expert opinion, presence on the EPA list of water pollutants (Wade, 1988), and known groundwater ubiquity scores (Gustafson, 1989), which are developed to screen leachability of pesticides by means of organic sorption coefficient and halflife in soil (Table 3.1).

The final list of pesticides selected for analyses was also conditioned by the availability and existence locally of methods for analysis. This meant that not all pesticides could be selected because the analytical methods were either not existent or feasible to do. For example, analyses for aldicarb could not be incorporated in the study because of prohibitive costs and logistic difficulties in ferrying large numbers of samples to specialised laboratories elsewhere.

A total of 31 pesticides were identified through this process. (Table 3.4).

Analyses were conducted jointly by the Analytical Chemistry laboratories of the Peninsula Technicon (PENTECH) in Cape Town and the State Forensic (SF) Laboratory in Cape Town. The latter laboratory undertook analyses conducted as a battery for all 31 pesticides in line with their statutory function of providing a screening service for monitoring of pesticide residues on foodstuffs. Based on their preliminary results and on anticipated findings, the PENTECH laboratory developed in-house capacity to analyse water samples for the insecticides BHC (gamma, beta and delta isomers), 4,4-DDT and 4,4-DDE, dichlorvos, chlorpyrifos and endosulfan (isomers I and II and endosulfan sulphate). The SF Laboratory thus acted as a preliminary screen.

Because relatively few pesticides<sup>3</sup> other than chlorpyrifos<sup>4</sup> and endosulfan<sup>5</sup> were detected on screening by either the State laboratory or the ARC laboratories (used for quality assurance collaboration - see below) the project laboratory at PENTECH did not pursue establishing methods for measuring pesticides other

<sup>&</sup>lt;sup>3</sup> These included ipriodione, azinphos-methyl, priothiofos, deltamethrin and fenanimol detected on 6 occasions at low levels at 10 different sites over the course of the project. See Chapter Four for more details.

<sup>4</sup> The chemical description of chlorpyrifos is 0.0-diethyl 0-3,5,5-trichloro-2 pyridyl phosphorothiate.

<sup>&</sup>lt;sup>5</sup> The chemical description of endosulfan is: 6,7,8,910,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepine 3-oxide.

than chlorpyrifos and endosulfan. There were no detections of BHC (gamma, beta and delta isomers), 4,4-DDT and 4,4-DDE, or dichlorvos by the PENTECH laboratory in the pilot phase of the project in any of the samples taken in the Hex River Valley.

	AREA (N, Y = SIGNIFICANT USAGE; N = NO SIGNIFICANT USAGE)				
PESTICIDE	HEX RIVER (N = 25)	Grabouw (n = 22)	Piketberg (n = 27)		
Azinphosmethyl	Y	Y	Y		
Bromopropylate	Y	Y	Y		
Bupirimate	N	Y	Y		
Captab	N	Y	Y		
Chlorpyrifos	Y	Y	Y		
Copper oxychloride	Y	Y	Y		
Cypermethrin	Y	Y	Y		
Demeton-S-methyl	N	N	Y		
Dichorvos	Y	Y	Y		
DNOC	N	Y	Y		
Dimethoate	Y	N	Y		
Endosulfan	Y	Y	Y		
Esfenvalerate	Y	N	N		
Ethylene Bromide	Y	N	N		
Fenamiphos	Y	Y	Y		
Fenarimol	Y	Y	Y		
Fenvalerate,	Y	Y	Y		
Folpet	Y	Y	Y		
Formothion	Y	Y	Y		
Iprodione	Y	Y	Y		
Methyl Parathion	Y	N	Y		
Mevinphos	Y	N	N		
Penconazole	Y	N	N		
Propioconazole	N	N	Y		
Prothiofos	Y	Y	Y		
Pyrefenox	Y	N	N		
Simazine	Y	Y	Y		
Terbuconazole/	Y	Y	Y		
Tridimenol					
Trichlorfon	Y	Y	Y		
Vanmidothion	N	Y	Y		

### Table 3.4: Main pesticides used in the three study areas

Additional to the above organics, a subset of analyses were conducted on samples for Copper content as part of undergraduate training by students in Analytical Chemistry at the Peninsula Technicon. A number of copper-based fungicides are in widespread use in fruit farming in the Western Cape, and it was anticipated that useful information on copper levels in water might be obtained. However, copper is a trace element essential for human function, is not regarded as an endocrine disruptor of note, and is ubiquitous in natural water sources. Toxicity of copper is usually related to high levels of over-exposure. Thus, it did not qualify in terms of criteria listed above as a pesticide for analysis in this study. Accordingly, this sub-study is not presented in any detail in the text of this report. However, readers are referred to Appendix E for a fuller description of the findings of this sub-study.

## 3.4 ANALYSES

#### SAMPLE EXTRACTION

The PENTECH Laboratory used solid phase extraction for analyses following EPA methods (EPA, 1995a; EPA, 1995b). All samples were extracted within 7 days of collection. The water samples were prefiltered by vacuum filtration through S&S filter paper (ref. No. 334508) to remove particulate matter before extraction. Bond Elute Extraction Cartridges (C18, 10ml LRC (Loose Reservoir Cartridge), 500 mg sorbent massi was used in extraction procedure. The column was first conditioned with 2 column volumes (2 X 10 ml) ethyl acetate and 1 column volume (1 X 10 ml) of methanol and 1 column volume (10 ml) of deionised water.

All solvents used were high-pressure liquid chromatography grade. 250 ml of filtered water sample was slowly aspirated through the column at a rate of 20 - 25 ml per minute under vacuum. The column was then washed with 1 column volume (10 ml) of deionised water and then thoroughly dried for 15 minutes under vacuum. The pesticides were then eluted into a borosilicate glass vial using 2 samples of 10 ml ethyl acetate. The ethyl acetate was then evaporated off at room temperature. 1 ml hexane was then added to the glass vial to redissolve the residue. This solution was now ready for GC analysis.

#### ANALYTICAL METHODOLOGY

Analytical standards (> 98% purity) were used to prepare standard solutions (EPA, 1995). The extracted samples were subjected to gas chromatography for identification and quantification. All compounds were determined using a Varian 3300 GC equipped with an electron capture detector (ECD). 2  $\mu$ l sample was injected onto a capillary column with a BPX 5 stationary phase. The temperature program was 170 °C initially increased at a rate of 7°C/min to 290 °C and held for 5 minutes at that temperature. Injector and detector temperature were 250 °C and 300 °C, respectively. Although the PENTECH laboratory aimed to make use of an autosampler to cope with the volume of assays in the course of the project, software incompatibilities precluded use of the instrument in the course of the study.

The PENTECH members of the team trained a specific staff member (RI) taken on for the project to manage the analyses as well as having the assistance of students in analytical chemistry. The need to appoint a specific staff member was prompted in January 1998 by the increasing volume of analyses required over the project.

Methods used by the SF laboratory were similar to that of the Pentech laboratory. The SF laboratory used solid phase extraction and a methyl sillicon CC column and a C18 ec column for sample prep. The temperature programme was as follows: temperature was held at 170 °C for 0.5minutes, increased at 20 °C per minute to 195 °C and held for 1.75 min, then increased at 30 °C per minute to 280°C where it was held for 2 minutes and then increased at 30 °C per minute to 295 °C where it was held for 2 minutes were reported without Quantification Limits.

The Agricultural Research Council (ARC) laboratory participating in a Quality Assurance programme (see below) used a multiresidue method described in Manual of Pesticide Residue Analysis, Vol1, p.383-400. The sample extracts were analysed on a gas chromatograph equipped with EC detector and a 2m 3% OV-17 column. Using a temperature starting at 200 degrees Celcius, the alpha-endosulfan, beta-endosulfan and endosulfan-sulphate eluted at 6.4,8.3 nd 9.4 minutes respectively. Chlorpyrifos eluted at 5.4 minutes.

## 3.5 QUALITY CONTROL AND QUALITY ASSURANCE

Quality Control measures implemented in the PENTECH laboratory included:

- Sampling and analysis of duplicate measures at least once per sampling run.
- A reagent blank and spike were run with each set of samples.
- Recoveries of below 70% or in excess of 130% of spike concentration prompted investigation and, if necessary reanalysis.
- Mixed standard solutions were injected prior to sample injections and peak shape, resolution and
  response evaluated by comparison with previous chromatograms to ensure that the instrument was
  operating properly.

Where samples gave inordinately low recoveries (21 runs, involving 22% of the total of 783 samples, mainly for chlorpyrifos), the results have still been reported but have been highlighted in tables. The mean and range for recoveries were also calculated for analyses for endosulfan and chlorpyrifos.

A more detailed description of Sampling Protocol, including collection, preservation, handling, and equipment, and laboratory procedures are contained in Appendix C.

A Quality Assurance protocol (see Table 3.5) was established with the laboratories of the Agricultural Research Council (ARC) and the SF laboratory. The former runs a GLP-accredited facility. Eleven runs of parallel samples were forwarded to the SF laboratory over the course of 1998 (4 from Piketberg, 2 from Grabouw and 5 from Hex River) and two sets to the ARC in March and August 1998 (from the Hex River). The set on the 12<sup>ch</sup> August 1998 therefore included a set of samples submitted to all 3 laboratories simultaneously (PENTECH, SF and ARC). Inter-laboratory comparisons enabled estimation of bias. In addition, one triplicate set of multiple samples (n = 7 for each laboratory) taken from a single sampling point in the Hex River (Bdr) was sent to all 3 laboratories in June 1998. This enabled estimation of bias and precision in inter-laboratory agreement.

Samples for the SF laboratory were held overnight at 5° C and transported within 24 hours to the SF for extraction and analysis. Samples for the ARC laboratories were couriered to the ARC laboratories using polystyrene containers to achieve temperature control. In August and September 1998, sampling point Bdr was sampled twice and the second sample given a false identifier (I) to blind the laboratories to assist assessment of QA. QA procedures in the study are summarised in Table 3.5 and the results discussed in detail in Appendix G.

DATE	SAMPLES INVOLVED	LABORATORIES	METHOD	MEASURING
March 1998, and August 1998	Split samples (n = 2) from all 8 different sampling points in Hex River	ARC and PENTECH	One sample of each pair sent to each lab.	Inter-laboratory agreement: bias
May 1998	8 samples from one sampling point in Hex River split into 3.	ARC + PENTECH + SL	One sample of each triplet sent to each lab.	Inter-laboratory agreement: bias and precision
April 1998 to December1998*	Split samples (n = 2) from all 8 different sampling points in Hex River	ARC and SL	One sample of each pair sent to each lab.	Inter-laboratory agreement: bias

## Table 3.5: Quality Assurance Testing: Outline of Sampling comparisons conducted

ARC = Agricultural Research Council; SL = State Laboratory

Although comparisons with the State Laboratory continued throughout the study, the SL was unable to provide effective quality assurance analyses after September 1998 - see text. Whereas the extraction methods used by the SF laboratory follow that used by PENTECH closely, the ARC laboratories use liquid-to-liquid extraction for its analysis. All three laboratories use GC methods with Electron Capture Detectors (ECDs) but with different columns and temperature programmes. The ARC laboratory made use of a 2m 3% OV-17 column, using a temperature programme starting at 200°C.

Note that the pesticides identified and quantified at the PENTECH and at the SF laboratories were not confirmed on a second column nor by GC /MS method. In the course of the study, we were informed that analyses at the SF laboratory had been delayed by the analysis of a sediment sample that disrupted the GC column dedicated to pesticide analyses. The impact of this event on the pick-up from the SF laboratory and on QA analyses is difficult to predict and is discussed in Chapter 4 under section 2.

# 3.6 FARM SURVEYS ON WATER USE AND KNOWLEDGE, ATTITUDE AND PRACTICE

To meet the objective of assessing the practices of farm residents in relation to water, farm surveys were conducted on a sample of farms in the study areas. Because of logistic difficulties, only two of the study areas (Hex River and Grabouw) could be surveyed, and these surveys were only completed very late in the project. Access to both areas was arranged through the local producers' organisations, partly accounting for the delay in completion date.

A pilot study was conducted early in the project to field test the questionnaire. This was carried out in the Slanghoek valley region, some 25 km from the Hex River with farming conditions thought to be similar to that pertaining in the Hex River area.

#### 3.6.1 SAMPLING

Cross-sectional surveys were conducted of farms in the study areas, as indicated in Table 3.6 below. For the study areas, two sampling strategies were used. One arm selected a random sample of 25 farms from each study area based on a listing obtained from the Producers' Associations in those areas. In addition to the random sample, the farms on which sampling took place were also included in the survey.

For each farm, interviews were sought with the owner or manager, one pesticide applicator, one farm worker non-applicator, and one farm resident not working on the farm. Liaison with the farm owner or manager meant that the workers participating in the study were not randomly selected.

#### 3.6.2 QUESTIONNAIRE

Interviews explored water usage (sources at home and in the field for drinking and non-drinking purposes), contamination of water sources, drift, domestic use of pesticides or containers and knowledge of, and training in pesticide safety. Interviews were conducted in Afrikaans and administered by the project coordinator and students from the PENTECH Public Health Department. Surveys took place in 1997 and 1999.

DATE AND SITE	SAMPLE TYPE	SAMPLE N	PARTICIPANT	PARTICIPANT SUBJECTS
June 1997: Slanghoek Valley	Pilot: All farms in Slanghoek Valley	18	12	7 farm owners 3 managers 12 spray operators 9 farm workers 9 non-farm workers
October 1999: Grabouw / Vyeboom	Study farms	5	2	2 managers 2 sprav operators 2 farm workers 2 non-farm workers
	Random sample	40	29	7 owners 23 managers 29 spray operators 28 farm workers 25 non-farm workers
October 1999: Hex River Valley	Study farms	6	4	2 managers 3 spray operators 3 farm workers 3 non-farm workers
	Random sample	40	13	10 managers 14 spray operators 16 farm workers 12 non-farm workers
TOTAL		109	60	19 owners 40 managers 60 spray operators 58 farm workers 51 non-farm workers

Table 3.6:	Field surveys	for water usage	and knowledge
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#### 3.6.3 ADDITIONAL SURVEY DATA

While the project was ongoing, additional opportunities arose to collect data on another farming community near Cape Town (Stellenbosch) where the Department of Community Health was conducting a health survey. The survey included a random sample of 53 farms and 665 households in the period August to October 1998. As part of a household questionnaire information was collected from respondents on sources of water and use of farm dams for swimming. This data are also included in Chapter 5 for comparison.

## 3.7 ESTIMATION OF DIETARY CONSUMPTION

Initial plans for the estimation of dietary consumption included the incorporation of a detailed dietary inventory as part of the farm-based surveys to identify all potential sources of pesticide intake. However, following consultation with a nutritional expert at the Medical Research Council (personal communication, Dr L Bourne, MRC, January 1998), it was decided to simplify the exercise by using a standard 2 ( of water consumption as an average daily water intake for an adult.

Concentrations of pesticides (only endosulfan and chlorpyrifos were used in this exercise because of the low number of detects of other agents) found in water at each of the sampling points used for drinking in the three study areas were used to estimate potential dietary exposures experienced by users. Two models were used in a sensitivity analysis:

 Use of the highest concentration found at the sampling point applied to average daily pesticide intake from water. b) Use of a root mean square concentration to derive a proxy for average daily pesticide intake from water. Only results with acceptable recoveries achieved in the laboratory (> 70% or < 130%) were used to derive this estimate, so as to reduce error margins.

In both cases, results were modeled assuming a 60kg adult consuming 2I of water per day to generate total pesticide consumed through drinking water. Results were compared to the ADIs cited by the WHO/IPCS (IPCS, 1999) to estimate the proportion of ADI represented by this exposure. The percentage could then be compared to the models used in current standard setting (WHO, 1993a; EPA, 1999) that assume that between 1 and 10% of dietary intake through drinking water.

# 3.8 FEEDBACK OF RESULTS, ETHICS AND STAKEHOLDER PARTICIPATION

All participants in the study were guaranteed of confidentiality, and participation in the field surveys took place only after respondents had the study fully explained to them, and were able to give informed consent. Care was taken by the researchers to ensure that no farm workers suffer any adverse consequence as a result of their participation in the study (job loss, housing loss, etc.)

Co-operation of key stakeholders in the three study areas was crucial to the progress of the project. In the Hex River area, the project team concluded an agreement with the Hex River Producers Association (see Appendix F) as the basis for ongoing research. The main element to the agreement was confirmation of regular feedback, and providing the Producers' Association with opportunity to comment on the findings. During the course of the project, three meetings were held in De Doorns to give feedback and further communication will be ongoing. The Producers Association and the Hex River Irrigation Board played an invaluable role in providing data to the research team on chemicals used in the region, on farming patterns and geography, and commenting on research findings. Access to sites was also facilitated by the Association.

In the Grabouw region, the technical officer for a large apple co-operative provided access to and information for sampling points. A similar agreement to that with the Hex River Producers Association, but less formal, was reached with the local farmers association, as the basis for cooperation in the study. Links were also established through the Chair of the Producers Association in Grabouw with the Palmiet River Water Catchment Taskteam, with whom some of the relevant project data were shared.

In the Piketberg area, access to sampling sites was obtained through the assistance of local pesticide company staff, and local environmental health officers working for rural local authorities. The Western Cape Agricultural Association office has also been helpful in facilitating contacts for the project.

Cooperation from Dr Andre de Klerk and Mr Kobus Hartman from Nietvoorby and UNIFRUCO, respectively, greatly assisted in this project, partly in response to requests from the Hex River Producers.

Feedback of results is critically important and will continue over the next period as the Steering Committee concludes its recommendations on the project. In addition, results will be disseminated in the scientific literature, at scientific meetings and in the non-scientific media to ensure maximal dissemination to appropriate target groups. It is important for relevant government departments to be informed of the study findings, particularly the different departments with responsibilities for water quality and safety so as to inform policy development. Further, non-governmental organisations, particularly those in the environmental sector, will also be involved.

# Chapter 4:

# RESULTS

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# 4.1 QUANTIFICATION LIMITS

Quantification Limits were estimated to indicate the concentration of a pesticide in water above which results could provide a quantitative estimate of the pesticides concentration with a sufficient (95%) degree of confidence. Analyses in the PENTECH laboratory to estimate the quantification limits for the chlorpyrifos and endosulfan calculated the standard deviation for a series of 7 assays of each pesticide standard, and multiplied the standard deviation by 2. The quantification limits for the PENTECH laboratory analyses were thus found to be  $0.05 \ \mu g/l$  for chlorpyrifos and  $0.1 \ \mu g/l$  for endosulfan.

		EPA METHOD		
PESTICIDE	CONCENTRATION OF STANDARD USED	EMPIRICAL MEAN VALUE	EMPIRICALLY-DERIVED* QUANTIFICATION LIMIT	QUANTIFICATION LIMIT (EPA, 1995B)
Chlorpyrifos	0.080	0.096	0.052	Not available
Alpha-endosulfan	0.171	0.103	0.108	0.030
Beta-endosulfan	0.182	0.206	0.134	0.030
Endosulfan sulphate	0.266	0.290	0.130	0.030

#### Table 4.1: Quantification limits for chlorpyrifos and endosulfan $(\mu g/t)$

This report has not used the more conventional term 'Detection Limit' which implies the absence of a pesticide below a certain threshold, but rather the term 'Quantification Limit' which acknowledges the degrees of uncertainty at very low concentrations, where quantification is not possible with any meaningful degree of accuracy. By citing quantification limits, we indicate explicitly the limits of quantification. Where evidence for a pesticide's presence has been detected at levels below Quantification Limits, the results are presented in full, but qualified with acknowledgement that the results lie below the limits of quantification. The results are presented in full to allow the reader maximum opportunity to interpret best the findings.

Thus, results are reported throughout as follows:

- All detections for chlorpyrifos at levels below 0.05 µg/t have been reported in parentheses to indicate these are levels below our quantification limits. For example, chlorpyrifos at (0.02 µg/t).
- All detections for endosulfan isomers and endosulfan sulphate at levels below 0.1 µg/l have been
  reported in parentheses to indicate these are levels below our quantification limits. For example,
  endosulfan at (0.08 µg/l).
- All results for chlorpyrifos or endosulfan where no peaks were detected on the GC are reported as ND (not detected).
- Where samples were not taken from particular sampling points on particular runs (for example, flow
  rate too poor to generate sufficient volume for samples), results have been reported as NS (not
  sampled).

# 4.2 QUALITY ASSURANCE AND QUALITY CONTROL

Details of the Quality Assurance measurements for the 3 study areas over the course of the project are contained in Appendix F. Both intra- and inter-laboratory variation were measured with the participation of the laboratories of the Agricultural Research Council (ARC), the State Forensic (SF) services and the Peninsula Technicon (PENTECH) using a defined protocol (see Chapter 3, Table 3.5).

It should be borne in mind that variability between laboratories in analytical measurements may be large without implying any of the results are invalid, particularly when laboratories are measuring pesticides at very low concentrations (parts per billion) as is the case in this study. The reasons for such variation may reflect the inherent instability of the samples and may relate to the timing of sampling, the presence of time delays, and other factors that may differentially affect the "decay" of organic compounds. Additionally, a large part of the variation in results may be attributable to the adsorption of pesticides onto different species in the water, and different methods of sample preparation may detect different fractions of the species present (personal communication, Dr Phillip Kempster, institute Water Quality Studies). While QA analyses attempt to control for these factors as far as possible, it is not possible to standardise such conditions entirely, and it is not unusual for such differences to be encountered in usual analytical practice. Thus QA analyses for organic chemicals need to be interpreted with these constraints in mind. Indeed, because a single reading is always itself the product of a process of inherent variability with a laboratory, normative practice in some instances emphasises an analytical range as being the appropriate way to present a single finding.

Furthermore, when one of the participant laboratories is an analytical research laboratory geared to the analysis of pesticides, it is quite likely that greater attention will be paid to precautions and procedures than occurs at laboratories where analyses are routine.

Given these considerations, what may be more important from a QA perspective at very low concentrations is that results should consistently be able to:

- identify qualitatively the presence of the same pesticides across different laboratories, and report
  similarly the qualitative absence of the same pesticide, where such pesticide is not detected,
- show a consistent gradient in concentration patterns for different samples analysed by the same laboratory.- i.e. where a pesticide is found in differing concentrations in a number of samples analysed by one laboratory, another laboratory should demonstrate a similar gradient of concentrations, even if discrepancies arise between laboratories in the absolute concentrations.

Based on the above criteria, the findings of QA in Appendix G appear to suggest acceptable agreement and precision of measurements conducted at the PENTECH laboratories for endosulfan and chlorpyrifos. Strong qualitative agreement for most sampling points emerged in the comparisons for laboratories in 1998. For example, QA analyses in the Hex River valley (table A.7.1) in March and April 1988, showed reasonable agreement for the presence of pesticides (11 of 20 possible detections were events where both laboratories reported detections) and strong agreement on the absence of pesticides (41 of 50 possible non-detections). Moreover, agreement for high vs. low results was also commonly found across sample points, giving an overall pattern of consistency.

Intra-laboratory assessments for precision appear to yield comparable results across laboratories (see Table A.7.5 in Appendix G). It is noteworthy that although recoveries less than 70% were noted for a number of analyses for chlorpyrifos at PENTECH (36% of the total 400 analyses for chlorpyrifos but less than 8% of the 383 analyses for endosulfan), these would tend to underestimate the concentrations obtained in the study. In total, the mean recoveries for 43 determinations for chlorpyrifos was 67% while that for

endosulfan for the same number of determinations was 71%. Whereas a low recovery may tend to invalidate the result from a single analysis, assessing the overall picture of analytical results from a range of samples, requires assessment of the mean and range of recoveries for the whole population of samples. This is particularly important when analysing the results of a number of samples, as is the case in this study.

There were problems with comparisons with the SF laboratory towards the end of the study. This was largely due to the consequences of a sediment sample (McGregor, 1999) being analysed on the SF GC late in 1998 which disrupted the functioning of the GC column. This precludes meaningful interpretation of the data obtained from the SF laboratory from September 1998 onwards for inter-laboratory agreement. However, a number of factors provide grounds for believing that the levels of precision and accuracy achieved early in the study were maintained throughout the study:

- Patterns detected in the Hex River valley area in the first 4 months of the study by the PENTECH laboratory were more or less reproduced one year later, giving a consistent pattern across 12 months.
- Intralaboratory procedures and QC did not change at PENTECH.

In summary, the results of the QA analyses thus suggest that the laboratory analytical procedures followed in this study were able to achieve adequate precision and inter-laboratory agreement, consistent with normative practice for such strategies. Discrepancies that were detected are entirely consistent with normative variation obtained in such procedures and were relatively small. Most importantly, the QA analyses provide sufficient ground for making reasonable inferences from the main findings of the study.

# 4.3 FIELD RESULTS

Preliminary results from pilot studies in 1997 indicated that only a limited number of pesticides were being detected in rural water sources in the region. The two most commonly detected were the insecticides endosulfan and chlorpyrifos. For this reason, the PENTECH laboratory chose to concentrate specifically on measuring these two agents. Results presented below for chlorpyrifos and endosulfan are therefore from the PENTECH laboratory. However, where other agents were detected by the SF laboratory, these results are cited in Tables 4.6 and 4.11. Endosulfan data are quoted as the sum of its isomer forms plus endosulfan sulphate (i.e. total endosulfan), unless otherwise specified.

#### HEX RIVER

Given its soil and hydrological characteristics (Table 3.2), the Hex River Valley probably represented the scenario with maximum likelihood for identifying pesticide pollution of water of the three study areas.

Tables 4.2 to 4.5 list endosulfan (as total endosulfan in  $\mu$ g/() and chlorpyrifos ( $\mu$ g/() levels, detected by the PENTECH laboratory in the Hex River valley from February 1998 to May 1999, respectively. Where the SF laboratory detected other pesticides for the Hex River valley, these are also indicated in Table 4.6.

The highest levels of contamination are consistently found at point Bdr, which is a closed sub-surface drain, collecting drainage from a number of neighbouring vineyards (see also Figure 4.1). Virtually no pesticides were detected in the open drain Cdr, which dried up completely towards the end of the study. Because Bdr is a drain that collects drainage from a number of different farms, this might explain why it was consistently more contaminated than the open drain at Cdr. Where pesticides other than endosulfan and chlorpyrifos were also detected by SF laboratory screening, these were most commonly at Bdr (Table 4.6).

Little evidence of contamination was found in the single dam sample D before September 1998 (Tables 4.2 and 4.4), but consistent contamination occurred afterwards with both endosulfan and chlorpyrifos. One explanation for this might relate to the concentration of the dam water with increasing use of dam water for irrigation. The dam at site D is an earth dam so that adsorption to soil or sediments may occur. However, there was no evidence of significant pH changes in the dam water isee Appendix P that may have prompted potential release from sediments to have explained this phenomenon. The half-life of endosulfan is 120 days and prolonged persistence in dam water may be consistent with a concentration effect. In any event, from October onward, both chlorpyrifos and endosulfan are in use in the region.



Figure 4.1: Endosulfan and Chlorpyrifos levels in sampling point, Bdr: A sub-surface vineyard drain in the Hex River Valley

Of the 2 open reservoirs sampled Ar contains spring and Br contains spring and borehole water. Both were erratically contaminated, and generally at low levels.

River contamination (see Figures 4.2 and 4.3) by both endosulfan and chlorpyrifos at points E, F and G appeared to peak in mid-valley (F) and was present in smaller quantities at the lower valley (point G) after confluence with a tributary. Because this suggested dilution by inflow, further sampling was conducted at a point (L) which lies between F and G. Results showed that point L had similar levels of contamination as G, suggesting that dilution occurs between L and F. No obvious points source (e.g. pesticide mixing points) were identified along the course of the river (although a mixing stand is sited some 30 m from the river at

L). However, this site (L) was only sampled 4 times. No inference could be drawn from the sampling of a site (K) on another river which joins the Hex River, because virtually no contamination was found the three times that it was sampled.

Temporal trends need to be considered. Chlorpyrifos is generally sprayed during May, mid-July to end of August, while endosulfan is sprayed during September to mid October. Irrigation occurs in September to May (about 125mm per month).

Low levels of contamination were detected during the spraying months across most of the sites. However, for the most contaminated sites (see Figures 4.1 to 4.3), concentrations did not necessarily match the timing of spraying, and seemed rather to coincide with period of maximum irrigation. Endosulfan contamination was highest in the peak spraying time in September 1998 at point F (mid valley on the Hex River) but was also raised in the periods February to April in 1998 and 1999, which is the period of maximum irrigation. Similarly, chlorpyrifos appeared to peak in both river points and Bdr in the period February to April In both years.



Figure 4.2: Endosulfan levels in the Hex River Valley: Sampling points E, F and G on the Hex River



Figure 4.3: Chlorpyrifos levels in the Hex River Valley: Sampling points E, F, G on the Hex River

The first autumn rains meeting the criteria for trigger rains fell in the Hex River on 10 May 1998 and 14 April 1999. The data are equivocal for either any dilution or washout effects for either chorpyrifos or endosulfan. Sub-surface drain detections (particularly Bdr) are consistently present throughout the year, although there is little evidence to discern a washout effect in relation to the rain trigger.

Given the main irrigation period during summer months, it appears far more plausible that constant irrigation washout is more important as a mechanism for both endosulfan and chlorpyrifos reaching surface and sub-surface waters.

Low levels of contamination were also found in the shallow drain (H) and from the water of a tap (J), both of which supply water used for drinking purposes. The implications of these findings are discussed in more detail in Chapter 5.

Low levels of Fenarimol, Prothiofos and Deltamethrin were also detected by the SF Laboratory, again predominantly at the Bdr site. These detections were all in the range of 0.06 to  $1.4 \, \omega g/t$ , and are relatively consistent with the timing of use of these particular pesticides in the area. These findings, although not that significant in themselves, help to support the construct validity of the overall results of the study.

In summary, detections of endosulfan and chlorpyrifos were widespread in the Hex River region at generally low levels. However, some sites were clearly "hot-spots" with regular detections at significant levels. These included the sub-surface drain Bdr and the mid-point of the river, F. Of the three main competing potential mechanisms (rain washout, irrigation and spray activities), irrigation appears to be the most important mechanism, although some evidence of a temporal relationship to spray activities could be discerned.

DATE			SI	TES AND C	ONCENTR/	ATION IN .	. <b>q</b> /:		
DATE	E	F	G	Cdr	Bdr	Ar	Br	D	н
11/2/98	ND	0.24	ND	ND	0.19	0.44	0.16	ND	NS
18/2/98	ND	0.32	ND	ND	0.37	0.11	ND	ND	NS
25/2/98	ND	0.24	ND	ND	0.18	(0.08)	ND	ND	NS
4/3/98	ND	0.29	ND	ND	2.22	0.28	0.204	ND	NS
11/3/98	ND	0.16	ND	(0.07)	1.53	0.16	ND	ND	NS
18/3/98	ND	0.22	ND	ND	1.81	0.14	ND	ND	NS
25/3/98	ND	0.20	ND	ND	1.10	(0.08)	ND	ND	NS
22/4/98	ND	0.26	ND	ND	0.43	ND	ND	ND	ND
12/5/98	ND	ND	ND	ND	(0.04)	ND	ND	ND	ND
19/5/98	ND	(0.06)	(0.03)	ND	0.23	0.06	NS	ND	ND
12/8/98	(0.03)	(0.04)	ND	ND	(0.03)	(0.02)	0.20	ND	ND
23/9/98	(0.03)	1.56	ND	NS	(0.01)	(0.02)	NS	0.2	ND
21/10/98	ND	(0.04)	0.26	NS	ND	0.19	(0.09)	(0.05)	0.23
12/11/98	ND	ND	ND	NS	0.13	ND	ND	ND	ND
18/11/98	ND	ND	ND	NS	0.58	ND	(0.06)	0.58	ND
13/1/99	ND	ND	ND	NS	NS	ND	ND	0.25	0.89
24/2/99	ND	1.02	0.45	NS	1.84	ND	0.51	0.47	ND
17/3/99	NS	1.25	0.19	NS	3.86	1.02	ND	0.35	ND
07/4/99	NS	0.54	ND	NS	0.79	ND	ND	(0.09)	ND
20/4/99	0.35	0.29	(0.05)	NS	1.48	NS	0.79	(0.08)	ND
26/4/99	0.47	0.27	ND	NS	0.59	ND	NS	0.2	NS
13/5/99	(0.02)	(0.03)	NS	NS	(0.03)	ND	NS	ND	NS
NS = Not sa	mpled								

## Table 4.2: Endosulfan levels detected in the Hex River Valley

Table 4.3: Endosulfan levels detected in the Hex River Valley. Other Sites

DATE	SITES	AND CONCE	INTRATION I	N µg/t
DATE	L	ĸ	L	M
23/9/98	(0.03)	ND	ND	NS
21/10/98	ND	ND	NS	NS
12/11/98	ND	NS	ND	NS
18/11/98	ND	0.4	ND	NS
13/1/99	NS	NS	NS	NS
24/2/99	0.15	NS	0.37	NS
17/3/99	0.62	NS	NS	NS
07/4/99	ND	NS	NS	NS
20/4/99	NS	NS	NS	NS
26/4/99	NS	NS	NS	NS
13/5/99	0.43	NS	NS	ND
VS = Not sa VD = Not de ) = Below	mpled etected guantificat	ion limit of	0.1 µg/(	

DATE		SITES AND CONCENTRATION IN µg/(												
DATE	E	F	C	Cdr	Bdr	Ar	Br	D	н					
11/2/98	ND	0.29	ND	ND	11.11	0.06	0.14	ND	NS					
18/2/98	ND	ND	ND	ND	0.49	ND	ND	ND	NS					
25/2/98	ND	ND	ND	ND	3.14	ND	ND	ND	NS					
4/3/98	ND	ND	ND	ND	2.51	ND	0.17	ND	NS					
11/3/98	ND	0.19	0.10	1.14	19.13	0.17	ND	0.15	NS					
18/3/98	ND	0.13	ND	ND	7.81	ND	ND	ND	NS					
25/3/98	ND	ND	ND	ND	2.31	ND	ND	ND	NS					
22/4/98	ND	0.18	ND	ND	1.13	ND	ND	ND	ND					
12/5/98	ND	ND	ND	ND	1.42	ND	ND	ND	ND					
19/5/98	0.50	0.09	(0.04)	0.06	2.54	(0.04)	NS	0.06	ND					
12/8/98	(0.04)	0.08	0.07	ND	0.36	(0.03)	(0.03)	0.33	0.03					
23/9/98	(0.06)	0.21	0.02	NS	1.34	(0.01)	NS	0.29	0.02					
21/10/98	ND	0.05	ND	NS	0.19	ND	ND	0.08	ND					
12/11/98	ND	0.08	ND	NS	0.57	ND	(0.04)	0.06	ND					
18/11/98	ND	ND	ND	NS	ND	ND	ND	ND	0.03					
13/1/99	0.14	0.34	ND	NS	NS	0.17	ND	0.09	0.10					
24/2/99	0.11	0.25	0.107	NS	14.83	0.11	0.12	0.24	ND					
17/3/99	NS	0.4	0.31	NS	0.20	0.24	0.17	0.13	0.17					
07/4/99	NS	3.38	0.19	NS	40.36	ND	ND	0.18	0.24					
20/4/99	0.48	1.90	0.35	NS	17.97	NS	0.13	0.39	0.27					
26/4/99	0 1	0.66	0.12	NS	0.19	0.09	NS	0.19	NS					
13/5/99		0.03	NS	NS	0.33	ND	NS	0.02	NS					

# Table 4.4: Chlorpyrifos levels detected in the Hex River Valley

# Table 4.5: Chlorpyrifos levels detected in the Hex River Valley. Other Sites

	SITES AND CONCENTRATION IN µg/(								
DATE	L	к	L	M					
23/9/98	(0.02)	ND	ND	NS					
21/10/98	ND	ND	NS	NS					
12/11/98	ND	ND	ND	NS					
18/11/98	ND	0.09	ND	NS					
13/1/99	NS	NS	NS	NS					
24/2/99	0.09	NS	0.31	NS					
17/3/99	0.21	NS	NS	NS					
07/4/99	0.47	NS	NS	NS					
20/4/99	ND	NS	NS	NS					
26/4/99	ND	NS	NS	NS					
13/5/99	ND	NS	NS	ND					
IS = Not san ID = Not de ) = Below Recoveries	npled tected quantificati	on limit of (	0.5 µg/t						

DATE	SITES AND CONCENTRATION IN µg/												
DATE	E	F	C	Cdr	Bdr	Ar	Br	D	н				
11/2/98									NS				
18/2/98									NS				
25/2/98									NS				
4/3/98									NS				
11/3/98									NS				
18/3/98									NS				
25/3/98									NS				
22/4/98					1.4 Fenarimol	•		•					
12/5/98													
19/5/98	0.08				0.082   Fenarimol		NS						
12/8/98		Delta-		-			Delta-		Delta-				
23/9/98													
21/10/98		•			0.06 Fenarimol	•							
12/11/98				NS									
18/11/98					0.6 Fenarimol								
13/1/99				NS	NS								
24/2/99				NS									
17/3/99	NS			NS									
07/4/99	NS			NS									
20/4/99				NS		NS							
26/4/99				NS			NS		NS				
13/5/99			NS	NS			NS		NS				

### Table 4.6: Other pesticides detected in the Hex River Valley (Forensic Laboratory)

#### PIKETBERG

Tables 4.7 and 4.8 present total endosulfan and chlorpyrifos levels for Piketberg from May 1998 to April 1999, respectively. There were no detects of other pesticides reported by the SF laboratory for this period.

Low levels of contamination were found in all sites, and were most obvious during February and March 1999, corresponding to the irrigation period. Many of these sites include points used to derive potable water for drinking purposes (P1b, P3b, P7b, P4, P8t).

Both pesticides were detected in the water of the purification scheme supplying drinking water to a big area in the West Coast region (P8t), especially the endosulfan level in October 1998. This latter time period coincides with peak spraying of endosulfan, probable in the surrounding fruit and grape growing areas. Endosulfan levels also peaked in two of the borehole samples (P1b and P7b) shortly after the spraying period, suggesting movement of the pesticide through the soil after application.

Generally low levels of contamination were found in the two sites on the Berg River (P5 and P6) although one site p6 was not sampled consistently due to inaccessibility. Chlorpyrifos was generally detected more frequently than endosulfan, but a moderately high level of endosulfan was found in January 1999. The Berg River drains water from a large area of the Western Cape where intensive fruit farming and vineyard activity occurs upstream. Thus detects in the water of the Berg may only partly reflect local applications.

Low levels of contamination were noted for both total endosulfan and chlorpyrifos in the open dam (P3d). Endosulfan levels were somewhat correlated in time with endosulfan levels detected in the stream (P4) which drains the dam (P2d) above on the mountain. Water from this stream (P4) is purified for drinking for a community of about 250 people. Contamination seems to be more pronounced during the irrigation period, as in the Hex River.

In summary, the findings suggest low levels of detects of endosulfan and chlorpyrifos at numerous sites. No detections were made by the SF laboratory of other pesticides from sampling points in the Piketberg area.

DATE	SITES AND CONCENTRATION IN µg/(												
DATE	P1b	P2d	P3b	P4r	PSr	P6r	P7b	P8t					
13/5/98	0.13	ND	ND	(0.02)	ND	ND	NS	NS					
20/5/98	NS	ND	NS	ND	ND	ND	ND	ND					
1/7/98	ND	(0.09)	ND	ND	ND	ND	ND	ND					
2/9/98	ND	0.12	ND	(0.01)	(0.04)	ND	(0.02)	NS					
7/10/98	(0.05)	0.24	0.249	ND	ND	(0.07)	(0.01)	26.31					
11/11/98	013	0.20	(0.01)	0.20	(0.07)	0.25	1.15	(0.06					
25/11/98	ND	ND	ND	ND	ND	ND	ND	ND					
27/01/99	ND	ND	ND	ND	1.05	NS	ND	1.123					
17/02/99	0.47	0.67	ND	0.18	0.1	NS	0.21	(0.09					
10/03/99	0.44	0.13	ND	0.36	0.34	NS	0.59	0.16					
31/03/99	ND	ND	ND	0.24	ND	NS	ND	ND					
22/04/99	ND	(0.08)	(0.08)	ND	ND	NS	0.27	ND					
28/04/99	ND	ND	ND	ND	ND	ND	ND	NS					

# Table 4.7: Endosulfan levels detected in Piketberg

DATE		SITES & CONCENTRATION IN ug/												
DATE	P1b	P2d	P3b	P4r	P5r	P6r	P7b	P8t						
13/5/98	0.06	0.12	0.06	0.31	(0.03)	0.46	NS	NS						
20/6/98	NS	ND	NS	ND	ND	ND	ND	ND						
1/7/98	0.09	(0.03)	0.06	(0.03)	(0.04)	(0.04)	(0.03)	0.05						
2/9/98	ND	0.07	ND	(0.03)	0.06	(0.04)	(0.04)	NS						
7/10/98	ND	(0.02)	(0.02)	ND	(0.04)	(0.02)	(0.02)	0.05						
11/11/98	ND	(0.02)	(0.01)	(0.01)	0.05	(0.04)	0.09	(0.01)						
25/11/98	ND	ND	ND	ND	ND	ND	ND	ND						
27/01/99	ND	0.12	0.09	0.17	0.70	NS	ND	ND						
17/02/99	0.1	0.15	ND	0.12	0.22	NS	0.11	0.16						
10/03/99	0.23	(0.04)	0.8	0.17	0.39	NS	0.19	0.21						
31/03/99	ND	ND	0.4	ND	0.16	ND	ND	ND						
22/04/99	ND	80.0	0.09	ND	0.29	NS	0.18	ND						
28/04/99	0.09	0.1	(0.04)	0.1	0.08	0.09	0.08	NS						
NS = Not sa	mpled													

# Table 4.8: Chlorpyrifos levels detected in Piketberg

#### GRABOUW / VYEBOOM

Tables 4.9 and 4.10 present total endosulfan and chlorpyrifos levels, detected in Grabouw from April 1998 to May 1999, respectively. Where the SF laboratory detected other pesticides, these are also indicated in Table 4.11.

Low levels of contamination were detected in all the sites. Endosulfan contamination seemed to occur more frequently than chorpyrifos, although the latter is sprayed more regularly.

Contamination in all sites was detected consistent with the timing of spraying activities on farms in the area, (endosulfan sprayed during October and December; chlorpyrifos sprayed in August-September, and November - February), with endosulfan levels being raised after the October spray (in November) and the December spray (January to March 1999). The period February - March also represents the period following maximum irrigation applications and may thus pick up significant sub-surface drainage resulting from irrigation.



Figure 4.4: Endosulfan levels from sampling points in the Palmiet River (Grabouw/Vyeboom)



Figure 4.5: Chlorpyrifos levels from sampling points in the Palmiet River (Grabouw/Vyeboom)

The two open dams (C1d and C5d) were also contaminated consistently with endosulfan but less so with chlorpyrifos. Concentrations of endosulfan were also generally higher than chlorpyrifos and seemed to persist in the dams well beyond the period of application (Figures 4.6 and 4.7). Data on pH collected with sampling (Appendix F) did not suggest any mobilisation of sediments by pH changes as an explanation.

Sampling sites supplying water used for drinking yielded fairly consistent low levels of contamination for both endosulfan and chlorpyrifos. Particularly high levels for the dam (G2d) that supplies water to one household, for both endosulfan and chlorpyrifos were noted. There was intermittent presence of both endosulfan and chlorpyrifos (at low levels) in the stream (G7d) feeding the major dam supplying drinking water to Metropolitan Cape Town.



Figure 4.6: Endosulfan levels from sampling points in dams: Grabouw/Vyeboom



Figure 4.7: Chlorpyrifos levels from sampling points in dams: Grabouw/Vyeboom

Low levels of iprodione, azinphos-methyl and penconazole were also detected by the Forensic Laboratory on screening at time consistent with these pesticides' use in the area (Table 4.11).

In summary, the findings in Grabouw / Vyeboom are similar to other areas, with significant detects of chlorpyrifos and endosulfan in many of the sampling sites, including a number used for drinking water. As in other areas, irrigation appears to be an important mechanism for movement of pesticides to water. The results showing endosulfan in Grabouw dams are consistent with findings of Davies (1997) who also identified endosulfan as a common contaminant of dams in the Grabouw region. The concentrations detected in this study were of similar order to those found by Davies.

DATE		SITES & CONCENTRATION IN µg/												
DATE	G3r	G4r	C7d	G1d	G5d	G2d	CST	C6b	G9r					
23/4/98	(0.01)	ND	(0.09)	(0.06)	(0.08)	1.08	NS	ND	NS					
7/5/98	ND	ND	(0.09)	0.32	(0.09)	0.81	(0.09)	NS	NS					
27/5/98	(0.06)	0.59	ND	0.24	ND	1.78	ND	NS	NS					
29/7/98	ND	ND	ND	ND	ND	0.16	NS	NS	NS					
6/9/98	ND	ND	ND	(0.03)	0.70	(0.05)	(0.07)	NS	NS					
12/10/98	ND	0.10	0.20	(0.07)	ND	0.10	ND	NS	NS					
17/11/98	0.18	0.98	0.90	1.09	1.61	4.41	0.49	NS	NS					
2/12/98	0.62	ND	0.82	0.88	0.79	9.11	0.54	NS	NS					
18/1/99	0.50	1.09	1.14	0.34	1.2	5.84	0.59	0.26	NS					
18/2/99	0.30	1.38	NS	0.96	0.50	NS	0.80	NS	NS					
03/3/99	0.47	(0.03)	0.54	0.56	0.63	9.50	1.06	NS	NS					
24/3/99	0.914	ND	0.91	ND	0.45	6.44	1.77	ND	NS					
15/4/99	0.55	ND	0.15	0.16	0.50	1.85	0.88	NS	0.29					
23/4/99	ND	0.27	ND	ND	0.21	NS	0.17	NS	NS					
05/5/99	ND	ND	ND	ND	0.10	ND	NS	ND	ND					
IS = Not sa	mpled													

Table 4.9:	Endosulfan	levels	detected	in Grabouw
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# Table 4.10: Chorpyrifos levels detected in Grabouw

DATE		SITES & CONCENTRATION IN µg/												
DATE	G3r	G4r	G7d	G1d	G5d	G2d	GSt	C6b	G9r					
23/4/98	ND	ND	(0.02)	ND	(0.04)	0.12	NS	ND	NS					
7/5/98	ND	ND	0.05	0.06	0.06	ND	ND	NS	NS					
27/5/98	(0.04)	0.10	ND	(0.03)	ND	0.07	ND	NS	NS					
29/7/98	ND	ND	ND	ND	ND	(0.01)	NS	NS	NS					
6/9/98	ND	(0.01)	ND	ND	ND	0.06	(0.04)	NS	NS					
12/10/98	ND	ND	0.1	0.15	ND	ND	ND	NS	NS					
17/11/98	0.12	ND	0.18	ND	ND	ND	ND	NS	NS					
2/12/98	ND	ND	ND	ND	ND	ND	0.52	NS	NS					
18/1/99	0.15	0.14	0.24	0.14	0.32	0.39	0.07	0.06	NS					
18/2/99	0.18	0.66	NS	ND	0.14	ND	ND	NS	NS					
03/3/99	ND	ND	ND	ND	ND	1.62	ND	NS	NS					
24/3/99	ND	ND	ND	0.2	ND	1.28	0.32	ND	NS					
15/4/99	0.28	ND	0.31	0.07	0.23	0.47	ND	NS	0.16					
23/4/99	ND	ND	0.21	ND	0.41	NS	0.12	NS	NS					
05/5/00	ND	ND	0.13	0.15	ND	0.07	NS	ND	0.10					

DATE		SITES & CONCENTRATION IN µg/(												
DATE	G3r	G4r	G7d	C1d	C5d	G2B	CST	C6b	C9r					
23/4/98	Iprodione		Azinphos-		Azinphos-	Iprodione		-	-					
7/5/98								NS	NS					
27/5/98								NS	NS					
29/7/98							NS	NS	NS					
6/9/98								NS	NS					
12/10/98		-		Pencon-				NS	NS					
17/11/98								NS	NS					
2/12/98								NS	NS					
18/1/99									NS					
18/2/99						NS		NS	NS					
03/3/99								NS	NS					
24/3/99									NS					
15/4/99								NS						
23/4/99						NS		NS	NS					
05/5/99									NS					
VS = Not sa	ampled													

# Table 4.11: Other pesticides detected in Grabouw (Forensic Laboratory)

#### OVERALL DETECTIONS

If one reviews the overall profile of detections, it is clear that detections were common in all three areas.

Chlorpyrifos was detected most frequently in Piketberg, 62 (66%) out of 94 times sampled compared to Hex River, 96 (52%) out of 184 times and Grabouw 51 (49%) out of 104 times. Endosulfan was found most frequently in Grabouw, 72 (69%) out of 104 times compared to Hex River 85 (46%) out of 184 times and Piketberg, 37 (39%) out of 94 times (Table 4.12).

Table 4.12 shows the proportion detected above our QL, and proportion above 0.1 "g// (EEC limit) in the three areas, and compares total detections stratified by whether the sample sites were groundwater or surface water.

# Table 4.12: Number of detections in the three areas sampled, and detections stratified by groundwater or surface water

PESTICIDE, AREA AND NUMBER OF DETECTS (PERCENTAGE)								
LEVEL	CHLORPYRIFOS				ENDOSULFAN			
	HEX	PIKET-	GRABOUW	TOTAL	HEX	PIKET-	GRABOUW	TOTAL
ALL	96 (52)	62 (66)	51 (49)	209 (55)	85 (46)	37 (39)	72 (69)	194 (51)
> QL	83 (45)	41 (44)	40 (38)	164 (43)	60 (33)	24 (26)	59 (57)	143 (37)
> EEC	64 (35)	21 (22)	28 (27)	113 (30)	60 (33)	24 (26)	59 (57)	143 (37)
	Ground	iwater	Surface	Water	Groundwater		Surface Water	
ALL	29 (	55)	180	(55)	17 (32)		177 (47)	
>QL	23 (	43)	141	141 (43)		12 (23)		40)
> EEC	25 (	47)	148 (45)		12 (23)		131 (40)	
ALL : All c	detections							

The slightly higher frequency of detection, especially of endosulfan and its metabolites, in Grabouw compared to Hexriver and Piketberg might be explained by the more frequent rainfall and the spraying of endosulfan during the irrigation period. The more frequent levels of contamination by chlorpyrifos in Piketberg, although at low levels is unexpected because it is not sprayed in the wheat farming areas and the soil and climatic conditions are not more conclusive to contamination than Grabouw and Hexriver. However, this finding might be explained by inputs into the Bergriver by surrounding fruit and grape farming areas outside the area of investigation.

Although the number are based on small samples (only 5 sites in the three study areas, totalling 53 samples over the study), detections of chlorpyrifos at low levels appears as common in groundwater sources as for surface water (about 43%), but endosulfan detections slightly lower for groundwater (23%) compared to surface water (40%).

It is also worth noting that the SF laboratory detected sporadically a number of other pesticides in both the Hex River and Grabouw/Vyeboom areas that are commonly used in deciduous fruit farming. These detections (of azinphos-methyl, fenarimol, iprodione, deltamethrin, penconazole and prothiofos) occurs at times more or less consonant with usage of these agents in the industry, and at relatively low levels (below  $2 \mu g/0$  but not as low as detections achieved in the PENTECH laboratory<sup>1</sup>. However, their presence in the samples adds consistency to the picture obtained and to the construct validity of the overall results.

Both cholrpyrifos and endosulfan, and some of the other pesticides detected in the study are considered to have a low pollution likelihood (Custafson, 1989). Despite this they were detected consistently in all three areas in both groundwater and surface water. Other factors such as soil characteristics, shallow water tables and intensive spraying probably explain the presence of these pesticides in water. Previous studies (Vighi and Funari 1995, Jabbar *et al*, 1993, California Environmental Protection Agency, 1996) have shown that these factors are important in pesticide contamination of water. Had the PENTECH laboratory been able to undertake regular analyses of pesticides such as Iprodione (which is extensively used in all three areas), azinphos-methyl (that has a high pollution likelihood), and simazine and vanmidothion (high usage and pollution likelihood), we might have established similar patterns for these pesticides. This is especially likely in Piketberg where the use of endosulfan and chorpyrifos is only for fruit farming and does not occur in the wheat farming areas. However, in light of the SF laboratory screening findings of a few detections of ipriodione and azinphos-methyl, these suppositions are only tentative and require further exploration.

As found previously by Domagalski (Domagalski, 1997), irrigation seem to be an important trigger for both leaching and run-off events. In that study, high levels of contamination was found in irrigation drainage water flowing into the river, and in this study the enclosed drain in Hexriver and dam sites in Grabouw (P1d, P5d, P6d) showed high levels of contamination during the irrigation period. Our findings suggest irrigation as a more important factor than rainfall, consistent with previous research in the same study area (Weaver, 1993).

<sup>1</sup> PENTECH quantification limits were 0.1 ug// for endosultan and 0.05 ug// for chlorpyrifos.

# 4.4 OVERVIEW: FIELD RESULTS IN RELATION TO REGULATORY STANDARDS AND TO OTHER RESEARCH FINDINGS

How do the results compare to health and other regulatory standards?

Although the WHO does not provide a health-based standard for drinking water for either chlorpyrifos and endosulfan, the EPA does post Health Advisory levels for short term (1-day and 10-day), longer-term (7 years or 10% of an average lifetime) and for lifetime exposures for chlorpyrifos in drinking water for adults and children (Table 4.13). The levels for children are 30  $\mu$ g/t for all durations of exposure and for adults are 100  $\mu$ g/t or 20  $\mu$ g/t, depending on duration. The Australian Drinking Water Guidelines also cite 30 mg/t as its Health Value for endsulfan, based on a calculation derived from 10% of an ADI.

A much lower standard is held by the California Inland Surface Water Plan (CAISWP) California Environmental Protection Agency, 1996) with an endosulfan water quality criterion of  $0.9 \ \mu g/t$  (30 day average). Even lower is the European Community (1980) universal standard of  $0.1 \ \mu g/t$  and  $0.5 \ \mu g/t$  for a single pesticide and total pesticides, respectively. There are no South African (South African Department of Water Affairs, 1996 or WHO (WHO, 1992) guideline values for all pesticides investigated in the study. Standards to protect aquatic ecosystems are far lower than those for human health.

HUMAN HEALTH'	HUMAN HEALTH'		Pesticide & Standard (µg/l)		
			Endosulfan	Chlorpyrifos	
USEPA Health	10 kg child	1 day	n/a	30	
Advisory		10 day	n/a	30	
		(7 years)	n/a	30	
	70 kg adult	(7 years)	n/a	100	
		lifetime	n/a	20	
	DWEL		n/a	100	
California	30 day average		0.9	n/a	
EEC			0.1	0.1	
Australian Healt	h Value (10% ADI)		30	n/a	
World Health Or	ganisation (WHO)		n/a	n/a	
QUATIC SAFETY	•				
Australian			0.01	0.01	
South Africa			0.003	n/a	

#### Table 4.13: Comparison of Standards: Human Health, Aquatic Safety

n/a = not available;

Sources:

<sup>e</sup> European Community, 1980, USEPA, 1986; National Health and Medical Research Council, and Agriculture and Resource Management Council of Australia and New Zealand, 1996; California Environmental Protection Agency, 1996

From Dallas & Day 1993

In relation to all these health-based standards, results reported in this study are generally low. The level of chlorpyrifos contamination in all three areas was generally low in relation to the EPA lifetime drinking water health advisory and DWEL, but moderate to high in relation to the stringent European Community single pesticide standards. The level of contamination in the enclosed drain in the Hex River Valley (Bdr) was consistently in range of lifetime EPA Health Advisory for drinking water for adults, but this is not a site used for drinking water. Endosulfan contamination in all three areas was also moderate to high when compared to the CAISWP and EEC standards and the levels of the other pesticides also mostly exceeded EEC standards. The levels of both pesticides in most of the study sites where water is directly used for drinking consistently exceeded the EEC standard but not the health-based standards from the EPA, CAISWP or Australia. The implications of these findings for human health are discussed in more detail in the final two chapters.

Relatively few studies have previously detected endosulfan (Vighi and Funari; 1995; Oskam *et al.*, 1993; California Environmental Protection Agency, 1996, Vighi and Funari 1995, California Environmental Protection Agency, 1996). Monitoring in Texas between 1984 and 1997 found the presence of endosulfan in only 1% of surface water samples (Texas Center for Policy Studies, 1999). The levels found in this study are consistent with the range (0.1-100  $\mu$ g/l) found in groundwater (Vighi and Funari 1995; Vighi and Funari 1995; Vighi and Funari 1995; California Environmental Protection Agency, 1996, and California Environmental Protection Agency, 1996) and surface water (Oskam *et al.*, 1993).

Espigares *et al*, found chlorpyrifos at least once in all of the 22 points sampled on the Guadalquivir River in Spain in 1997 at mean concentrations that ranged from 0.01  $\mu$ g/i and 0.47  $\mu$ g/i. Chlorpyrifos was also detected at slightly lower concentrations (range 0.006  $\mu$ g/i to 0.32  $\mu$ g/i) in another study that tested a new nested surface monitoring network to measure variability in pesticide concentrations in the San Joaquin River Basin during the irrigation season (Domagalski, 1997). High quantities were also found during a spill in a UK river (Raven *et al*, 1989). In contrast, chlorpyrifos was not detected in a study that monitored the seasonal occurrence of pesticides and other organic pollutants at the mouth of tributaries of the Nile as they flow into the Mediterranean Sea (Abassy *et al*, 1999) nor in another investigating residue contamination of the Coho Salmon in the Great Lakes (Clark *et al*, 1984).

Contamination by both endosulfan and chlorpyrifos found in all three areas in this study appears more consistently than found previously in other studies, probably a function of increased frequency of sampling (Domagalski, 1997). Spraying of endosulfan and chlorpyrifos in Grabouw which ranges from 0.5 - 1.5 kg active ingredient per hectare, seems higher than in developed countries.

Of particular note was that this study contrasted to some extent with previous research conducted in the Hex River Valley in 1990, where no evidence was found for pesticides reaching ground water (Weaver, 1993). However, that study identified a different set of pesticides for analysis and focused primarily on ground rather than both ground and surface water. In addition, analyses for Weaver's study were conducted by the laboratories of the South African Bureau of Standards (SABS) using analytical techniques for which the quantification limits were substantially higher than in the present study (lowest limits of detection given in Weaver's study as  $0.5 \ \mu g/i$  as compared to limits in this study of 0.05 or  $0.1 \ \mu g/i$ ).

Nonetheless, one sampling point in the 2 studies were identical (site H), and the findings of this study do suggest that low levels of water contamination are occurring in both surface and to a lesser extent in ground water. Of importance is the observation that the problem is not confined to the Hex River but is ubiquitous in all 3 study areas chosen for investigation. Out of 382 samples, there were 30% detects above the EEC limit of 0.1  $\mu$ g/l, for chlorpyrifos and 37% for endosulfan.

One important limitation to this monitoring is the reliance on grab sampling, with the result that intermittent monitoring may give false estimates of true exposures, or inadequate characterisation of contamination patters. For example, Domagalski (1997) showed that thrice weekly sampling of surface water in the San Joaquin River Basin was more than twice as likely to identify concentrations exceeding State water standards than single weekly sampling. Efforts to develop methods that sample water sources on a continuous basis, to provide an integrated assessment of water contamination by pesticides should be explored. In summary, the field results have demonstrated widespread detections of low levels of endosulfan and chlorpyrifos in water sources in farming areas in the Western Cape. Concentrations have generally been low, particular for ground water sources, and temporal patterns generally consistent with irrigation impacts and, to a lesser extent timing of spray activities. QA measurements provide adequate support for the validity and reliability of the data on which these findings are based. The implications for human health are explored in the next chapter.

# Chapter 5:

# HUMAN HEALTH

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This chapter explores different considerations related to human health arising from the study. Knowledge, Attitudes and Practices of rural farm residents in relation to water and pesticides assessed from a set of farm-based surveys conducted in the study areas are presented and discussed. In addition, the implications for human health of the concentrations of pesticides detected in this study are discussed in the latter part of the chapter.

# 5.1 KNOWLEDGE, ATTITUDES AND PRACTICES OF RURAL FARM RESIDENTS IN RELATION TO WATER AND PESTICIDES

Fifty-six farms in total participated in the surveys in the three regions. All study farms as well as a random sample of farms in two of the study areas were chosen. Demographic characteristics of respondents are summarised in Table 5.1. Participants were mostly male, and average age was in the late 30's, with Grabouw having the oldest participants (average age = 46 years). Water sources for domestic uses are summarised in Tables 5.2 (by farm as unit) and 5.2a (by respondent as unit).

SITE	SAMPLE(FARMS)	ACE (YE	ARS)	GENDER	
		MEAN (SD)	RANGE	M	F
Slanghoek	Pilot, n = 40 (12)	33.0 (8.6)	18-61	38	2
Grabouw / Vyeboom	Random sample n = 112 (29)	39.8(11.2)	19-74	86	26
	Study farms, n = 8 (2)	45.0 (10.2)	28-64	7	1
	All Grabouw participants n = 120 (31)	40.3 (11.2)	19-74	93	27
Hex River	Random sample, n = 53 (13)	34.7 (11.1)	18-63	44	9
	Study farms, n = 16 (4)	36.8 (11.9)	22-65	11	5
	All Hex River participants n = 69 (17)	35.2 (11.3)	18-65	55	14
TOTAL	229 (60)	37.5 (11.2)	18-74	186	43

# Table 5.1: Demographic characteristics of study participants: Knowledge, Attitudes and Practices in relation to water and pesticides

In the Hex River Valley and Grabouw/Vyeboom areas, two arms to the samples were included: Study farms were those where water sampling took place, while the random sample was drawn from all other farms in the respective regions to achieve a representative sample for those areas.

PURPOSE	SOURCE REPORTED*	SLANGHOEK	CRABOUW / VYEBOOM	HEX RIVER	ALL FARMS
_		n = 12	n = 31	n = 17	n = 60
	Water storage dam	50%	7496	65%	67%
	Fountain / borehole	58%	55%	76%	62%
Drinking	Rainwater entrapment	8%	1%	0%	396
	Farm dam	8%	71965	23.5%	45%6 <sup>\$</sup>
	River	8%	10%6	0%	7%6
	Water storage dam	50%	74%	65%	67%
Domostic use	Fountain / borehole	58%	55%	76%	67%
other than	Rainwater entrapment	8%	1%	0%	3%
drinking	Farm dam	8%	7196 <sup>s</sup>	23.5%	45965
	River	8%	10%	0%6	7%
	Water storage dam	25%	90%	71%	72%
	Fountain / borehole	58%	35%	77%	52%
Field	Rainwater entrapment	0%	396	0%	2%
ablutions	Farm dam	8%	80%5	35%	53%65
	River	50%	10%	0%	15%
	Other: sub-surface drain	17%	0%	696	5%
Recreation	Swimming in farm dam	66.7%	29%	2996	48%

## Table 5.2: Water Sources by purpose and by area, as percentage of farms

 Reported as supplied for the farm. Percentages are not mutually exclusive as respondents may report more than one source.

<sup>5</sup> Includes farm water storage dams

Groundwater and water from relatively pristine mountain sources appear to be the most important source for drinking for the farming community. Relatively few rural residents are dependent on surface water for drinking\*. Sources of water for domestic purposes closely mirrors that for drinking. For use in the field (both drinking and othen, river water is used (35%) in the Slanghoek area and farm dams in moderate proportions in all three areas. In the Grabouw area, water from the Groenland water scheme is stored in farm dams for drinking on many farms. Thus, water sources used for drinking on farms appear to be mainly from protected sources, although non-drinking usage and usage while in the field appears to make use of more surface water. However, the majority of respondents still are using relatively protected water.

The risks of pesticide drift appear significant (Table 5.4). About a third of respondents reported living within 10m of the nearest site of spraying. Seven (11%) respondents reported noting that pesticides from local spray had within the preceding 6 months drifted into their nomes (Table 5.4).

PURPOSE	SOURCE REPORTED*	SLANGHOEK	CRABOUW / VYEBOOM	HEX RIVER	ALL RESPONDENTS
		n = 40	n = 120	n = 69	n = 229
	Water storage dam	30%	58%	5296	52%
Brinking	Fountain / borehole	55%	40%	58%	48%
Drinking	Rainwater entrapment	5%	1%	0%	196
	Farm dam	8%	47%6 <sup>s</sup>	9%	28%55
	River	596	3%	0%	2.6%
	Water storage dam	30%	79%	57	63%
Field	Fountain / borehole	27%	24%	55%	34%
ablutions	Sub-surface drains	8%	0%	7%	496
	Farm dam	1196	61%5	16%	38%55
	River	3296	4%	0%	8%
Recreation	Swimming in farm dam	22%	14%	15%	17%

### Table 5.3: Water Sources by purpose and by area as percentage of respondents

 Reported as available by respondent. Percentages are not mutually exclusive as respondents may report more than one source.

<sup>s</sup> Includes farm water storage dams

#### Table 5.4: Distance from pesticide spraying activity by area as reported by farm residents

DISTANCE FROM HOUSEHOLD		SLANGHOEK	GRABOUW / VYEBOOM	HEX RIVER	ALL RESPONDENTS	
		n = 40	n = 120	n = 69	n = 229	
Nearest	< 10m	58%	30%	30%	35%	
sprayed	10 - 50m	33%	52%	45%	46%	
Orchard / vineyard	> 50m	10%	17%	25%	18.5%	

In addition, opportunities presented for multiple sources of exposure appear to be relatively high (Table 5.5). A sizeable number of respondents used pesticides, either for domestic pest control or for nome gardening, and about half reported obtaining these pesticides from the farm store. However, re-use of pesticide containers was low, reported by only 9% of farm residents, and was always reported as being for the purpose of serving as a garbage bin. Simultaneously, awareness of the hazards of pesticides was reported as high, with farm workers scoring slightly more highly than farm owners or managers.

RISK	SLANGHOEK	GRABOUW / VYEBOOM	HEX RIVER	ALL RESPONDENTS
	n = 40	n = 120	n = 69	n = 229
Reported spray drifting into home	18%	13%	4%	11%
Use of pesticides at home for pest control	30%	48%	36%	41%
Use of pesticides for home garden	13%	42%	29%	32.6%
Of those using pesticides, what proportion obtain pesticide from farm	33%	58%	51%	53%
Use of pesticides at home in past 6 months	30%	62%	50%	54.6%
Use of pesticide container at home	15%	12%	0%	9%
Knew Pesticides were dangerous to their health	88%	93%	94%	92%
Farmers	70%	84%	94%	85%
Farm workers	93%	96%	94%	95%

# Table 5.5: Risk Activities, knowledge and attitude toward pesticides on farms reported by farm residents

The surveys suggest that a number of different potential routes of exposure for farm residents may be important to consider. In particular:

#### Through water:

In Grabouw, the storage of drinking water in farm dams is widespread. If dams are contaminated as a result of proximity to pesticide spraying, as appears to be the case from results in Chapter Four, this may be a route of exposure worth attention and control. Up to 18% of farm workers reported spray drifting into their homes, tending to confirm the significance of this mode of exposure. Swimming in farm dams (16.8%) may present an additional source of exposure, although probably minor in quantity.

#### Though routes other than water:

Between 30 and 58% of farm residents live in very close proximity (<10ml to orchards, vineyards or fields subject to pesticide application, increasing opportunities for exposure through drift. A moderate percentage of farm residents make use of pesticides at home, of which about a half is obtained from farm sources. Use of containers occurs at a low level, but reportedly only for use for garbage. Reuse of containers for water storage did not appear to occur at all.

In general, however, awareness of pesticides as a health hazard appears relatively good, and was better amongst farm workers than amongst farmers. The positive effects of education reported by some of the employers in the area appear to be borne out by very low levels of re-use of containers, which augurs well for public health and occupational hygiene measures need to control pesticide exposure. Collateral evidence from the survey of farms conducted in Stellenbosch in 1998 suggest that the pattern in this area is not dissimilar to that in the Slanghoek, Grabouw and Hex River areas (see box).

#### Water and Sanitation Conditions: Farm Survey in the Stellenbosch area: DOPSTOP Project, Aug-Oct 1998

665 households on 53 randomly chosen farms

- Just over 50% of respondents made use of borehole water for drinking.
- However, 9 respondents (1%) made use of river water, and 19% made use of dams for water used for drinking. This is a total of about 20% using surface water
- 23% dependent on bucket or pit latrines for toilet
- Of these, 10 families use a communal pit
- 27% have taps outside their houses.
- Of these, 46% are communal taps
- 93% of households reported a dam on the farm
- Of these, 45% reported farm residents use the dam for swimming

Source: DOPSTOP Project Research Report, October 1999.

# 5.2 DIETARY CONSUMPTION

Table 5.6 lists sampling points where water was used for drinking purposes. A set of assumptions was required in order to estimate daily dietary consumption of pesticides in drinking water in the study areas. These assumptions are simplistic in the extreme but are used heuristically in order to derive a rough estimate of total dietary intake in relation to published values for an Acceptable Daily Intake (ADI). The assumptions include the following:

- The grab samples are representative of a population distribution of levels pertaining in the sampled sites and can be used to extrapolate to consumption over the year.
- The nature of the exposure is cumulative and peak exposures or exposures of increased intensity
  are of no relevance to estimation of health implications of dietary intake other than their
  contribution to the average daily intake over a prolonged period.
- Only sampling sites reported as providing drinking water are examined.
- Consumption of water is assumed to be 2 r for an adult. Additional fluid intake in other beverages is assumed to be additional to drinking water.
- The average body weight of an adult is assumed to be 60kg.

Note that in this model, exposure is assumed to be to a single pesticide. Possible additive or synergistic effects of exposure to several different pesticides cannot be accounted for. Moreover, the methodology does not account for endocrine disrupting properties of chemicals, which might occur at concentrations far lower than convention NOAEL and NOELs.

The modeling in Table 5.7 assumes two scenarios: A worst case scenario where drinking water concentrations are characterised at the highest concentration detected at the site; and a scenario where the concentrations of the detections found at each site are averaged using a root mean square conversion. These are then used to estimate total daily intake of pesticide and compared to published ADIs (IPCS, 1999) to calculate a percentage of ADI derived through water consumption.

AREA	POINT	POPULATION				
Grabouw	G7	Feeder stream to dam supplying 51% of Cape Town's drinking water				
	C6	Supplies 3 adults on a farm (Owners)				
	G8	Tap in Office, representative of the water supply for about 50 residents on farm				
Piketberg	P1	Farm community of about 200 people using the borehole for drinking water				
	P3	Farm managers house - about 5 adults and children				
	P4	Moravian village of about 200 residents using stream for drinking water				
	P7	Borehole on wheat farm supplying about 15 farm residents				
	P8	Tap at outlet of water purification scheme supplying water to West Coat (about 150 000 people)				
Hex River	L	Tap at Irrigation Board, representative of the reticulated drinking water supply to the Hex River Valley, including town residents in De Doorns				
	н	Deep well, supplying about 50 farm residents				

# Table 5.6: Sampling points where local populations use water for drinking in the three study areas

Of importance is the consideration that the assumptions used in this modeling are vulnerable to many confounding factors. Clearly, not all consumed water will be from the water point identified by the study, and may be taken in beverage form or other supplies. This might lead to an overestimation of risk. However, other factors may underestimate risk. Workers in hot and sunny environments may increase their intake of water in field conditions, and data earlier in this chapter suggest that workers in the field are more likely to use surface water sources when in the fields. Moreover, vulnerable subjects, such as children, have higher water consumption per kg body weight and will therefore have greater risk than the adults used in our modeling. While many of these factors add significant margins of uncertainty, the results provided here are useful to explore methods for standard setting for the South African context.

What the tables suggest is that only a small proportion of the ADI may be contributed by contamination of drinking water for these populations. Of the two pesticides, endosulfan is of greater importance because of a lower ADI and a generally higher concentration found. Only in the case of the peak concentration of endosulfan for the site providing water for the water purification system for the West Coast in Piketberg, did the percentage of the modeled ADI exceed 10%. All the average estimates except that for the same site providing water for the water purification system, the percentage ADI did not exceed 1%. **Given the use by the WHO of a range of 1 to 10% of ADI contributed by pesticides in drinking water, in modeling of health risks due to pesticides, it may be reasonable to infer that the levels found in drinking water in this study fall below levels that would be of immediate concern.** In particular, the levels for both endosulfan and chlorpyrifos at the site for the stream feeding the Theewaterskloof dam (G7) that is a major supplier of urban drinking water for Cape Town, were at concentrations that approximated to less than 1% of an ADI.

					ROOT MEAN	DAILY II	NTAKE
	DOINT	PEAK CONCEN-	DAILY INTAKE BASED ON PEAK		SQUARE	BASED ON ROOT MEAN SQUARE CONCENTRATION	
AKEA	POINT	TRATION (ug/t)			CONCENTRATION		
					(µg/i)		
			(µg/kg)	%ADI		(µg/kg)	%ADI
ENDOSULFAN	1						
Grabouw	G6	0.26	0.009	0.14	0.13	0.004	0.07
	G7	1.14	0.038	0.63	0.53	0.017	0.30
	G8	1.77	0.059	0.98	0.74	0.025	0.41
Piketberg	P1	0.44	0.015	0.24	0.15	0.005	0.09
	P3	0.25	0.009	0.14	0.31	0.010	0.17
	P4	0.36	0.012	0.20	0.14	0.005	0.09
	P7	0.27	0.009	0.15	0.22	0.007	0.12
	P8	26.31	0.877	14.6	10.74	0.360	6.00
Hex River	J	0.62	0.021	0.34	0.27	0.009	0.15
	н	0.89	0.030	0.49	0.25	0.008	0.14
CHLORPYRIF	DS .						
Grabouw	G6	0.06	0.002	0.02	0	0	0
	G7	0.31	0.010	0.10	0.12	0.004	0.04
	C8	0.52	0.017	0.25	0.19	0.006	0.06
Piketberg	P1	0.23	0.008	0.80	0.08	0.003	0.03
	P3	0.77	0.026	0.26	0.32	0.011	0.11
	P4	0.31	0.010	0.10	0.12	0.004	0.04
	P7	0.19	0.006	0.60	0.09	0.003	0.03
	P8	0.21	0.007	0.70	0.08	0.003	0.03
Hex River	1	0.21	0.007	0.70	0.11	0.004	0.04
	н	0.27	0.009	0.90	0.14	0.005	0.05
ENDOSULFAN:	ADI < 0.006	mg/kg bw (IPCS, 19	999)				
CHLORPYRIFOS	S: ADI < 0.01	mg/kg bw (IPCS, 19	999)				
Note: Only res	sults used w	here recoveries we	ere > 70% a	nd < 130	96.		

# Table 5.7: Modeling of daily intake of pesticides for study populations using selected sampling points for drinking water (µg/t)

However, there are some issues to consider that may alter the significance of these exposures. Rural populations may experience considerable exposures through routes other than drinking water to that experienced by non-rural residents (see for example, Tables 5.4 and 5.5). Moreover, the toxic effects of endocrine disruption may occur at levels far lower than current risk assessment methodologies cater for. Nonetheless, the margins of error inherent in the modeling would have to be quite substantial to elevate the levels sufficiently to represent immediate dangers to human health. For example, although the worst-case (highest concentration) scenario is not a realistic model, it does alert one to the fact that the margin of error would have to be very large to negate this additional risk.

What do these levels mean in practice? As pointed out in Chapter 4, the levels found in this study generally fall below various guidance standards issued in other countries, except for the stringent criteria held by the EEC, and in relation to dietary intake, levels do not appear to warrant immediate threats to human health. However, much of our present knowledge about dose-response effects in relation to chronic impacts of pesticides is limited by lack of adequate data, and thresholds for concern are being continually revised downward as more empirical evidence emerges.

Chlorpyrifos is an organophoshate and has been associated with a number of health effects including neurological, respiratory and reproductive effects. The WHO classifies it as moderately toxic (class II) to humans. Endosulfan is classified as class II and has been shown in vitro to have oestrogenic effects comparable to estradiol (Soto et al, 1994). Both Endosulfan and Chlorypifos are listed as endocrine disruptors (see Appendix D) and both pesticides are very toxic to aquatic life (DWAF, 1996). Thus, although the contamination by these pesticides of sources used for drinking water occurs at low levels, their presence, and their potential for bioconcentration and bioaccumulation, should warrant further attention. The implications for human health and surveillance strategies are discussed in more detail in the next chapter.

# CHAPTER 6:

# **GENERAL DISCUSSION**

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# 6.1 STUDY FINDINGS IN RELATION TO PROJECT OBJECTIVES

In terms of the aim of the study set out in Chapter One, most of the main objectives have been met. We have identified study areas of concern (Hex River, Piketberg and Grabouw/Vyeboom), where the likelihood of pesticides entering ground and surface water may be anticipated to be higher than for other regions (objective 1), and have been able to measure the presence of pesticides at low concentrations in these areas of concern (objective 2). Reliable and valid methods for the accurate determination of the main pesticides in rural water in the Western Cape (endosulfan and chlorpyrifos) have been established at the Peninsula Technicon laboratories, and the practicability of detection of pesticides at low levels confirmed (objective 3). By relating the detections to data on spray patterns, climate, irrigation practices and other factors, we have been partly able to interpret the results so as to characterise the extent to which pesticides contaminate rural water supplies in the region (objective 4). However, the exact mechanisms, routes and agricultural risk activities associated with entry of pesticides into rural water sources could not be adequately addressed in this study, and is the subject of a recommendation for future research.

Non-occupational routes of human exposure (objective 5) and a profile of rural water sources for drinking and ablution (objective 6) have been explored in this study through a series of user surveys. Although initially intended to be linked to a full dietary intake survey, assessment of the health impacts through food and water intake (objective 7) was curtailed and substituted by modeling using normative water intake figures. Thus the modeling of human health impacts was somewhat simplified, although useful comparisons to the Acceptable Daily Intake (IPCS, 1999b) enabled us to partially meet this objective.

# 6.2 REVIEW OF RESULTS

As is to be expected, the results show a wide degree of variability in the presence of detections and in concentrations of detections found between sites, and between regions, although relative consistency in the pesticides found (mainly chlorpyrifos and endosulfan). For example, in the Hex River sample site G (lowest point on the Hex River) yielded only one detection of endosulfan above the quantification limit in the course of the study, while point Bdr (sub-surface drain) consistently (17 out of 22 samples) yielded levels of endosulfan above the quantification limit (Table 4.7.1). Similarly, detections of total endosulfan were recorded above the PENTECH quantification limit in only 26% of samples taken in Piketberg but in 57% of samples in Grabouw/Vyeboom (Table 4.15).

To what extent is such variability attributable to laboratory error? Careful attention to standardised field and laboratory protocols for sampling, extraction and analysis, as conducted in this study should have successfully minimised the contribution to variability in results from intra-laboratory error. Furthermore, application of Quality Assurance (QA) procedures in this study sought to bolster the confidence we could place in the results.

When measuring pesticides at very low concentrations (parts per billion), as was done in this study, variability between laboratories in analytical measurements may seem relatively large without implying lack of validity. The inherent instability of the samples, the timing of sampling, and the presence of time delays may differentially affect the "decay" of organic compounds. Additionally, adsorption may occur of pesticides onto different species in the water, and different methods of sample preparation may detect different fractions of the species present. While QA analyses attempt to control for these factors as far as possible, it is not possible to standardise such conditions entirely, and it is not unusual for such differences to be encountered in usual analytical practice. In this light, QA results in this study provide sufficient reassurance that the PENTECH laboratory results are a valid reflection of the true situation, particularly when averaged over a population of samples. In the Quality Assurance programmes with the SF and ARC laboratories, the PENTECH results showed good agreement in the early stages of the project for discriminating qualitatively for the presence or absence of selected pesticides, as well as agreeing on the patterns of high versus low concentration. Table A.7.5 in the Appendix, in particular, illustrates most clearly consistent patterns for detections at low levels with reasonable agreement between all three participating laboratories.

There were difficulties encountered with Quality Assurance comparisons in the second half of the project, largely related to disruption of the GC column at the SF laboratory by a sediment sample. However, the consistency of the PENTECH findings across the two spraying seasons, and strict adherence to quality control procedures support our belief that the PENTECH results offer a good overview of the extent of the problem. PENTECH results for samples taken from dams in the Grabouw/Vyeboom area were also consistent in the detection, and concentrations of endosulfan and chlorpyrifos in the study by Davies conducted on dams in the same region (1997).

Moreover, there is a specificity to the results which supports the inference that measurable levels of endosulfan and chlorpyrifos were consistently found across study sites. Unlike the case with endosulfan and chlorpyrifos, there were no detections of BHC (gamma, beta and delta isomers), 4,4-DDT and 4,4-DDE, or dichlorvos by the PENTECH laboratory in the pilot phase of the project in any of the samples taken in the Hex River Valley. Moreover, the SF laboratory did sporadically detect other pesticides in high use in the Hex River and Grabouw/Vyeboom areas (iprodione, azinphos-methyl). The former group of pesticides would not be expected to be identified in the survey areas, while the latter might be anticipated to be present in low concentrations. This pattern thus further strengthens the postulated validity of the overall findings.

The strategy of using the SF laboratory to screen for pesticides had both positive and negative effects. It rapidly enabled the project team to focus on the main pesticides of concern through developing sensitive analytical methods with substantially lower levels of detection than previously encountered in field studies (Weaver, 1993), as well as providing opportunity for ongoing quality assurance comparisons. However, the project team may well have underestimated the scope of the problem by reliance on the SF laboratory for pesticides other than chlorpyrifos and endosulfan, since the quantification limits for the SF laboratory were not subject to the same criteria as that for the PENTECH laboratories. Low concentration of commonly used pesticides in Grabouw (such as iprodione, azinphos-methyl and simazine) may well have escaped detection as a result of this strategy. However, even were this to be the case, it is important to remember these are very low concentrations, and conclusions similar to those made for endosulfan and chlorpyrifos regarding health impacts would most likely have been made. At the very least, the screening by the SF laboratory excluded high levels of contamination that would have posed immediate threats to human health.

# 6.3 DISCUSSION OF CRITICAL FINDINGS

What are the most important findings to emerge from this study and how do we place these findings in a policy perspective for South African environmental managers?

The percentage of detects in this study was relatively high, and consistently so across different sampling sites within study areas, and across study areas. Patterns emerged that emphasised surface run-off and sub-surface movement through the soil following irrigation as an important route for entry of pesticides into shallow water sources. This was particularly marked in the Hex River, where one sub-surface drain (Bdr) yielded consistently high levels of both chlorpyrifos and endosulfan. Trigger rainfall appeared to be less important as a precipitant for movement of these two pesticides. Contamination of surface water in dams also emerged as an issue, particularly in the Grabouw/Vyeboom area, often consistent with periods of local application, suggesting direct entry of pesticides from spray activity into dam waters. These findings are consistent with previous research in the same area which demonstrated widespread presence of both endosulfan and chlorpyrifos but at much higher concentrations found in our study (Davies, 1997).

# Table 6.1: International literature on endosulfan and chlorpyrifos in ground and surface water comparisons to South African data.

AUTHOR (YEAR)	TYPE OF STUDY	AVERAGE LEVEL (µg/t)	RANGE	FREQUENCY OF DETECTION (%)	WATER
	Endos	ulfan Studi	es		
Vighi & Funari, 1995	Literature Review of Groundwater monitoring – international, 1987 - 1993	0.3	0-0.4	No data	Ground- water
Oskam et al, 1993	Overview of Dutch Water pollution	No data	No data	No data	Surface
California Environmental Protection Agency, 1996	Californian monitoring results July 1995 – June 1996	0.45*	0-0.45	2 out of 297 wells	Ground- water
Texas Pesticide Information Network, 1999	Texas monitoring results 1984 – 1997	No data	No data	1% over a 10 year period	Surface
Davies, 1997	Dams in Elgin / Grabouw, SA	23.15	0 - 626	27 out of 28 dams	Surface
Current study, 1998-99	Borehole, dam, drain, river water in W Cape, SA	0.41	0 - 26.31	51% of 383 samples	Surface and ground- water
	Chiorp	yrifos Studie	\$		
Espigares et al, 1997	River Basin sampling in Spanish agricultural area, 1989/90	0.070	0-0.33	All 22 sampling points had at least one detection	Surface
Abassey et al, 1999	Nile River Basin sampling, Egypt, 1995- 1997	0	o	o	Surface
Domagalski, 1997	Monitoring over 5 months in San Joaquin basin, agricultural area California, 1992	0.17	0.006-0.32	80 – 100% across three sampling areas	Surface
Raven, 1989	Monitoring river after spill	1			Surface
Gilliom et al. 1999 US Geological Survey in	Routine monitoring - urban	N/a	23% of samp 3% of samp	ples > 0.01µg/( les > 0.05µg/(	Surface and shallow
20 geographical regions	Agricultural areas		10% of samples > 0.01µg/( 2% of samples > 0.05µg/(		ground- water
Davies, 1997	Dams in Eigin / Grabouw, SA	1.33	0 - 138 µg/(	11 out of 28 dams	Surface
Current study, 1998-99	Borehole, dam, drain, river water in W Cape, SA	0.42	0 - 40.36	55% of 400 samples	Surface and ground- water

Based on two positive finding of 0.45 µg/t

# Cited as "high levels" in Henriques et al, 1997.

The frequency of detections of chlorpyrifos in surface and groundwater in this study (both around 43%) appears higher than results from routine monitoring in Texas (Texas Pesticide Information Network, 1999) or California (California Environmental Protection Agency, 1996) but similar to results from field studies of rivers in agricultural areas (Espigares et al, 1997: Domagalski, 1997). One explanation might be that because routine monitoring is far more sporadic than monitoring conducted under research conditions, the likelihood of detections is lower (Domagalski, 1997).

In the published studies where endosulfan and chlorpyrifos were detected, the range of concentrations reported was similar to this study, with the maximum averages of the order of magnitude of 0.3 to 0.4 ag/l. Unlike the Spanish and Californian studies, Abbassey, et al (1999) did not detect chlorpyrifos in water of the Nile basin. It is not clear whether the use of chlorpyrifos is sufficiently high in Egypt to result in significant contamination.

Although relatively few of the published studies give detailed data on maximum levels (California Environmental Protection Agency, 1996; Domagalski 1997), the data from this study (and indeed in the other local study by Davies (1997)) suggest that maximum levels found locally are substantially higher than studies internationally. Maximum concentrations found in this study for chlorpyrifos (40.4  $\mu$ g/c in the Bdr sampling point in the Hex River) and for endosulfan (26.3  $\mu$ g/c in the P8t sampling point in Piketberg) are, respectively about to 80 to 90 orders of magnitude higher than those maxima reported California (California Environmental Protection Agency, 1996; Domagalski 1997).

It should be borne in mind that this study purposively sought out sites where probabilities of pesticides reaching water were high and is therefore not representative of the overall situation with regard to pesticide pollution by agricultural pesticides. In contrast, most of international studies cited above were typically conducted on integrated samples representative of the target population. The data in Table 6.1 should therefore be interpreted with the proviso that we are examining what may be worst case scenarios – study areas with all factors conducive to pesticides reaching water – favourable climate, soil and hydrology, coupled with high usage. On the other hand, the limitations of reliance on grab sampling in this study may have resulted in missing peak concentrations and influenced results in the null direction. Comparisons of maximum levels may therefore be of particular importance in contrasting our results to that of other studies.

How do we make sense of these data in terms of what would be acceptable contamination? Two approaches to setting standards for drinking water were outlined in detail in Chapter Two.

The health-based approach adopted by agencies such as the World Health Organisation (WHO), and the US Environmental Protection Agency (EPA) and followed by many countries such as Australia, uses a proportion of dietary intake attributable to water intake in relation to the ADI to estimate acceptable levels of a contaminant in drinking water. The derivation of the ADI or a Reference Dose (US EPA) is dependent on various risk assessment assumptions and inclusion of safety factors. In contrast, **the policybased approach** adopted by the European Unions sets permissible levels of pesticides at the lowest limit of analytical capability, as a tool to drive down all exposures to pesticides. Such an approach is also predicated on the primary application of the precautionary principle and the recognition of scientific uncertainty in risk assessment.

Placing this study's results in relation to these standards, although the detections were at relatively low concentrations, when compared to EU standards, between 22 and 57% of samples analysed yielded detects. This suggests that if judged against a policy-based standard such as the EU's, water pollution by pesticides is a matter of concern. Indeed, compared to some of the literature from Europe on frequencies of detection (see Chapter 2 for more detail) it would appear that pollution by pesticides in the selected areas in this study occurs more frequently than in those countries where water quality is regularly monitored.

In contrast to the policy-based EU standards, few of the detections approached concentrations of the order of those associated with health-based standards (such as the EPA or WHO approaches). Furthermore, modeling of the concentrations as a percentage of ADI did not identify any immediate concerns for human health. Of all the sampling points in the 3 study area, only one of the 30 points yielded a contribution of more than 1% of an ADI when modeled on the root mean square endosulfan concentration in a daily intake of 2 r of water by a 60kg adult (Table 5.6). Thus, given the existing scientific base for regulatory standards, immediate threats to human health from pesticides in water do not appear to emerge from the data.

However, some caveats should be made in considering the implications for human health in light of criticisms of current risk assessment procedures that form the basis of human health standards (see for example the discussion on page 33 in section 5.3.3). Firstly, the current scientific models that inform risk assessment do not adequately address toxicity of combinations of chemicals, as is often found in water monitoring results in both developed and developing countries, and as was the case in this study. Moreover, relatively few pesticides have been adequately researched with a view to establishing standards for drinking water. Indeed, neither the EPA nor the WHO offer regulatory standards for either endosulfan or chlorpyrifos (EPA does provide a guideline for the former), and the Australian standard for chlorpyrifos is simply a simplified percentage of an ADI, reflecting the lack of precise science in the standard setting process.

Secondly, drinking water may be only one of many routes of exposure for rural communities. Although risk assessment models do make some effort to take into account other routes of potential exposure to pesticides, unique additional exposures may exist for rural communities in developing countries, including South Africa. Data in this study has shown that farm residents may be potentially subject to spray drift by virtue of residential arrangements on farms, commonly make use of pesticides at home for gardening and domestic pest control and may pick up small additional exposures through swimming in contaminated dams. Moreover, given an environment of poor nutrition, and many other factors increasing the vulnerability of adults and children on farms, risk from low concentrations of pesticides in drinking water that may be of marginal importance for healthy urban populations, may be of critical importance for farming populations. This is particularly so where they have ample opportunities for other routes of exposure to mixtures of pesticides. It is therefore not surprising that the EPA has recently introduced changes to its screening models for risk assessment that aim to produce more accurate estimates of pesticides in drinking water by examining more carefully the assumptions implied in back calculating Drinking Water Levels of Comparison, (DWLOC) used to derive a Maximum Contaminant Level (MCL) (EPA, 1999).

Thirdly, it is of concern that a small number of sites in this study where water is directly used for drinking, yielded detections of both chlorpyrifos and endosulfan. Although these concentrations were generally very low levels, endosulfan is well-recognised as an endocrine disruptor, and it is known that endocrine disrupting effects occur at concentrations much, much lower than other kinds of toxic effects (Colborn *et al*, 1986). Current risk assessment procedures do not take endocrine disrupting impacts into account in standard setting and the EPA is only now beginning to explore methodologies to incorporate the science

related to endocrine disruption in its risk assessment procedures<sup>1</sup>. The fact that endosulfan was so widely distributed in this study, despite a half-life said to be relatively short for organochlorine compounds, is unusual and may be partly explained by the strategy of seeking "high probability" sampling sites with

The EPA Endocrine Screening and Testing Advisory Committee (EDSTAC) plans to establish a screening programme for over 150000 chemicals to help inform EPA's regulatory actions. EPA Administrator Carol Browner is quoted in October 1998 as saying "Science has only recently come to understand the potential threats posed to public health from endocrine disruptors. The national screening programme recommended by the committee is a critical first step in our efforts to identify and health threats from these substances and ensure that human health and the environment are protected." Cited in EDSTAC report on the World Wide Web: <u>http://www.epa.gov.opprintr/opptendo</u>, 7<sup>th</sup> October, 1998.
sandy soils and little organic matter. Moreover, at least two of the sites (G7 in Grabouw/Vyeboom, and P8 in Piketberg) included sites supplying potentially large human populations.

Thus although the concentrations found do not exceed current health based standards nor the ADI-based models, the results of the study do provide pointers for taking action on two important policy questions that underlay this study.

#### a) Should there be monitoring for pesticides in water in South Africa?

Given the extent of scientific uncertainty and trends in the current policy environment in South Africa, there appear to be sufficient grounds to warrant some form of surveillance of water for pesticides on a routine basis. Future international standard setting is likely to shift thresholds for endocrine disrupting chemicals downwards, and the lack of data in South Africa make rational policy decisions on pesticides difficult. Moreover, other policy commitments to international conventions will impose similar responsibilities. For example, the United Nations Environment Programme, (UNEP) Convention on Persistent Organic Pollutants (POPs) will demand the South African government undertake a range of related surveillance activities (and in all probability a phase-out program) for selected high-risk (POP) pesticides.

Existing data from this study suggest that even in a relatively affluent province such as the Western Cape, with a well-developed infrastructure, the levels of risk for rural residents, while low, are not inconsequential. With the growth of the informal agricultural sector and of small-scale farming, these risks are likely to be multiplied. If the precautionary principle is to be consistently acted upon by government departments, enough evidence exists from this study to warrant closer attention to pesticides in water in the form of routine or systematic monitoring, even in the absence of proven excursions above current health-based standards, such as they presently exist.

#### b) Should regulatory standards be developed for pesticides in South African waters, and if so, what kinds of standards?

At present, we are faced with the choice of health-based standards based on current risk assessment methods (e.g. EPA, WHO, etc), or policy-based standards used to drive down usage of pesticides and meet the precautionary principle (EU standards). Clearly lower thresholds may carry higher costs for prevention or remediation, and South Africa may find it difficult to compete with well-resource developed countries in its environmental management practices. However, it would appear reasonable from the data that application of international health-based standards of the EPA and the WHO would not present an overly burdensome set of thresholds for practical use in South Africa. At the very least, such standards will provide a measure of health protection not presently available to ordinary South Africans, and which the Constitution seeks to achieve<sup>2</sup>.

The question as to whether the much more stringent policy-based standards such as the EU's should be considered could perhaps best be left to consultative multistakeholder processes such as the National Chemicals Profile to be convened by the DEAT in 2000. Greater input from all parties might help to clarify the relative benefits and burdens of implementing such an approach to standard setting.

<sup>&</sup>lt;sup>2</sup> Section 24 in Chapter 2 (the Bill of Rights) of the South African Constitution indicates that "everyone has the right to an environment that is not harmful to their health or well-being; and to have the environment protected ... through reasonable legislative and other measures that prevent pollution and ecological destruction ...\*

#### 6.4 OTHER ISSUES TO EMERCE FROM THE STUDY

A striking feature of the farm user surveys was the relatively high levels of awareness demonstrated by farm workers and employers of the health hazards associated with pesticides. Moreover, particular high-risk behaviours such as the re-use of pesticide containers were reported as virtually absent, although a number of environmental (drift from spray activity in the field and orchard) and behavioural (domestic use of pesticides) factors that may contribute to exposure remained present. While this high level of reported awareness may to some extent reflect a reporting bias, we are not aware that the size of such bias would be so large as to invalidate the findings. It is thus encouraging that many rural residents were able to identify important dangers of pesticides. This may be the result of training programmes run by agricultural employers over past months and such programmes, mandatory in terms of occupational health legislation<sup>3</sup>, should be encouraged. Such high levels of awareness may make easier reduction in risk activities (e.g. poor hygiene in pesticide applications) and compliance with standards for pesticides in water, should the DWAF introduce such legislation.

One key element essential to surveillance is the availability of data on usage patterns. In this study, such data were not easily available, despite numerous legislative requirements for the regular and accurate maintenance of records in relation to chemical hazards<sup>4</sup>. To some extent, this reflects the culture in agriculture of non-regulation, or a tradition of operating outside of the formal regulatory framework (London, 1998; London and Rother, 1998). While this is likely to change gradually, it should be recognised that any effective surveillance system needs to make use of multiple sources of data. Sound environmental management of pesticides would require an effective system for monitoring the sale and application of pesticides. Use registries or release registries are routinely required in other countries and such data would be essential to interpreting monitoring data from water sources in South Africa.

In order to undertake surveillance, attention needs to be given to establishing the capacity to undertake such analyses. Research in this study took a capacity development approach to ensuring a historically disadvantaged research institution could successfully develop accurate and valid methods for analyses. We believe that the project was successful in meeting one of its key sub-objectives to move towards establishing quantification limits lower than previous studies and more consistent with the levels of sensitivity demanded by current developments in risk assessment. More so, this was done whilst achieving adequate quality control and quality assurance in measurements. Despite this, it is clear that further improvements in sensitivity would greatly assist risk assessment research. The use of an autosampler in the Gas Chromatograph (now installed at PENTECH but not available during the course of the project) would facilitate the use of replicate samples, with the attendant improvement of the precision of the analyses. The EPA and the US Geological Services (admittedly using different methods to that used in our study) report quantification limits of the order of 10 to 100 times lower (using GC-MS) than that achieved in our study (Gilliom *et al*, 1999; Environmental Protection Agency, 1999).

Achieving this level of sensitivity, which is required for protection of aquatic biota, presents significant challenges. Traditional approaches to measuring pesticides in water should be supplemented by alternative, less costly methods. Bioassays are clearly the most important opportunity but other methods (such as immuno-assays) should be explored. Although the research team was able to set up collaboration

<sup>&</sup>lt;sup>3</sup> The Hazardous Chemical Substance Regulations (Department of Labour, 1995) mandate employers to provide extensive training on hazardous chemicals to workers potentially exposed to such hazards.

<sup>&</sup>lt;sup>4</sup> For example, the Hazardous Substances Act (Department of Health, 1973) requires anyone selling a Class I pesticide to maintain a register of the purchaser, type and quantity of chemical sold. Similarly, the Hazardous Chemical Substance Regulations (Department of Labour, 1995) similarly require employers to maintain records of environmental measurements for pesticides for 20 years. In total, 14 different pieces of legislation, involving 7 different government departments pertain to pesticide use in South Africa (Rother and London, 1998).

with the team of Prof. Van Wyk at Stellenbosch, it was unfortunately unable, for logistic reasons, to extend this to a number of other opportunities for collaboration with other key researchers in the field of bioassay development.

Further extension of these skills are needed, both in the specific institutions, and more generally in the environmental health community. Further, capacity at local government level to manage monitoring programmes should also be developed since many technical personnel charged with key inspection and enforcement functions with regard to water quality do not have adequate training or sensitivity to the issues. Practical guidelines to facilitate monitoring in this regard would be very useful.

One of the major limitations of surveillance methods is the reliance on grab sampling. Methods that integrate exposures over time and /or detect peak concentrations in a given time interval would greatly assist the interpretation of data from surveillance. During the course of the study, exploratory testing of solid phase extraction micro-fibres was undertaken in vitro, to achieve a measure of water contamination better integrated over time was conducted. However, preliminary findings with these Solid-Phase Micro-Extractors (SPME) fibres were not encouraging because of substantial inconsistencies in recoveries achieved in the laboratory using diluted standards for an endosulfan/chlorpyrifos mix. However, the testing conducted was not properly set up as an experiment and was interpreted qualitatively. There is thus a need for exploring alternative methodologies that can successfully characterise continuous and fluctuating exposures in water sources more effectively.

Measures to control the loss of pesticides to ground water need to be considered. Although this study was unable to identify in sufficient detail the precise farm practices responsible for egress of pesticides to water, generic measures may well be appropriate. These include training of farmers and farm workers in pesticide safety, and particularly on environmental hazards. Such training should be able to engage with farm residents in ways that enables farmers and farm workers to take ownership of the environmental consequences of farming practices. Particularly for farm workers, in a resource constrained and socially controlled environment, this demands particularly sensitive methods, geared towards empowerment and self-efficacy. Other interventions of a technical nature would include containment liners to mixing points used in orchards, fields and vineyards to prevent spillage at mixing sites, which should be routine farm practice.

However, data in this study suggested that irrigation was a major factor driving the entry of pesticides to water bodies in the areas surveyed. This suggests that, to some extent, pollution of water sources is occurring under "normal" farming practices and not as a result of accidental or unintentional point source releases (e.g. mixing sites). The main remedial measure under such circumstances would be to encourage pesticide reduction as an overall restraint on the amount of active ingredient reaching environmental media. Integrated Pest Management should be widely encouraged to meet this objective. Further detailed research into the precise farming activities associated with these low-level exposures would also be desirable. A last issue to emerge from the data is the need for sound epidemiological studies that can begin to quantify the actual risk associated with the levels of endosulfan and chlorpyrifos found in this study. Epidemiological studies are frequently flawed by the lack of accurate data on exposures of rural populations, with the result that possible inferences may be invalidated by misclassification. Our study has generated consistent findings of low levels of pesticides in rural water sources, and can provide muchneeded data that can help to answer aetiological questions about the health impacts of these low levels of pesticides in drinking water. The ability to boister such important research is a valuable spin-off of the study. However, at the same time as conducting such research, implementation of the precautionary principle should inform generic moves towards reducing potential hazards, no matter what the degree of scientific uncertainty. Based on the discussion above, the final chapter summarises our conclusion and presents a number of recommendations for action by various authorities and stakeholders.

# CHAPTER 7:

# RECOMMENDATIONS

In developed countries, concerns for the health effects of water pollution by pesticides are sufficiently well-recognised for the monitoring of water sources for organic and inorganic contaminants to be prioritised (Oskam *et al*, 1993). However, for most developing countries, the capacity and infrastructure for addressing the control of chemical pollution of water sources is extremely limited. This study suggests that although pesticide pollution of water has not previously received adequate attention in South Africa, evidence for widespread, consistent, albeit generally low-level contamination by pesticides is present in rural water sources in selected regions of the Western Cape. It should be remembered that the regions sampled were chosen purposively as potential 'worst-case' scenarios with the highest likelihood of pesticides reaching water, and are therefore not representative of all agriculture. However, as illustrative extreme cases, they demonstrate that pesticides can and do reach water sources in rural farming areas of South Africa in low concentrations. Moreover, the reliance on grab sampling in this study may act to underestimate the extent of the problem.

We have no reason to believe that the situation in other farming areas of the country would be substantially different to that obtained in this study, and therefore surmise that similar studies of purposively chosen sites in other Provinces might yield similar patterns of detections.

The widespread extent of the low levels of detection therefore warrant greater attention to establishing reliable mechanisms for surveillance of water sources for pesticide pollution in the future.

Furthermore, although few of the detections of endosulfan and chlorpyrifos approached concentrations of the order of those associated with health-based standards of the WHO and EPA, and therefore, did not appear to pose immediate threats to human health based on current scientific approaches to international risk assessment, South African waters cannot be assumed to be adequately protected in the absence of drinking water standards that include pesticides and their metabolites. Risk assessment methods, as discussed in Chapters 2 and 7, which take account of the multiplicity of exposure routes, of aggravating socio-environmental factors, and mixtures/metabolites should be incorporated in a specific process of standard setting for pesticides in water, taking account of different water uses.

Thirdly, although rural populations may experience diverse potential routes of exposure to pesticides other than water, awareness of the hazards of pesticides is relatively high and recognised risky practices (such as reuse of pesticide containers) are very rarely reported. Regulatory standards should therefore be able to capitalise on this relatively highly developed awareness to ensure adequate compliance and protection of human health. The positive impacts of rural health and safety training initiatives by employers and employees may be reflected in this high level of awareness and should be encouraged further.

#### Recommendations

The Project Team therefore makes the following recommendations:

#### 1. THE NEED FOR MONITORING OF WATER FOR PESTICIDES

- 1.1 The DWAF should actively pursue development of surveillance and monitoring methodologies to protect water supplies from pollution by pesticides. Data in this study justify the conclusion that surveillance is warranted.
- 1.2 Local government capacity, particularly in rural areas, to implement monitoring of water sources for pesticide poisoning should be audited and strengthened.

- 1.3 In addition, rural communities should be provided with simple, cost effective tools to undertake monitoring of their own water supplies.
- 1.4 Practical guidelines for water monitoring for pesticides should be developed for all for personnel (community or governmental) charged with inspection and enforcement functions.
- 1.5 DWAF should also seek ways to ensure that data in support of surveillance activities on farms is effectively captured. In particular, every effort should be made to ensure that toxic release inventories and use inventories for pesticides should be available and used for surveillance purposes. DWAF should liaise with other government departments to co-ordinate and maximise the impact of such measures.
- 1.6 This study has focused on the extreme end of a spectrum, concentrating on areas where pesticide pollution was anticipated to be most likely. By introducing routine surveillance on a broader basis, DWAF should seek to ensure that it maps a representative sample of all agricultural areas, so as to characterise the overall state of water pollution due to pesticides, both extreme and average. These data should serve as the basis for monitoring temporal trends in the country.

#### 2. STANDARDS

- 2.1 Established international health-based standards, such as those developed by the WHO and the EPA, although not without criticism, should be adopted by the DWAF as a means to offer a level of protection consistent with the provisions of the South African Constitution.
- 2.2 Pursuit of more rigorous policy-based standards, such as those set down by the European Union, should be considered within the framework of an appropriate national multistakeholder process such as the National Chemicals Profile initiative to be undertaken by the DEAT in 2000.
- 2.3 Risk assessment in relation to pesticides should inform the setting of water standards, not only for drinking water but for other uses, and should be undertaken in recognition of the context of rural farm workers' additional exposures, and concomitant vulnerability factors. Methods used should be able to take account of cumulative risks from many sources and over time.

#### 3. IMPROVEMENTS IN ANALYTICAL METHODS

- 3.1 Methodologies that offer the possibility of producing assessments of exposure that integrate fluctuating concentrations over time should be explored. In particular, the utility of Solid-Phase Micro-Extractors (SPME) fibres should be adequately assessed in vitro and under field use for possible adoption as part of a monitoring programme.
- 5.2 Further research involving methods which have lower levels of detection should be explored, particularly with the view of informing risk assessment and standard setting for ecotoxicological purposes.
- 3.3 Traditional GC and GC-MS pesticide analytical methods should be supplemented with alternative methods such as bioassays and immunoassays, subject to adequate field testing, validation and cost-effectiveness evaluation.

#### CONTROL OF EXPOSURES

- 4.1 Policy measures that seek to avoid potential contamination of environmental media and reduce leaching should be encouraged: Integrated Pest Management, Containment liners at mixing sites, training, and general movement toward pesticide reduction.
- 4.2 DWAF should enlist the support of key partners to encourage research directed at identifying the precise farming activities that are amenable to intervention to reduce potential egress of pesticides to water sources.

4.3 Behavioural determinants of pesticide pollution should be addressed by encouraging health, safety and environment training to employers and employees in farming communities. Any training provided on health and safety should include the hazards to the environment amongst the full spectrum of safety information and be geared to empowerment of rural residents. Particular attention should be given to empowering rural residents to protect themselves and their communities from adverse consequences of unintended pollution.

#### 5. HEALTH OUTCOME STUDIES

- 5.1 Studies should be done to capitalise on the careful exposure data obtained in this study. Such studies can address many of the difficulties in typical epidemiological research by improving on the quality of exposure assessment. This research can put South Africa at the cutting edge of public health / environmental health research, and can help to provide informed risk assessment for standard setting.
- 5.2 Studies that specifically examine the importance of spray drift in human health impacts appear warranted given the frequency with which human habitation abuts onto areas of pesticide spray. Agencies other than the Water Research Commission (such as the Medical Research Council, and the Agricultural Research Council) should be encouraged to pursue this avenue.
- 5.3 The benefits of high levels of awareness should be related to improved health status amongst rural farm residents. Research to evaluate the impact of safety training on the health of farm workers and employers will assist lobbying for greater resources for the control of pesticide pollution in rural farming areas.

# CHAPTER 8:

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### APPENDIX A:

### SUMMARY OF INTERNATIONAL STANDARDS FOR PESTICIDES IN DRINKING WATER (mg/l)

#### APPENDIX A: INTERNATIONAL STANDARDS FOR PESTICIDES IN DRINKING WATER (mg/l)

	USEPA									
Type of Standard:	MCL	C	hild Advisori	es	A	dult Advisor	ies	Advisory at	Australian	WHO
	standard	I day	10 day	Longer term	Longer term	DWEL	Lifetime	10-4 Cancer Risk		
Pesticide		Child	Child	Child	Adult	Adult	Adult	Adult		
Acifluorfen		2	2	0.1	0.4	0.4		0.1		
Alachlor	0.002	0.1	0.1			0.4		0.04	0.002	0.02
Aldicarb	0.007					0.035	0.007		0.001	0.01
Aldicarb sulfone	0.007					0.035	0.007			
Aldicarb sulfoxide	0					0.035	0.007			
Aldrin			0.0003	0.0003	0.0003	0.001		0.0002	0.0003	0.0003
Ametryn		9	9	0.9	3	0.3	0.06		0.05	
Ammonium Sulfamate		20	20	20	80	8	2			
Atrazine	0.03	0.1	0.1	0.05	0.2	0.2	0.003		0.02	0.002
Bentazon		0.3	0.3	0.3	1	1	0.2		0.03	0.03
Bromacil		5	5	3	9	5	0.09		0.3	
Butylate		2	2	1	4	2	0.35			
Carbaryl		1	1	1	1	4	0.7		0.03	
Carbofuran	0.04	0.05	0.05	0.05	0.2	0.2	0.04		0.01	0.005
Carbon tetrachloride	0.005	4	0.2	0.07	0.3	0.03		0.03	0.003	
Chloramben		3	3	0.2	0.5	0.5	0.1			
Chlordane	0.002	0.06	0.06			0.002		0.003	0.001	0.0002
Chlorpyrifos		0.03	0.03	0.03	0.1	0.1	0.02			
2,4-D	0.07								0.03	0.03
DCPA		80	80	5	20					
Diazinon		0.02	0.02	0.005	0.02	0.003	0.0006		0.003	
Dieldrin		0.0005	0.0005	0.0005	0.002	0.02		0.0002	0.0003	
Diphenamid		0.3	0.3	0.3	1	1	0.2		0.3	
Diphenylamine		1	1	0.3	1	1	0.2			
Diquat	0.02					0.08	0.02		0.005	
Disulfoton		0.1	0.1	0.003	0.009	0.001	0.0003		0.003	
Endosulfan									0.03	
Endothall	0.1	0.8	0.8	0.2	0.2	0.7	0.1		0.1	

#### Summary of International Standards for Pesticides in drinking water (mg/l)

The Quality of Surface and Groundwater in the Rural Western Cape with regard to Pesticides Page A-1

APPENDIX A: INTERNATIONAL STANDARDS FOR PESTICIDES IN DRINKING WATER (mg/l)

	USEPA									
Type of Standard:	MCL	0	hild Advisori	es	A	dult Advisori	es	Advisory at	Australian	WHO
	standard	I day	10 day	Longer term	Longer term	DWEL	Lifetime	10-4 Cancer Risk		
Pesticide		Child	Child	Child	Adult	Adult	Adult	Adult		
Ethylene dibromide	0.00005	0	0	0				0.00004	0.001	
Fenamiphos		0.009	0.009	0.005	0.002	0.09	0.002		0.0003	
Fonotos		0.02	0.02	0.02	0.07	0.07	0.01			
Glyphosate	0.7	20	20	1	1	4	0.7	-	1.0	
Heptachlor	0.0004	0.01	0.01	0.005	0.005	0.02		0.0008	0.0003	0.00003
Heptachlor epoxide	0.0002	0.01	0.01	0.0001	0.0001	0.0004		0.0004	0.0003	0.00003
Hexachlorobenzene	0.001	0.05	0.05	0.05	0.2	0.03		0.002		0.001
Hexachlorocyclopentadi ene	0.05					0.2				
Lindane	0.0002	1	1	0.03	0.1	0.01	0.0002		0.00005	0.002
Malathion		0.2	0.2	0.2	0.8	0.8	0.2			
MCPA			0.1	0.1	0.4	0.05	0.01			0.002
Methomyl		0.3	0.3	0.3	0.3	0.9	0.2		0.03	
Methoxychior	0.04	0.05	0.05	0.05	0.2	0.2	0.04		0.3	0.02
Methyl parathion		0.3	0.3	0.03	0.1	0	0			
Metolachlor		2	2	2	5	3.5	0.07		0.3	0.01
Metribuzin		5	5	0.3	0.5	0.5	0.1		0.05	
Naphthalene		0.5	0.5	0.5	1	0.1	0.02			
Oxamyl	0.2	0.2	0.2	0.2	0.9	0.9	0.2		0.1	
Paraguat		0.1	0.1	0.05	0.2	0.2	0.03		0.03	
Pentachiorphenol	0.001	1	0.3	0.3	1	1		0.03	0.01	0.009
Picloram	0.5	20	20	0.7	2	2	0.5		0.3	
PCB's	0.0005							0.0005	0.0005	
Prometon		0.2	0.2	0.2	0.5	0.5	0.1			
Pronamid				0.8	3					
Propachlor		0.5	0.5	0.1	0.5	0.5	0.09			
Propazine		1	1	0.5	2	0.7	0.01		0.05	

#### APPENDIX A: International Standards for Pesticides in Drinking Water (mg/l)

Type of Standard:	USEPA									
	MCL	Child Advisories		Adult Advisories			Advisory at	Australian	WHO	
	standard	I day	10 day	Longer lerm	Longer term	DWEL	Lifetime	10-4 Cancer Risk		
Pesticide		Child	Child	Child	Adult	Adult	Adult	Adult		
Simazine	0.004	0.004	0.07	0.07	0.07	0.2	0.004		0.02	0.002
Tebuthiuron		3	3	0.7	2	2	0.5			
Terbacil		0.3	0.3	0.3	0.9	0.4	0.09		0.03	
Terbulos		0.005	0.005	0.001	0.005	0.05	0.0009		0.0005	
Toxaphene	0.003							0.003	0.003	
Trifluralin		0.08	0.08	0.08	0.3	0.3	0.005	0.5	0.05	0.02

Sources:

National Health and Medical Research Council, and Agriculture and Resource Management Council of Australia and New Zealand, 1996; USEPA 1986; WHO, 1993b

MCL : Maximum Contaminant Level

DWEL : Drinking Water Equivalent Level

## APPENDIX B:

### SOIL DATA FOR STUDY AREAS

#### THE SOILS OF SELECTED AREAS IN THE WESTERN CAPE; THEIR INTERNAL DRAINAGE AND CATION ADSORPTION CAPACITY

Reviewed by: Mr S van Niekerk and Mr J van Zyl, Elsenberg Agricultural College

#### HEXRIVER VALLEY

Land types:	la 22, Hb 40
Dominant soils:	Sloping to gently sloping, moderately deep to deep grey sand (FERNWOOD and DUNDEE soil forms)
Present land use:	Irrigated table grapes.
Water movement:	These sandy soils have a rapid infiltration and permeability. Soil water will move down until it reaches impermeable or slowly permeable rock or saprolite. It will then flow laterally down to the nearest river. Probably only a small percentage will reach a groundwater aquifer.
Cation adsorption capacity:	Low

#### GRABOUW AREA

Land type: Dominant soils:	c 264 Moderately deep (30 - 60 cm) red and reddish brown light to medium textured soils on moderately permeable clayey
material	(HUTTON and OAKLEAF forms).
Present land use:	Irrigated fruit (apple and pear).
Water movement:	Most excess rain and irrigation water will percolate to moderate depth but end up in the rivers.
Cation adsorption capacity:	Moderate to Moderately High.
Land types:	Fa 139 and Fa 173
Land types: Dominant soils:	Fa 139 and Fa 173 Shallow, medium textured soil on moderately weathered shale(Glenrose form). Soils with a dense clay layer between the topsoil and the shale also occur (SWARTLAND and ESTCOURT forms).
Land types: Dominant soils: Present land use:	Fa 139 and Fa 173 Shallow, medium textured soil on moderately weathered shale(Glenrose form). Soils with a dense clay layer between the topsoil and the shale also occur (SWARTLAND and ESTCOURT forms). Fruit under irrigation and pine plantations.
Land types: Dominant soils: Present land use: Water movement:	Fa 139 and Fa 173 Shallow, medium textured soil on moderately weathered shale(Glenrose form). Soils with a dense clay layer between the topsoil and the shale also occur (SWARTLAND and ESTCOURT forms). Fruit under irrigation and pine plantations. Mainly lateral movement over the clayey subsoil at shallow depth. Most rain and irrigation water should end up in rivers with a small percentage percolating to great depth.

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#### APPENDIX B: Soil Data for Study Areas

#### VYEBOOM

Land types:	Fa 211 High rainfall area			
Dominant soils: (i) (ii)	Clovelly, Avalon, Pinedene Light to medium textured yellow soils, commonly with slowly permeable clayey subsoil from about 70 cm. (CLOVELLY, AVALON and PINEDENE soil forms). Shallow sandy soils on wet, slowly permeable clay or soft saprolite (ESTCOURT, CARTREF, and GLENROSA soil			
Present land use: Water movement:	forms). Mainly pome fruit under irrigation. Very little deep percolation. Water will tend to flow laterally over the impermeable clay and land up in the river/dam.			
Cation adsorption capacity	Moderate on the Clovelly, Avalon and Pinedene soils. Low on the Estcourt and Cartref soils.			
Land types:	Dd 103 and Fa 207			
Dominant soils:	Shallow medium textured, soils on relatively fresh Bokkeveld shale (GLENROSA form). In the case of Swartland form soils a discontinuous clay layer occurs between the topsoil and the shale.			
Present land use:	Greater part of area under rain-fed small grain with the rest			
Water movement:	In most of these soils the shales are sufficiently unweathered to allow deep percolation of rain or irrigation water. However,percolation is not deep enough to prevent most of this water to end up in the river.			
Cation adsorption capacity:	Moderate to Moderately Low.			

#### ON TOP OF PIKETBERG MOUNTAIN

Land types:	Ac 482
Dominant soils:	Sandy, moderately deep, yellowish and reddish soils
	(CLOVELLY and HUTTON soil forms)
Present land use:	Apples and pears under irrigation.
Water movement:	Water will move rapidly through the soil profile until it reaches saprolite or sandstone at depths ranging from 600 to about one metre. A large proportion will then move laterally down slope towards the nearest river while the rest will percolate down cracks and cleavages and may end up in the Berg River.
Cation adsorption capacity:	Low to Moderately Low.

#### APPENDIX B: Soil Data for Study Areas

#### PIKETBERG PLAIN

Land types:	Da 177, Da 178
Dominant soils:	Shallow fine sandy loam over dense, structured clay with
weathered	Malmesbury phyllite deeper down (SWARTLAND soil form).
Present land use:	Rain-fed small grain.
Water movement:	Rainwater should move down to the clay material. Once the topsoil is saturated surface run-off with ensue. There will also be some lateral movement over the clay. Most of the surplus water will end up in the nearest drainage line while a small percentage will percolate deep and may reach a deep (commonly saline) water table.
Cation adsorption capacity:	Moderate
Land types:	Ab 213, Ab 214
Dominant soils:	Moderately deep to deep, medium to heavy textured red soils (HUTTON soil form)
Present land use:	Rain-fed small grain.
Water movement:	The largest portion of the rainfall goes back into the atmosphere through evapotranspiration. A small percentage may percolate deep and reach the saline groundwater and a small percentage may end up in the rivers.

Cation adsorption capacity: Moderately High to High (especially phosphate sorption).

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## APPENDIX C:

### **PROTOCOL FOR FIELD SAMPLING, SAMPLE PREPARATION AND ANALYSIS**

#### SAMPLING PROTOCOL FOR PESTICIDE ANALYSIS

#### SAMPLING EQUIPMENT

- Grab sample bottle amber glass, 1ℓ or bigger fitted with screw cap lined with Teflon or clean aluminium foil. If amber bottles are not available, protect sample from light.
- The bottles must be washed with water, rinsed with acetone or methylene chloride or methanol and air dried to minimize contamination.

#### SAMPLE COLLECTION, PRESERVATION AND HANDLING

- 1. Grab samples must be collected directly into the bottle without rinsing it.
- 2. Samples should preferably be chilled to 4°C or below from time of collection until extraction.
- 3. It is recommended that at least 3( of water be collected to represent one sample from one water source.
- If samples will not be extracted within 72 hours of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide or sulphuric acid.
- All samples must be extracted within 7 days of collection and extracts stored at 4°C and completely analyzed within 40 days.
- 6. A sample collection report to filled in every time a set of samples are collected (Appendix A).
- 7. Sampling bottles must be clearly labeled showing sample number, date and name of sample collector.
- At least 1 sampling site will be sampled and analyzed in duplicate under identical conditions per sampling run.

#### CLEANING OF GLASSWARE

- 1. Clean all glassware as soon as possible after use by rinsing it with the last solvent used in it.
- This should be followed by detergent washing with hot water and rinses with tap water and deionized water.
- The glassware can then be rinsed with acetone and pesticide quality hexane.
- After air drying the glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.
- 5. Glassware should be stored inverted or capped with aluminium foil.

#### REAGENTS

- Only high purity reagents and solvents must be used. Purification of solvents by distillation in an allglass system may be required.
- 2. Reagents:
  - (a) Deionized water
  - (b) Acetone, hexane, isooctane and methylene chloride pesticide quality or equivalent

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- (c) Ethyl ether pesticide quality or equivalent
- (d) Sodium sulphate (ACS) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.
- (e) Stock standard solutions 1 mg/ml.

#### SAMPLE EXTRACTION

#### Liquid - liquid extraction

All samples were extracted within 7 days of collection. One liter of sample was extracted in a 21 separatory funnel with 60 ml methylene chloride (three times) and the combined extracts passed through a drying column containing about 10g of anhydrous sodium sulphate. The extract was then concentrated on a rotary evaporator until the volume has been reduced to about 5 ml. Fifty ml of hexane was added to the round bottom flask and again concentrated to about 5 ml. The concentrated extract was then quantitatively transferred to a 10 ml volumetric flask and diluted to 10 ml with hexane. The solution was now ready for injection into the gas chromatograph. All solvents used in the extraction were high pressure liquid chromatograph grade.

#### Solid Phase Extraction

The water samples were prefiltered by vacuum filtration through S & S filter paper (ref. No. 334508) to remove particulate matter before pesticide extraction.

Bond Elute Extraction Cartridges (C18, 10 ml LRC, 500 mg sorbent mass) was used in extraction procedure. The column was first conditioned with 2 column volumes (2 x 10 ml) ethyl acetate and 1 column volume (1 x 10 ml) of methanol and 1 column volume (10 ml) of deionized water. All solvents used were high pressure chromatography grade. 250 ml of filtered water sample was slowly aspirated through the column at a rate of 20 – 25 ml per minute under vacuum. The column was then washed with 1 column volume (10 ml) of deionized water and then thoroughly dried for 15 minutes under vacuum. The pesticides were then eluted into a borosilicate glass vial using 2 amples of 1 ml ethyl acetate. The ethyl acetate was then evaporated off a room temperature. 1 ml hexane was then added to the glass vial to redissolve the residue. The solution was now ready for GC analysis.

#### Analytical Methodology

Ten pesticides were screened in the water samples. Analytical standards (> 98% purity) were used to prepare standard solutions. The extracted samples were subjected to gas chromatography for identification and quantitation. All compounds were determined using a Varian 3300 GC equipped with an electron capture detector (ECD). 2 µL sample was injected onto a capillary column with a BPX 5 stationary phase. The temperature program was 170°C initially increased at a rate of 7°C/min to 290°C and held for 5 minutes at that temperature. Injector and detector temperature were 250°C and 300°C, respectively. The pesticides identified and quantified have not been confirmed on a second column detector, neither has it been confirmed by GC/MS.

#### **Quality Control Measures**

- 1. Duplicate samples to be sampled and analysed at least once per sampling run.
- A reagent blank and spike to be run with each set of samples. The spike, in addition of a known amount of compound may contain up to 8 different pesticides.
- If the recoveries of the spiked components fall below 70% or rise above 130% the cause will be investigated to determine if the spike or the entire series need to be reanalyzed.
- Mixed standard solutions were injected prior to sample injections and peak shape, resolution and response evaluated by comparison with previous chromatograms to ensure that the instrument was operating properly.

## APPENDIX D:

### PESTICIDES LISTED AS POTENTIAL ENDOCRINE DISRUPTORS

WORLD WILD LIFE FUND CANADA lists the following as endocrine disruptors (Source: http://www.wwfcanada.org/hormone-disruptors/science/frameset.html)

2.4.5-T	DBCP
2.4-D	DDT
alachior	DDT metabolites
aldicarb	dicofol
amitrole	die)drin
atrazine	endosulphan
benomyl	esfenvalerate
beta - HCH	ethylparathion
carbaryl	fenvalerate
chlordane	lindane
cypermethrin	heptachlor

h-epoxide kelthane kepone malahion mancozeb maneb metiram metribuzin mirex

nitrofen oxychlordane permethrin synthetic pyrethroids toxaphene transnonaachlor methoxymyl tributyltin oxide methoxychlor trifluralin vinclozolin zineb ziram

#### The German list of endocrine disruptors (Bruhn et al, 1998)

Endocrinely Active	Potentially Endocrinely Active
Atrazine	2.4.5 Trichlorophenoxyacetic acid
2.4 dichlorophenoxyacetic acid	Ziram
amitrole	Metiram
metribuzin	Nonachlor (cis- and trans-)
Nitrofen	Aldrin
Trifluralin	Dicofol
Thiram	Pyrethroids
Maneb	2.4 Dicholorphenol
Zineb	
Macozeb	
HCB	
PCP	
Fenarimol	
Carbaryl	
Chlordane	
β-НСН	
γ-HCH	
Parathion	

US Physicians for Social Responsibility - List of known or suspected reproductive and developmental toxins, used in Massachusetts (Schettler et al, 1996)

parathion	benomyl	dicofol
malathione	maneb	cypermethrin
diazanon	nabam	fenvelerate
chlorpyrifos	zineb	ethylene bromide
tetrachlorvinphos	thiram	ethylene oxide
acephate	vinclozin	dicamba
dimethioate	paraquat	methoxychlor
carbaryl	atazine	2,4 D
lindane	cyanazine	
endosulphan	dieldrin	

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## APPENDIX E:

### SUB-STUDY: COPPER LEVELS IN WATER SAMPLES FROM THE HEX RIVER

#### INTRODUCTION

Heavy metals are all metals with atomic number greater than 20, except for alkali metals, alkaline earth metals, lanthanides and actinides. Most of these metals (for example copper (Cu), lead (Pb) and zinc (Zn)) are of importance in life, but they can be highly toxic when present in high quantities and thus be regarded as pollutants.

Heavy metal concentrations in natural systems may be derived from two primary sources ie. through nature and also through man's activities. Soil constitutes the natural sources, but except for a few cases, the amounts added by natural means are less than those added by man's activities.

Copper, lead and zinc are examples of metals that can be considered as pollutants when present in large amounts. The Hex River Valley is situated in an agricultural area of grapes (vines). Farmers use pesticides to control and take care of their crops. Pesticides are available in different forms, for example, insecticides, fungicides, etc. Copper is introduced into the river in the form of copper oxychloride which is classified as a fungicide. Copper compounds are very toxic to fish and other animal life in streams and are extremely toxic to algae and other vegetable life in rivers.

Lead can be introduced into rivers in the form of lead arsenate which is chemical compound that is classified under fungicides. Lead compounds are toxic to all forms of life. Zinc on the other hand can be introduced into river systems in the form of zinc oxide. As with other metals, zinc can be lethal to human and aquatic life when present in large quantities.

The introduction of metals as water pollutants into a river system can either be direct or indirect. The direct introduction includes using toxic chemicals for controlling some members of the water community and the indirect introduction includes depositions from vehicles (eg leaking oil or petrol on roads). These are washed into the river system during rainy seasons.

Heavy metals are very harmful to human health because they are either not broken down or they take long to be broken down. The trace elements of most concern to human health are Copper (Cu), Lead (Pb) and Zinc (Zn) which result in chronic ailments such as:

Copper:	Causes skin and eye irritation. May lead to blindness.
Lead:	Metabolic and neuropsychological disorders
	i.e. anemia and lowered IQ.
Zinc:	Causes irritation to the nose, throat and skin. May cause cancer.

#### INDUSTRIAL POLLUTANTS

Diluted and dispersed sites can allow toxic chemicals to pollution groundWater, even though the theory behind them is that natural chemicals and biological processes will render the wastes harmless as it seeps through the underlying soil. Fears about diluted and disperse pollution have led several countries to limit land filling to containment sites. These sites are lined with impermeable material such as clay or plastics or built over impermeable soil. However, heavy rain can cause the sites to overflow and some of the chemicals. Particularly industrial solvents can eventually penetrate the lining. The liquid draining from a waste dump may contain a large range of concentrated pollutants such as heavy metals, solvents, NH<sub>3</sub>, phenols and cyanides. These Pollutants are sometimes trapped in drains around the sites and then pumped back on top of the site. Very little is known of how leacheates may react during their movement through unsaturated zone to the water table. Toxic waste disposal is a growth industry; other waste is pumped directly into rivers or into water authority sewers.

#### TYPES OF HEAVY METAL POLLUTANTS

#### LEAD

Lead is probably the best documented of all known poison, lead reaches us in several ways. Lead in petrol has been a major public issue in recent years. Lead in paint, particularly the older high-lead varieties, has caused a number of fatalies. The major factor governing the amount of lead in the water is the presence of salt, acid, water, but pipe length and condition the time the water has stood in the pipe or tank and the rate at which the water flows through the system all make their contribution. Lead arsenate is an insecticide. Three types exist: neutral type Pb3(AS04)2. Acid type PbHAS04, Basic type Pb50H(AS04)3. The acid type is the Stable and widely used. Its physical and chemical properties are melting point 270°C, it is insoluble in water. It is insoluble in dilute nitric acid and caustic alkalis. Lead arsenate is a white powder containing 60% Lead and 21.5% arsenic. Lead arsenate has been used as a pesticide for mandibulation types of insects. It is however, prone to produce residues of soluble arsenic which become Phytotoxic to plant bodies. The toxic effect is particularly pronounced in insects With alkali digestive juices. For agricultural application a solution of 25 to 38g of Lead arsenate in 10t of water is made up. To reduce the phytotoxic action, lime Bordeau liquid or up to twice the quantity of lime is added. In industry, inhalation and in agriculture, accidental ingestion seem to be the most common modes of entry. Poisoning may occur during both the manufacture and application of Lead Arsenate insecticide. Lead and Arsenic excretion is mainly via the kidney, with Arsenic disappearing from the urine more quickly than Lead. Symptoms include nausea, vomiting, abdominal pain muscular cramps. Chronic poisoning is manifested by anorexia, weakness and hepatitis. Lead Arsenate dust can cause ulceration and perforation of the nasal septum. To prevent this, workers must wear protective clothing, respiratory protective equipment and must be fully informed of its hazards.
#### ZINC

Zinc oxide is a white powder insecticide which melts at 1975°C. It is soluble in acid and alkalis and insoluble in water. Zinc oxide fumes causes metal - fume fever, thirst, headache, pains in the limbs and a feeling of exhaustion.

#### COPPER

CuSO<sub>4</sub> is used to supplement pastures deficient in the metal as a plant fungicide. Copper Sulphate neutralized with hydrated lime, known as Bordeaux mixture is used for the prevention of mildew in vineyards. Workers who spray vineyards with Bordeaux mixture may suffer from pulmonary lesions (known as Vineyard sprayer's lung) and copper laden hepatic granulomas. Nausea, vomiting sweating, comma and death may result.

Excess copper can be toxic to plants and this liable to occur where copper Compounds are applied as fungicides, particularly on acid soils. Provineon and Mazoyer (1962) found copper toxicity in vineyards a few years after spraying with copper sulphate, at pH values less than 6 in the soil (as Mg, Ka). Generally copper remains isotopically exchangeable in acid soil is fixed in complex form in alkaline soils. Clay acids easily absorb copper added to soil. Copper is rapidly and strongly fixed by organic matter and copper deficiency is commonly found in high organic soils. Such a deficiency is almost a feature of newly prepared pest soils.

#### A NEED FOR PESTICIDES POLICY

A pesticides policy would provide central guidance on desired levels of use, a measure of control and surveillance, as well as research and development of alternatives to chemicals pesticides. An active research program is necessary to extend our knowledge of likely effects of chemical pesticides on human health and to expand the limits of what is possible to know. Direction from the government in the form of a national policy would enable a national assessment of the future or market-led strategy as at present.

### Results for water samples

SAMPLE	12-Aug		16-	Sep	14-Oct	
1	AA	ICP	AA	ICP	AA	ICP
AR	0.757	0.813	0.689	0.4158	7.374	9.81
BDR	0.004	0.0758	0.466	0.1848	0.337	0.3052
DD	8.303	8.435	0.446	0.1265	0.395	0.3308
E	0.027	0.0755	4.526	3.553	0.416	0.3267
F	0.716	0.605	0.636	0.1757	0.936	0.705
G	0.267	0.3127	0.774	0.2453	3.331	2.822

Table 1. Copper concentrations in water samples (ppm)

Table 2. Lead concentrations in water samples (ppm)

SAMPLE	12-Aug		16-Sep		14-Oct	
1	AA	ICP	AA	ICP	AA	ICP
AR	0.197	0.1155	1.151	0.1175	0.884	0.192
BDR	0.308	0.1155	1.173	0.1476	0,978	0.1713
DD	0.374	0.1155	1.421	0.1154	1.084	0.1821
E	0.398	0.1155	1.625	0.1857	1.185	0.1851
F	0.428	0.1155	1.662	0.1567	1.269	0.1982
G	0.335	0.1155	1.904	0.1205	1.398	0.2049

Table 3. Zinc concentrations in water samples (ppm)

SAMPLE	12-Aug		16-Sep		14-Oct	
1	AA	ICP	AA	ICP	AA	ICP
AR	0.563	0.4721	0.644	0.51	0.898	0.68
BDR	0.485	0.3856	0.562	0.4332	0.869	0.612
DD	0.483	0.406	0.53	0.4008	0.624	0.4302
E	0.502	0.3425	0.749	0.573	0.709	0.4768
F	0.539	0.3605	0.583	0.4118	0.539	0.3771
G	0.467	0.3718	0.764	0.56	0.904	0.622

Table 4. Copper concentrations in water samples (ppm) using Atomic Absorption (AA).

SAMPLE	12-Aug	16 Sep	14-Oct 7.374 0.337	
AR	0.757	0.689		
BDR	0.004	0.466		
DD	8.303	0.446	0.395	
E	0.027	4.526	0.416	
F	0.716	0.636	0.936	
G	0.267	0.774	3.331	

Figure 1. Cu concentrations in water samples using Atomic Absorption (AA).



SAMPLE	12-Aug	16-Sep	14-Oct 9.81 0.3052 0.3308	
AR	0.813	0.4158		
BDR	0.0758	0.1848		
DD	8.435	0.1265		
E	0.0755	3.553	0.3267	
F	0.605	0.1757	0.705	
G	0.3127	0.2453	2.822	

Table 5. Copper concentrations in water samples(ppm) using ICP

Figure 2. Cu concentrations in water samples using ICP



SAMPLE	12-Aug	16-Sep	14-Oct
AR	0.197	1.151	0.884
BDR	0.308	1.173	0.978
DD	0.374	1.421	1.084
E	0.398	1.625	1.185
F	0.428	1.662	1.269
G	0.335	1.902	1.398

Table 6. Lead concentrations in water samples(ppm) using Atomic Absorption (AA).

Figure 3. Pb concentrations in water samples using Atomic Absorption (AA).



SAMPLE	12-Aug	16-Sep	14-Oct 0.192	
AR	0.1155	0.1175		
BDR	0.1155	0.1476	0.1713	
DD	0.1155	0.1154	0.1821	
E	0.1155	0.1857	0.1851	
F	0.1155	0.1567	0.1982	
G	0.1155	0.1205	0.2049	

Table 7. Lead concentrations in water samples(ppm) using ICP.

Figure 4. Pb concentration in water samples using ICP



SAMPLE	12-Aug	16-Sep	14-Oct 0.898	
AR	0.563	0.644		
BDR	0.485	0.562	0.869	
DD	0.483	0.53	0.624	
E	0.502	0.749		
F	0.539	0.583	0.539	
G	0.467	0.764	0.904	

Table 8. Zinc concentrations in water samples(ppm) using Atomic Absorption (AA).

Figure 5. Zn concentrations in water samples using Atomic Absorption.



The Quality of Surface and Groundwater in the Rural Western Cape with regard to Pesticides Page E-9 Table 9. Zinc concentrations in water samples(ppm) using ICP.

SAMPLE	12-Aug	16-Sep	14-Oct
AR	0.4721	0.51	0.68
BDR	0.3856	0.4332	0.612
DD	0.406	0.4008	0.4302
E	0.3425	0.573	0.4768
F	0.3605	0.4118	0.3771
G	0.3718	0.56	0.622

Figure 6. Zn concentrations in water samples using ICP.



#### DISCUSSION OF RESULTS

This investigation had two main objectives. Firstly, to determine the concentration levels of heavy metals (Cu, Pb and Zn) in the Hex River Valley. It is very important to do so, because there are concentration levels under which the river will not be polluted and above which the river will be considered as being polluted. The department of Water Affairs has standard specifications which will help in deciding whether the river is polluted

or not.	Copper	< 1 ppm
	Lead	< 0.1 ppm
	Zinc	< 5 ppm

Secondly, another objective for this investigation was to compare two spectroscopic methods of analysis i.e. atomic absorption and atomic emission spectroscopy. AR (a reservoir sample), was polluted due to copper in the month of October and due to lead in all three months. Zinc concentrations were lower than the specification, therefore zinc will not be considered as a pollutant. BDR (a drain sample), was polluted only due to lead. Concentration levels of copper and zinc were so low as to be of no concern to users of groundwater in the Hex River Valley.

- DD (a dam sample), was polluted due to lead in all three months, due to copper only in August and never
  polluted due to zinc.
- E (a sample taken up-stream), was polluted due to lead in all three months, due to
- copper only in September and not polluted due to zinc.
- F (a sample along the river), was polluted only due lead in all three months and not polluted due to copper or zinc.
- G (a sample taken down-stream), was polluted due to copper in October, due to lead in all three months
  and not polluted due to zinc.

In most cases the ICP gave slightly higher readings than the AA. This means that Atomic Emission Spectroscopy is more sensitive than Atomic Absorption Spectoscopy.

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# APPENDIX F:

## AGREEMENT WITH THE HEX RIVER PRODUCERS ASSOCIATION

APPENDIX F: AGREEMENT WITH THE HEX RIVER PRODUCERS ASSOCIATION

### OOREENKOMS

#### MEMORANDUM VAN OOREENKOMS AANGEGAAN DEUR EN TUSSEN :

Die Universiteit van Kaapstad hierin verteenwoordig deur

van Privaatsak , RONDEBOSCH, 7700 (hierna die "UNIVERSITEIT" genoem)

. . 4

EN

HEXVALLEI PRODUSENTE VERENIGING hierin verteenwoordig deur

van : Posbus 193, DE DOORNS, 6875 (hierna die "VERENIGING" genoem)

AANGESIEN DIE UNIVERSITEIT EN DIE VERENIGING 'n ondersoek of ondersoeke wil laat instel op die effek wat die gebruik van landbou-chemiese spuitstowwe op die kwaliteit van die waterbronne in die Hexriviervallei het met die oog om die gegewens in die belang van die inwoners van die Vallei en in die belang van die land as geheel te tabelleer en te verwerk en te ontleed;

EN AANGESIEN voormelde doel nie effektief bereik kan word deur die ondersoeke op 'n ad-hoc basis te doen nie, maar sistematies volgens ooreengekome prosedures en deur middel van 'n ooreengekome struktuur;

NOU DAAROM kom die partye soos volg ooreen :

- 1. Die partye sal vir voormelde doel 'n Komitee saamroep bestaande uit :
  - a. Universiteit van Kaapstad as kontraktant ten opsigte van die Waternavorsingskommissie se navorsingsprojek;

2/....

b. 'n verteenwoordiger van die Hexvallei Produsente Vereniging;

- a verteenwoordiger van die Navorsingsinstituut vir Wingerdbou en Wynkunde;
- d. n verteenwoordiger van Unifruco.

soos van tyd tot tyd in samewerking met voormelde instansles aangewys.

- Voormelde Komitee sal op 'n gereelde basis vergader soos van tyd tot tyd, na die behoeftes van die tyd, deur die Komitee self bepaal.
- Die VERENIGING sal toesien dat sy lede hulle hartlike steun en samewerking aan die UNIVERSITEIT en aan voormelde Komitee lewer ten einde die nodige data te versamel en enige probleme wat uit sodanige data mag blyk te bestaan, aan te spreek.
- 4. Die UNIVERSITEIT sal so spoedig moontlik na ondertekening van hierdie ooreenkoms, 'n volledige voorstel aan die VERENIGING voorlê waarin al die verskillende stappe as wat nodig is om die navorsingsprojek deur te voer, sistematies uiteengesit word. Indien die VERENIGING inspraak wil lewer insake die stappe uiteengesit, sal die partye die nodige samesprekings voer ten einde die prosedure wat gevolg moet word gesamentlik te bepaal tot bevrediging van beide partye. Daarna sal die partye saam werk om die navorsing ooreenkomstig die prosedure te doen.
- Die partye sal in samewerking met die Komitee so spoedig moontlik die verskillende stappe soos bepaal, volg ten einde vas te stel of daar enige probleme in die Hexvallei bestaan vanweë die toediening van landbou-chemiese spuitstowwe.

Indien daar na die mening van die UNIVERSITEIT wel probleme bestaan, sal die Universiteit sy bevindings aan die Komitee voorlê wat so spoedig moontlik die bevindings sal ontleed en in samewerking met die UNIVERSITEIT, enige probleme sal probeer opios. Die gegewens soos verkry deur die UNIVERSITEIT sal nie publiseer word, of aan enige ander instansie of persone as die Komitee of die partye hiertoe, beskikbaar gestel word voordat die partye hiertoe nie deur bemiddeling van die Komitee geleentheld gehad het om insette te lewer op enige bevindings wat gemaak is en om die nodige besprekings daaroor te voer.

DR.

3/....

-3-

Indien die VERENIGING beswaar het teen die gegewens voorgelê of die interpretasie daarvan, sal die VERENIGING geregtig wees om enige geskille wat daar mag wees, vir mediasie aan die Waternavorsingskommissie voor te lê binne 14 (veertien) dae nadat die besware ontstaan het.

- Die UNIVERSITEIT sal geen vraelyste wat hulle beoog om onder produsente en/of ander groepe in die Hexvallei te versprei, na enige produsent en/of ander groepe stuur voordat dit nie vooraf aan die Komitee voorgelê is vir insae en kommentaar.
- Die VERENIGING sal self aanspreeklik wees vir enige koste verbonde aan die deelname van die VERENIGING se lid aan die werksaamhede van die Komitee.

UCT 27th GETEKEN TE hierdie op dag van Octabe AS GETU Marsh LONDON L namens DIE UNIVERSITEIT VAN KAAPSTAD avis 1 33/10/97 UNIVERSITY OF CAPE TOWN GETEKEN De Doorns TE OD hierdie Gde dag van November 1997 AS GETUIES These a & Aardaa. namens HEXVALLEI PRODUSENTE VERENIGING 2 Breadt

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# APPENDIX G:

## QUALITY ASSURANCE RESULTS INTERLABORATORY AGREEMENT

A Quality Assurance (QA) protocol (see Table 3.5 in the main text) was established with the laboratories of the Agricultural Research Council (ARC) and the State Forensic (SF) laboratory for the duration of the study. The purpose was to measure and to minimise bias and imprecision in study results so as to improve the validity of study findings. The QA protocol involved.

- A total of 11 runs of parallel samples were forwarded to the SF laboratory over the course of 1998 (4 from Piketberg, 2 from Grabouw and 5 from Hex River) and two sets to the ARC in March and August 1998 (from the Hex River).
- One set on the 12<sup>th</sup> August 1998 included samples submitted to all 3 laboratories simultaneously (PENTECH, SF and ARC). Inter-laboratory comparisons enabled estimation of bias.
- In addition to the above, a triplicate set of multiple samples (n=7 for each laboratory) taken from a single sampling point in the Hex River (Bdr) was sent to all 3 laboratories in June 1998. This enabled estimation of bias and precision in inter-laboratory agreement.
- In August and September 1998, sampling point Bdr was sampled twice and the second sample given a false identifier (I) to blind the laboratories.

QA procedures used in the study have been summarised in the main text in Table 3.5.

#### SOURCES OF VARIABILITY

Potential sources of variability that may give rise to discrepant results were addressed:

#### 1. Field sampling methods

For all the samples for different laboratories, the same sampling methods were used in the field.

#### 2. Time to analysis

As outlined in the main text, care was taken to try to reduce variability in the time taken for samples to reach participating laboratories. For example, samples for the SF laboratory in Cape Town were held overnight in a refrigerator at the PENTECH laboratory at 5°C and transported within 24 hours to the SF for extraction and analysis. Samples for the ARC laboratories were couriered to the ARC laboratories using polystyrene containers aiming to keep temperature reasonably constant.

#### 3. Extraction methods

Whereas the extraction methods used by the SF laboratory follow that used by PENTECH closely, the ARC laboratories used liquid-to-liquid extraction for its analysis.

#### 4. Analytical Methods

All three laboratories use GC methods with Electron Capture Detectors (ECDs) but with different columns and temperature programmes.

 Analyses at the PENTECH laboratory proceeded using a Varian 3300 GC equipped with an electron capture detector (ECD). 2 ul sample was injected onto a capillary column with a BPX 5 stationary phase. The temperature program was 170°C initially increased at a rate of 7°C/min to 290°C and held for 5 minutes at that temperature. Injector and detector temperature were 250°C and 300°C, respectively.

- The SF laboratory used a methyl sillicon GC column and a C18 ec column for sample prep. The temperature programme was as follows: temperature was held at 170°C for 0.5 minutes, increased at 20°C per minute to 195°C and held for 1.75 min, then increased at 30°C per minute to 280°C where it was held for 2 minutes and then increased at 30°C per minute to 295°C where it was held for 2 minutes. SF laboratory results were reported without quantification limits.
- The ARC laboratory made use of a 2m 3% OV-17 column, using a temperature programme starting at 200°C.

#### 5. Confirmation

Pesticides identified and quantified at the PENTECH and at the SF laboratories were not confirmed on a second column nor by GC /MS method. It is understood that the ARC laboratories as conforming to good laboratory practice would have confirmed all positives on a second method but no verification of this was confirmed during the study.

In the course of the study, we were informed that analyses at the SF laboratory had been delayed by the analysis of a sediment sample that disrupted the GC column dedicated to pesticide analyses. The impact of this event on the pick-up from the SF laboratory and on QA analyses is difficult to predict and is discussed below.

#### QUALITY ASSURANCE RESULTS

Details of the Quality Assurance measurements for the 3 study areas over the course of the project are contained in Tables A.7.1 to A.7.5. The first two tables (A.7.1 and A.7.2) contain results of split samples from the Hex River for interlaboratory comparisons. Table A.7.1 includes 1 week's samples comparing PENTECH to the ARC laboratory and 5 weeks of sampling involving comparisons with the SF laboratory. Table A.7.2 is a similar comparison for data from all three laboratories for the sampling run of 12<sup>th</sup> August 1999. Tables A.7.2 and A.7.3 include comparisons between PENTECH and SF laboratories for Grabouw and Piketberg, respectively. Table A.7.5 presents data from comparisons of multiple samples taken from one site in the Hex River (Bdr) to assess intra-laboratory agreement for bias and precision.

- a) In the March runs, PENTECH results were systematically higher than the ARC for chlorpyrifos but not for endosulfan. The ARC laboratory also did not detect chlorpyrifos peaks in 3 samples, which were all samples for which PENTECH identified chlorpyrifos at levels comfortably above our quantification limit.
- b) In the April runs, PENTECH results were in both qualitative (detection occurred in same sampling spots) and quantitative (magnitude of similar order) agreement with the State Laboratory.
- c) However, when the May runs took a range of samples from the same sampling point (previously showing peaks of chlorpyrifos and endosulfan), the bias between PENTECH and State laboratory increased somewhat, whereas that between the ARC and PENTECH was reduced for chlorpyrifos but appeared to increase for endosulfan species.
- d) In the August runs, agreement between PENTECH and State laboratory was of a reasonable order, across a range of concentrations. There was one exception in that the blinded duplicate specimen for Bdr produced a level of 0.435 μg/ℓ at PENTECH but was negative at the State laboratory. However, because the original sample for Bdr gave reasonably good agreement between the two laboratories (0.356 μg/ℓ and 0.22 μg/ℓ, respectively), we feel the PENTECH result shows reasonable consistency.

Note also that the intra-laboratory comparisons (Table A.7.5) showed comparable precision between the three laboratories, with PENTECH having the lowest Coefficient of Variation (CV) for the measurement of chlorpyrifos, and ARC having the lowest CV for endosulfan sulfate. However, CV's appeared to be dependent on mean concentrations, with greater precision achieved for higher mean concentrations.

#### DISCUSSION

Variability between laboratories in analytical measurements may be large without implying any of the results are invalid, particularly when laboratories are measuring pesticides at very low concentrations (parts per billion) as is the case in this study. The reasons for such variation may reflect the inherent instability of the samples and may relate to the timing of sampling, the presence of time delays, and other factors that may differentially affect the "decay" of organic compounds. Additionally, a large part of the variation in results may be attributable to the adsorption of pesticides onto different species in the water, and different methods of sample preparation may detect different fractions of the species present (personal communication. Dr Phillip Kempster, Institute Water Quality Studies). While QA analyses attempt to control for these factors as far as possible, it is not possible to standardise such conditions entirely, and it is not unusual for such differences to be encountered in usual analytical practice. Thus QA analyses for organic chemicals need to be interpreted with these constraints in mind. Indeed, because a single reading is always itself the product of a process of inherent variability with a laboratory, normative practice in some instances emphasises an analytical range as being the appropriate way to present a single finding.

Furthermore, when one of the participant laboratories is an analytical research laboratory geared to the analysis of pesticides, it is quite likely that greater attention will be paid to precautions and procedures than occurs at laboratories where analyses are routine.

Given these considerations, what may be more important from a QA perspective at very low concentrations is that results should consistently be able to:

- identify qualitatively the presence of the same pesticides across different laboratories, and report similarly the qualitative absence of the same pesticide, where such pesticide is not detected;
- show a consistent gradient in concentration patterns for different samples analysed by the same laboratory.i.e. where a pesticide is found in differing concentrations in a number of samples analysed by one
  laboratory, another laboratory should demonstrate a similar gradient of concentations, even if discrepancies
  arise between laboratories in the absolute concentrations.

Based on the above criteria, the findings of QA in this study appear to suggest acceptable agreement and precision of measurements conducted at the PENTECH laboratories for endosulfan and chlorpyrifos. Strong qualitative agreement for most sampling points emerged in the comparisons for laboratories in 1998. For example, QA analyses in the Hex River valley (table A.7.1) in March and April 1988, showed reasonable agreement for the presence of pesticides (11 of 20 possible detections were events where both laboratories reported detections) and strong agreement on the absence of pesticides (41 of 50 possible non-detections). Moreover, agreement for high vs. low results was also commonly found across sample points, giving an overall pattern of consistency.

There were problems with comparisons with the SF laboratory towards the end of the study. This was largely due to the consequences of a sediment sample being analysed on the SF GC late in 1998 (McGregor, 1999) which disrupted the functioning of the GC column. This precludes meaningful interpretation of the data obtained from the SF laboratory from September 1998 onwards for inter-laboratory agreement. However, a number of factors provide grounds for believing that the levels of precision and accuracy achieved early in the study were maintained throughout the study:

- Patterns detected in the Hex River valley area in the first 4 months of the study by the PENTECH laboratory were more or less reproduced one year later
- Intralaboratory procedures and QC did not change at PENTECH.

#### CONCLUSION

Results of the QA analyses suggest that the laboratory analytical procedures followed in this study were able to achieve adequate precision and inter-laboratory agreement, consistent with normative practice for such strategies. Discrepancies that were detected are entirely consistent with normative variation obtained in such procedures and were relatively small. Most importantly, the QA analyses provide sufficient ground for making reasonable inferences from the main findings of the study.

	PESTICIDES & CONCENTRATIONS IN (µg/l)									
DATE & SAMPLE ID	CHLOR	PYRIFOS	ALPHA- ENDOSULFAN		BETA- EN	DOSULFAN	ENDOSULFAN SULPHATE			
	Pentech	ARC	Pentech	ARC	Pentech	ARC	Pentech	ARC		
11/3/98										
Ar	0.17	0.04	ND	ND	0.06	ND	0.105	0.1509		
Br	ND	ND	ND	ND	ND	ND	0	0.0631		
Bdr	19.13	0.1	0.11	ND	0.28	0.41	1.248	16.79		
Cdr	1.14	ND	ND	ND	ND	ND	0.073	0		
Dd	0.15	ND	ND	ND	ND	ND	0	0		
E	ND	ND	ND	ND	ND	ND	0	0		
F	0.19	0.1	ND	ND	ND	ND	0.161	0.1361		
G	0.1	ND	ND	ND	ND	ND	0	0		
	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic		
22/4/98										
Ar	ND	ND	ND	ND	ND	ND	ND	ND		
Br	ND	ND	ND	ND	ND	ND	ND	ND		
Bdr	1.13	0.64	ND	0.01	ND	0.03	0.43	0.21		
Cdr	ND	ND	ND	ND	ND	ND	ND	ND		
Dd	ND	ND	ND	ND	ND	ND	ND	ND		
E	ND	ND	ND	ND	ND	ND	ND	ND		
F	0.18	0.12	ND	0.01	ND	0.03	0.25	0.18		
G	ND	ND	ND	ND	ND	ND	ND	ND		
19/5/98										
Ar	0.04	ND	ND	ND	0.019	ND	0.038	ND		
Br	NS	NS	NS	NS	NS	NS	NS	NS		
Bdr	2.54	1.42	0.08	ND	0.029	0.01	0.126	0.04		
Cdr	0.06	ND	ND	ND	ND	ND	ND	ND		
Dd	0.06	ND	ND	ND	ND	ND	ND	ND		

#### Table A.7.1 HEXRIVER QUALITY ASSURANCE RESULTS

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DATE & SAMPLE ID	CHLORPYRIFOS		ALPHA- ENDOSULFAN		BETA- END	OSULFAN	ENDOSULFAN SULPHATE	
	Pentech	ARC	Pentech	ARC	Pentech	ARC	Pentech	ARC
E	0.5	0.38	ND	ND	ND	ND	ND	ND
F	0.09	ND	0.02	ND	0.017	ND	0.024	ND
G	0.043	ND	0.01	ND	ND	ND	0.014	ND
23/9/98								
Ar	0.01	ND	ND	ND	0.02	ND	ND	ND
Br	ND	ND	ND	ND	ND	ND	ND	ND
Bdr	1.34	ND	0.1	ND	0.01	ND	ND	ND
Cdr	ND	ND	ND	ND	ND	ND	ND	ND
Dd	0.29	ND	ND	ND	0.06	ND	0.14	ND
E	0.06	ND	0.01	ND	0.02	ND	0.01	ND
F	0.21	ND	0.29	ND	0.66	ND	0.9	ND
G	0.02	ND	ND	ND	ND	ND	ND	ND
н	0.02	ND	ND	ND	ND	ND	ND	ND
1	1.29	ND	0.05	ND	0.15	ND	0.29	ND
J	0.022	NA	ND	NA	ND	NA	ND	NA
К	ND	ND	ND	ND	ND	ND	ND	ND
21/10/98								
Ar	ND	ND	0.02	ND	0.06	ND	0.11	ND
Br	ND	ND	0.05	ND	0.05	ND	ND	ND
Bdr	0.17	ND	ND	ND	ND	ND	ND	ND
Dd	0.08	ND	ND	ND	0.05	ND	ND	ND
E	ND	ND	ND	ND	ND	ND	ND	ND
F	0.05	ND	0.04	ND	ND	ND	ND	ND
G	ND	ND	0.03	ND	0.08	ND	0.15	ND
н	ND	ND	0.02	ND	0.09	ND	0.13	ND
J	ND	ND	ND	ND	ND	ND	ND	ND
K	ND	ND	ND	ND	ND	ND	ND	ND
18/11/98								
Ar	ND	ND	ND	ND	ND	ND	ND	ND
Br	ND	ND	0.06	ND	ND	ND	ND	ND
Bdr	ND	ND	ND	ND	0.13	ND	0.45	ND
Dd	ND	ND	0.09	ND	0.12	ND	0.36	ND
E	ND	ND	ND	ND	ND	ND	ND	ND
F	ND	ND	ND	ND	ND	ND	ND	ND
J	ND	ND	ND	ND	ND	ND	ND	ND

APPENDIX G: QUALITY ASSURANCE RESULTS : INTERLABORATORY AGREEMENT

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#### APPENDIX G: QUALITY ASSURANCE RESULTS : INTERLABORATORY AGREEMENT

			Table A.7	.2					
HEXRIVER QUAL	ITY ASSUR	ANCE RESUL	TS SAMPL	ES,	12/8/98,	PENTECH,	ARC A	ND FOREN	ISIC
		INTERLABO	RATORY	COM	PARISO	NS			

	C	HLORPYP	RIFOS	ALP	HA-ENDO:	SULFAN	BET	A-ENDOS	ULFAN	ENDO	SULFANS	ULPHATE
	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results
	Ex	Ex	Ex	ex	ex	ex	Ex	ex	ex	ex	ex	ex
Site	Pentech	ARC	Forensic	Pentech	ARC	Forensic	Pentech	ARC	Forensic	Pentech	ARC	Forensic
Ar	0.03	ND	0.02	ND	ND	ND	ND	ND	ND	0.02	ND	ND
Br	0.03	ND	0.04	0.01	ND	ND	0.04	ND	ND	0.15	ND	ND
Bdr	0.36	0.5	0.22	ND	ND	ND	ND	1.02	ND	0.03	0.18	ND
Cdr	ND	NA	NA	ND	NA	NA	ND	NA	NA	ND	NA	NA
Dd	0.33	NA	0.16	ND	NA	ND	ND	NA	ND	ND	NA	ND
E	0.04	ND	ND	ND	ND	ND	ND	ND	ND	0.03	ND	ND
F	80.0	0.12	0.04	0.02	ND	ND	ND	0.53	ND	0.02	ND	ND
G	0.07	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
н	0.02	ND	0.02	ND	ND	ND	ND	ND	ND	ND	ND	ND
1	0.44	0.4	ND	0.01	ND	ND	0.02	ND	ND	0.04	ND	ND
SP	0.21	ND	0.03	0.52	ND	0.4	2.91	ND	1.12	4.33	ND	1.54
D = Not S = Not	detected sampled	Base	arian ware b	-law 700								

APPENDIX G: QUALITY ASSURANCE RESULTS : INTERLABORATORY AGREEMENT

			PESTIC	CIDES & CONC	ENTRATION	IS IN (µg/i)		
DATE & SAMPLE ID	CHLOR	PYRIFOS	ALPHA-EN	DOSULFAN	BETA-END	OSULFAN	ENDOSULFA	N SULPHATE
	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic
29/7/98								
G1d	ND	ND	ND	ND	ND	ND	ND	0.04
G2b	0.01	ND	ND	ND	ND	ND	0.16	1
G3r	ND	ND	ND	ND	ND	ND	ND	ND
G4r	ND	ND	ND	ND	ND	ND	ND	ND
G5d	ND	ND	ND	ND	ND	ND	ND	0.04
G6b	NS	NS	NS	NS	NS	NS	NS	NS
G7d	ND	ND	ND	ND	ND	ND	ND	ND
GBt	NS	NS	NS	NS	NS	NS	NS	NS
06/9/98								
G1d	ND	ND	0.03	ND	ND	ND	ND	ND
G2b	0.06	ND	0.04	ND	0.01	ND	ND	ND
G3r	ND	NA	ND	NA	ND	NA	ND	NA
G4r	0.01	ND	ND	ND	ND	ND	ND	ND
G5d	ND	ND	0.02	ND	0.25	ND	0.45	ND
G6b	NS	NS	NS	NS	NS	NS	NS	NS
G7d	ND	ND	ND	ND	ND	ND	ND	ND
GBt	0.04	ND	0.05	ND	0.02	ND	ND	ND
12/10/98								
G1d	0.15	ND	ND	ND	ND	ND	0.07	ND
G2b	ND	ND	ND	ND	0.04	ND	0.06	ND
G3r	ND	ND	ND	ND	ND	ND	ND	ND
G4r	ND	ND	ND	ND	0.05	ND	0.05	ND
G5d	ND	ND	ND	ND	ND	ND	ND	ND
G7d	0.1	ND	0.06	ND	0.09	ND	0.08	ND
G8t	ND	ND	ND	ND	ND	ND	ND	ND

#### Table A.7.3 GRABOUW QUALITY ASSURANCE RESULTS

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#### Table A.7.4 PIKETBERG QUALITY ASSURANCE RESULTS

			PESTICI	DES & CONCE	INTRATIONS	5 IN (μα/ℓ)			
SITE & SAMPLE ID 20/5/98 P1B P2D P3B	CHLOR	PYRIFOS	ALPHA-EN	DOSULFAN	BETA-END	OSULFAN	ENDOSULFAN SULPHATE		
	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic	Pentech	Forensic	
20/5/98									
P1B	NS	NS	NS	NS	NS	NS	NS	NS	
P2D	ND	ND	ND	ND	ND	ND	ND	ND	
P3B	NS	NS	NS	NS	NS	NS	NS	NS	
P4R	ND	ND	ND	ND	ND	ND	ND	ND	
P5R	ND	ND	ND	ND	ND	ND	ND	ND	
P6R	ND	ND	ND	ND	ND	ND	ND	ND	
P7B	ND	ND	ND	ND	ND	ND	ND	ND	
P8T	ND	ND	ND	ND	ND	ND	ND	ND	
01/7/98									
P1B	0.09	ND	ND	ND	ND	ND	ND	ND	
P2D	0.03	ND	0.03	ND	0.06	ND	ND	ND	
P3B	0.06	ND	ND	ND	ND	ND	ND	ND	
P4B	0.03	ND	ND	ND	ND	ND	ND	ND	
P5B	0.04	ND	ND	ND	ND	ND	ND	ND	
P6B	0.04	ND	ND	ND	ND	ND	ND	ND	
P7B	0.03	ND	ND	ND	ND	ND	ND	ND	
Dat	0.05	ND	ND	ND	ND	ND	ND	ND	
12/9/98	0.00	110	110	ND	140	NU	NU	NU	
D1R	ND	ND	ND	ND	ND	ND	ND	ND	
PID	0.12	ND	0.02	ND	0.04	ND	0.07	ND	
P2D	ND	ND	0.02	ND	0.04	ND	ND.	ND	
P3D	0.02	ND	ND	ND	ND	ND	ND	ND	
P4M DED	0.03	ND	ND	ND	ND	ND	0.04	NU	
Pan	0.06	ND	ND	ND	ND	ND	0.04	ND	
POH	0.04	ND	ND	NU	ND	ND	NU	ND	
P/B	0.04	NU	ND	NU	NU	ND	ND	NU	
7/10/98	10	10	2.04	N/D	0.00	10	0.00	10	
P18	NU	ND	0.01	ND	0.02	ND	0.02	NU	
P2D	0.02	ND	0.03	ND	80.0	ND	0.14	ND	
P3B	0.02	ND	0.02	ND	0.09	ND	0.14	ND	
P4H	ND	ND	ND	ND	ND	ND	ND	ND	
P5R	0.04	ND	ND	ND	ND	ND	ND	ND	
P6R	0.02	ND	0.01	ND	0.04	ND	0.10	ND	
P78	0.02	ND	0.01	ND	ND	ND	ND	ND	
PBT	0.05	ND	0.06	ND	0.21	ND	26.04	ND	
11/11/98									
P18	ND	ND	ND	ND	0.06	ND	0.08	ND	
P2D	0.02	ND	0.03	ND	0.07	ND	0.11	ND	
P38	0.01	ND	ND	ND	ND	ND	ND	ND	
P48	0.01	ND	0.03	ND	0.09	ND	0.08	ND	
P5R	0.05	ND	0.01	ND	0.06	ND	ND	ND	
P6R	0.04	ND	0.05	ND	0.11	ND	0.10	ND	
P78	0.09	NA.	0.02	NA	0.35	NA	0.78	NA	
P8T	0.01	ND	0.01	ND	0.01	ND	0.04	ND	

	APPENDI	IX G:
QUALITY	ASSURANCE RESULTS : IN	VTERLABORATORY AGREEMENT

#### Table A.7.5 MULTIPLE SAMPLES TAKEN FROM ONE SITE (BDR) IN HEX RIVER: INTRALABORATORY AGREEMENT

18/6/98				PE	STICIDE	S & CONC	ENTRAT	ION IN (A	(g/2)			
	СН	ORPYR	IFOS	ALPHA	A-ENDOS	ULFAN	BETA	-ENDOS	ULFAN	EN	DOSULA	FAN TE
	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results	Results
	ex	ex	ex	ex	ex	ex	ex	ex	ex	ex	ex	ex
Site	Pentech	ARC	Forensic	Pentech	ARC	Forensic	Pentech	ARC	Forensic	Pentech	ARC	Forensic
Bdr 1	0.598	0.728	0.162	0.007	nd	nd	0.021	nd	nd	0.052	0.151	nd
Bdr 2	0.781	0.899	0.340	nd	nd	nd	0.007	nd	nd	0.019	0.140	nd
Bdr 3	0.836	0.618	0.272	nd	nd	nd	0.018	nd	nd	0.039	0.136	nd
Bdr 4	0.897	0.863	0.336	0.025	nd	nd	0.008	nd	nd	0.107	0.307	nd
Bdr 5	0.772	0.123	0.106	0.023	nd	nd	0.010	nd	nd	nd	0.224	nd
Bdr 6	0.723	0.630	0.354	0.007	nd	nd	0.031	nd	nd	0.027	0.194	nd
Bdr 7	1.071	0.801	0.31	0.041	nd	nd	nd	nd	nd	0.009	0.177	nd
Mean	0.811	0.602	0.272							0.034	0.186	
Standard Deviation	0.148	0.297	0.090							0.034	0.057	
Coefficient of variation	0.182	0.493	0.331							1.00	0.306	

# APPENDIX H:

## CLIMATIC DATA: PH, TEMPERATURE AND RIVER FLOWS

APPENDIX H: CLIMATIC DATA: PH, TEMPERATURE AND RIVER FLOWS

### **CLIMATIC DATA : HEX RIVER**

SITE	11/2/98	18/2/98	25/2/98	4/3/98	11/3/98	18/3/98	25/3/98	22/4/98	19/5/98	12/8/98	23/9/98	21/10/98	12/11/98	18/11/98	13/1/99	24/2/99	17/3/99	07/4/99	20/4/99	26/4/99	13/5/99
E																					
T	24	23.8	24	23	21	22	20		16	16	19	19.5	20.2	20	25	26			18	19	17.5
pH	7.2	8.1	7.54	6.93	6.92	6.79	6.89	6.87	6.99	8.25	6.27	6.35	8.06	6.9	6.13	6.65			7.01	6.89	7.24
S	n	n	n	n	n	n	n	n	n	N	n	У	У	n	У	n			n	n	n
FI	1	1	1	1	1	1	1	1	m	1	1	1		1	1	1			1	1	1
F																					
T	25	26	25	24	21	20	20		18	15	17	21	20.7	20.5	24	23	24	20	18	22	
pH	7.62	8.68	8.74	7.25	7.11	7.01	7.14	7.1	7.07	8.41	7.27	6.53	7.56	7.17	6.29	7.82	7.52		7.46	7.11	6.98
S	n	n	n	n	n	n	n	n	n	п	n	n	У	n	n	п	n	n	n	n	n
FI	1	1	1	1	1	1	1	1	m	M	1	1		m	1	m	1	m	m	1	1
G																					
T	22	23.5	22	22.5	22	21	20		16	17	17	18	21.8	19.5	24	22	25	20	19	21	
pH	7.12	8.13	8.26	6.85	6.7	6.62	6.76	6.6	6.87	8.46	5.79	5.77	7.2	6.05	6.01	6.47	5.58		6.64	6.86	
S	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	n	
FI	m	1	1	1	1	1	1	m	m	1	m	m		m	m	m	m	1	m	m	
Cdr																					
T	23	25	24	23	21	21	20		16	17											
pH	7.61	7.53	7.54	6.45	6.5	6.4	6.25	6.46	6.88												
S	n	n	n	n	n	n	n	n	n	n											
FI	1	1	1	1	1	1	1	1	m	1											
Bdr																					
T	25	27	25	27	22	23	20		18	15	17	20	19.7	23.5		30	30	23	20	22.5	20
pH	7.57	8.63	8.66	7.2	7.1	7.1	7.27	7.14	6.89	8.19	7.06	6.29	7.57	7.01		7.33	7.05		7.04	6.84	6.37
S	n	n	n	n	n	n	n	n	n	n	n	Y .	Y .	n		n	n	n	n	n	n
FI	1	1		-	1	1	-	1	1	m	1	1		m		m	m	1	1	1	1
Ar	0.062	0	0	0	0.167	0	0	0	0.036	0.03	0.01	0	0	0	0.169	0.106	0.24	0		0.089	0
T	23	25	24.5	25	22.5	22	19		14	12		20	16.1	18	23	21	23	21		21	21
pH	7.38	8.07	7.85	6.92	6.92	7.01	7.1	6.8	6.94	8.26		6.72	7.94	7.33	6.6	6.73	6.42			7.23	6.64
S	n	n	n	n	n	n	n	n	n	n		n	n	n	n	n	n	n		n	n
FI	m	m	1	h	1	-	1					m		m	m	m		m		m	m
Br													00.6								
T	25	25	24	25	22.7	21	21			14		20	23.1	18	20	26	25	23	18		
pH	7.37	7.74	8.21	6.87	6.82	6.84	7.03	6.26		8.32		7.16	8.3	7.33	6.38	7.48	7.29		7.18		
S	n	n	n	n	n	n	n	n		n		У	У	n	n	n	n	n	n		
FI		m	m		m					m		m		m		m			h		

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APPENDIX H: Climatic Data: pH, Temperature and River Flows

SITE	11/2/98	18/2/98	25/2/98	4/3/98	11/3/98	18/3/98	25/3/98	22/4/98	19/5/98	12/8/98	23/9/98	21/10/98	12/11/98	18/11/98	13/1/99	24/2/99	17/3/99	07/4/99	20/4/99	26/4/99	13/5/99
D																					
T	29	29	30	28	25	26	22		18	17	18	21		23	31	28	30	25	19	21	26
pH	7.99	8.63	8.84	7.29	7.09	7.27	7.26	7.53	6.98	8.51	7.93	7.86		8.17	7.61	7.75	7.91		7.53	8.78	7.86
S	n	n	n	n	n	n	n	n	n	n	n	n		n	n	n	n	n	n	n	n
FI	m	1	1	1	1	1	1	1	m	1	1			m	1	1	m	m	m	m	m
H																					
T										17	16	17	17.5	18	22	21	22	20	19		
pH										8.32	5.5	6.4	7.43	7.37	8.09	7.58	7.46		5.57		
S										n	n	n	n	n	13	п	n	n	n		
FI										1	1						m	m	m		
J											0.022	0	0	0		0.088	0.212	0.471			0
T											18.5	19.5	22.7	19		24.5	24	24			22
pH											8.56	6.7	7.9	7.27		6.55	6.43				7.04
S											n	n	y y	n		n	n	n			n
FI											1							m			
K												0		0.094							
T											11	20		18							
pH											6.34	6.4		7.13							
S											n	n		n							
FI											1	1		1							
L											0		0	0		0.311					
T											15.5		25.8	22		28					
pH											6.61		8	7.88		7.75					
S											n		У	n		n					
FI											1			1		1					
M																					0
T																					21
pH																					6.7
S																					n
FL																					m

T = Water temperature in degrees celcius

S = Spraying 1 km from site, y = yes, n = no

FI = Flow, I = low, m = medium, h = high

#### APPENDIX H: CLIMATIC DATA: PH, TEMPERATURE AND RIVER FLOWS

#### GRABOUW

Site					12/10/98	17/11/98	3	18/1/99	18/2/99	03/3/99	24/3/9	15/4/9	23/4/99	05/5/99
G3														
т	16	14	11	16		16.6		21	24		18	18	15	15
pН	6.76	6.95	7			7.36	7.42	6.51	8.08		6.4	6.5	7.16	7.48
S	n	N	N	N		N	N	N	N		N	N	N	N
FI	m	M	M	M		M	L	L	M		M	L	M	M
G4														
Т	11	17	12	17		16.6		24	29	23	21	17.5	20	18
pH	6.79	6.96	6.93	5.12		7.54	5.1	7.02	5.68	6.7	6.85	6.76	6.65	6.65
S	12.5	N	N	N		N	N	N	N	N	N	N	N	N
FI	m	M	M	L		M	M	M	M	M	M	M	M	M
G7d														
Т	18		12.5	17		18		25		24	24		15	16
pН	6.78	6.99	7	4.92		7.29	6.78	6.96		7.1	6.17	6.91	7	7.62
S	N	N	N	N		N	N	N		N	N	N	N	N
FI	L	M	н	L		M	M	L		L	L	L	L	L
G1d														
T	17	17	14	22		18.8		25.5	30	25	22.5	18	18	19
pH	6.93	7	7.09	6.73		8.96	7.42	7.85	7.83	7.54	7.13	6.74	7.04	6.99
S	N	N	N	N		N	N	N	N	N	N	N	N	N
FI	н	н	н	L			L	L	M	M	L	L	L	M
G5d														
Т	16	16	13	16		16.7		21	23	21	19	18	19	18
DH	6.84	6.99	6.93	5.81			5.45	6.27	6.06	6.34	6.23	6.47	6.5	6.51
S	N	N	N	N		N	N	N	N	N	N	N	N	N
FI	L	M	н	M			M	M	L	L	L	M	M	M
G2d														
T	15	17	19	29		15.5		29		29	23	15		
DH	6.77	6.99	7.07	6.2		8.1	7.12	7.09		7.42	6.47	7.02		
S	N	N	N	N		N	N	N		N	N	N		
FI	NA	NA	NA	M			NA	NA		NA	NA	NA		-
GBt														
T		16		18		17.7		22	26		22	21	21	
pH		6.99		6.26		8.09	5.83	6.63	6.4		6.82	6.72	6.67	
S		N		N		N	N	Y	N		N	N	N	
FI		M		NA			NA	NA	NA		NA	L	NA	
G6b														_
T	17							23			23			20
pH	6.88							6.64			6.47			7.01
S	N							N			N			N
FI	NA							NA			NA			
G9														
т												19		17.5
pH												6.93		7.07
S												N		N
FI												L		M

T S

FI

=

=

Water temperature in degrees celcius

Spraying 1 km from site, y = yes, n = no

= Flow, I = low, m = medium, h = high

#### APPENDIX H: CLIMATIC DATA: PH. TEMPERATURE AND RIVER FLOWS

#### PIKETBERG

Date	13/5/98	20/5/98	1/7/98	2/9/98	7/10/98	11/11/98	25/11/98	27/01/99	17/02/99	10/03/99	31/03/99	22/04/99	28/04/99
P1b													
T	16		14	19	19	23	25.5	23	22	25	21	18	22
pM	6.44		6.6	4.41	4.16	5.5	6.4	5.04	4.29	5.07	5.57	6.81	7.21
S	n		n	n	n	n	n	n	n	n	n	n	n
Fi	na		na	na	1	na							
P2d													
T	14	13	14	17	17	22	25	31	28	27	28	18	21
pН	6.94	7.02	7.01	5.92	5.5	5.75	5.52	5.77	5.81	6.32	6.97	7.06	5.92
S	n	n	n	n	n	n	n	n	n	n	n	n	n
FI	1	m	m	1	1	1	m	1	1		1	- 1	1
P3b													
T	16		15	18	18	24.5	20.5	20	29	26	27	17.5	20
pН	6.34		6.53	4.62	4.24	5.84	5.45	4.54	5.88	6.7		4.96	4.56
S	n		n	п	n	n	n	n	n	n	n	n	n
FI			m	m			na	na	1	na	na	na	na
P4													
Т	15.5	15	14	16	18	24	21	26	27	23	27	19	21
pH	6.84	7.01	6.99	6.28	5.35	6.87	6.88	6.63	6.05	6.61	6.8		7.5
S	n	n	n	n	п	n	n	n	n	п	n	п	n
FI	m	m	1	m	1	m	1	1	1	1	i	1	1
P5													
T	15.5	15	14	16	18.5	22	25	29	29	26	27	20	22
pH	6.84	6.95	6.96	7.67	5.72	6.67	7.17	6.9	6.11	6.84	6.4	6.8	6.48
S	n	n	n	n	n	n	n	n	n	n	n	n	n
FI	1	m	m	m	m	m	m	na	m	m	m	m	m
P6													
T	15.5	15.5	13	16	19	21	25						21
pH	6.85	7.02	6.75	8.75	6.31	6.68	6.67						7.52
S	n	n	n	n	n	n	n						n
FI	m	m	m	1	m	m	m						1
P7													
T		15	13	18	17	23	22	27	37	32	32	22	26
pH		6.92	7.02	6.64	5.22	5.59	5.5	5.47	5.86	6.61	6.08	6.95	7.14
S		n	n	n	n	n	n	n	n	n	n	n	n
FI		na	na	m		na	na	na	1	na	na	na	na
P8t													
T		17	16		20	25.5	26	31	28	27	28	21	
pН		6.99	7		6.33	6.53	7.14	6.8	7.43	7.85	6.8	6.85	
S		n	n		n	n	n	n	n	n	n	n	
FI		na	na		<b>na</b>	na	na	na	na	na	na		

т Water temperature in degrees celcius = S

FI

Spraying 1 km from site, y = yes, n = no -

Flow, I = low, m = medium, h = high =

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