# DEVELOPMENT OF AN INDICATOR METHODOLOGY TO ESTIMATE THE RELATIVE EXPOSURE AND RISK OF PESTICIDES IN SOUTH AFRICAN SURFACE WATERS

Report to the
**Water Research Commission**

by

**JM Dabrowski, K Schachtschneider, TA Ross, S Bollmohr and M Thwala**
CSIR

**WRC Report No. 1854/1/11**
**ISBN 978-1-4312-0157-0**

**September 2011**

## EXECUTIVE SUMMARY

### Project Background

A number of studies performed in South Africa illustrate that pesticides are frequently detected in surface waters across a variety of agricultural settings. Despite these findings, the potential impact of pesticides in South African surface waters has generally been a low priority and as such, has generally not been considered in aspects of water resource management. Although intensive monitoring and sampling can identify pesticide impacts, the cost of sampling and analysis makes this a highly costly exercise (particularly in the context of less developed countries). As a result there is a need to develop cost effective methods of predicting the environmental risks of pesticide use on a catchment specific basis.

The Department of Water Affairs and Forestry (DWAF) recently designed and implemented the National Toxicity Monitoring Programme (NTMP), which monitors toxicity and a number of priority toxic chemicals, the majority of which are pesticides. While monitoring and sampling can contribute to the assessment of the impact of pesticides in aquatic ecosystems, this is a very expensive exercise. Furthermore, the NTMP currently only monitors two current use pesticides (atrazine and endosulfan), while the remainder are banned persistent organic pollutants (POPs). The National Water Act (Act 36 of 1998) requires rivers to be classified according to a specific class and requires the establishment of resource quality objectives (RQOs). These are numeric or descriptive (narrative) goals for resource quality within which a water resource must be managed. RQOs are therefore designed to protect the desired class of a specific river. Given the highly toxic nature of pesticides and their risk towards ecological and human health, it is important that methodologies are developed to identify pesticides of concern as well as important areas of concern within agricultural catchments. Based on previous studies and water management initiatives in South Africa, it is clear that there is a need to identify priority catchments at risk of pesticide impacts in a cost-effective manner. In this respect, risk indicators may prove highly beneficial tools.

This study is designed to examine the application of pesticide risk indicators as a meaningful tool to predict the relative impacts of pesticides on water quality through integrating pesticide use, toxicity and physicochemical data of pesticides with site-specific geographic and climatic characteristics. It is anticipated that the developed methodology will allow users to assess and rank pesticides in terms of their risk (i.e. from low to high) to the aquatic environment, thereby encouraging informed and responsible decision making with respect to management, monitoring and mitigation of pesticides in agricultural catchments.

### Project Aims

1. To review the current status of pesticide contamination in South African water resources.
2. To assess the potential benefits of pesticide risk indicators as a lower-tier risk assessment tool in current South African water resource management initiatives (i.e. National Toxicity Monitoring Programme).
3. To develop a risk indicator methodology for estimating relative pesticide risks appropriate to the needs of South African water resource management initiatives.
4. To validate the predictions of the risk indicator methodology through field-based monitoring studies.

### Project Approach

- The approach of the project was first to review the extent of pesticide contamination in South Africa and assess the need for a pesticide risk indicator for identification problematic pesticides and identification of hotspots.

- Development of a risk indicator methodology which involved three major tasks
    1. Development of a theoretical risk indicator framework.
    2. Assessment of data requirements and availability in South Africa.
    3. Identification of runoff and spray drift models for prediction of environmental contamination.
    4. Implementation of the risk indicator through application in a catchment using catchment variables as input.
- Design and implementation of a field study to test the validity of the risk indicator.
- Validation exercise by comparing field monitoring data with the output of the risk indicator.

**Literature Review**

The literature clearly demonstrates that pesticides are frequently detected in South African surface waters, potentially posing risk to various components of the aquatic ecosystem. Despite this evidence, the potential impact of pesticides in South African surface waters has generally been a low priority and generally not considered in aspects of water resource management. Although intensive monitoring and sampling can identify pesticide impacts, the cost of sampling and analysis makes this a highly costly exercise (particularly in the context of less developed countries).

Risk indicators can be regarded as lower-tier risk assessment tools that provide a relative assessment of the environmental impact of pesticides through integration of ecotoxicological, environmental fate and pesticide use data. Risk indicators are regarded as useful tools in minimising off-site impacts of pesticides and can assist in decision making and policy formulation. Pesticide environmental risk indicators vary greatly in terms of their purpose, compartments, methodology and are often very broad in scope covering, for example, the impact on aquatic organisms, soil organisms, bees, occupational exposure and human health effects. Ideally, an indicator needs to deal not just with the inherent hazard of a pesticide but rather with the potential risk it poses. This involves taking into account the rate and method of application of the pesticide as well as environmental and site conditions and taking into consideration the asset threatened by use of that pesticide. Relative risk is assessed using site conditions (soil type, soil organic matter content, water input, slope of land, soil loss, recharge rate, depth of water table, etc.) and environmental conditions (rainfall and temperature). For each pesticide, the rate and method of application, its sorption and persistence properties, its toxicity to a range of receptor organisms (chosen to represent different trophic levels, e.g. algae, daphnia, fish and rat) is assessed. On a first level of assessment, risk indicators may be designed as instruments for predictive risk management approaches to offer preliminary insights into the *status quo* of pesticide risks. They may be developed to obtain baseline information about pesticide use and risks, focusing on one or more realistic hazardous scenarios, and they may guide the identification of potential *trouble spots* and *vulnerable areas* where risk reduction might be requisite. Furthermore, risk indicators can potentially highlight the most important route of contamination of surface waters (i.e. via runoff during rainfall or spray drift during pesticide application) and therefore provide valuable insight with respect to risk mitigation strategies for certain pesticides.

**Risk Indicator Framework**

The main purpose of the risk indicator designed in this project is to provide a qualitative indication of:

a) the relative exposure potential of a number of different pesticides applied in a catchment, and
b) the relative risk posed by these different pesticides to the aquatic ecosystem.

In producing this output, the indicator should be able to be used to:

a) identify high priority pesticides within a catchment based on their exposure and risk potential,
b) identify hotspots where exposure and risk may be relatively high, and
c) identify the main route of entry of pesticides into surface waters.

In order to fulfil the above-mentioned criteria, the developed risk indicator framework integrates pesticide application, geographical and hydrological characteristics of the catchment and physicochemical and toxicological properties of pesticides in a set of indices. This is achieved using relatively simple modelling techniques and input variables. A three step indicator framework was developed, incorporating a Pesticide Use Index (PUI), Pesticide Exposure Index (PeXI) and a Pesticide Risk Index (PeRI).

The PUI gathers information on crop area and pesticide application and assumes that contamination of a water resource is mostly dependent on the amount of pesticide used. Thus a highly used pesticide will result in relatively high contamination, while a less heavily applied pesticide will result in low contamination. For calculation of the PUI it is first necessary to calculate the total amount of pesticide applied in the catchment (Predicted Environmental Use – PEU). Three different levels of PEU can be calculated (i.e. PEU_1, _2 or _3), with PEU_1 representing the least detailed analysis, relying on estimates of crop area and application (through recommended application rates). A PEU_3 represents actual crop area and pesticide application data and is the most realistic estimate of pesticide use. PEU_2 represents an intermediate level of accuracy with either crop area or pesticide application being estimated. The PUI is calculated by expressing the total amount of each pesticide applied in the catchment as a ratio of the pesticide with highest total application. The PEU is used to calculate subsequent indices in the framework.

The PeXI provides a relative comparison of the exposure of different pesticides in surface water at different sites. Using the PEU as input; runoff and spray drift models are used to estimate the total loss of each pesticide in each catchment (Predicted Environmental Load – PEL). The PEL is integrated with hydrological data from each stream to provide an estimate of the Predicted Environmental Concentration (PEC). The PeXI is then calculated by expressing the PEC of each pesticide in each catchment as a ratio of the pesticide with the highest PEC across all catchments.

The PeRI provides an indication of the relative risk of each pesticide to the aquatic ecosystem in each stream assessed. Using the PEC as input, the toxicity to exposure ratio (TER) is calculated for each pesticide in each catchment by expressing the PEC as a ratio of the toxicity value for the pesticide. The toxicity value is derived using Species Sensitivity Distribution techniques. The PeRI is calculated by expressing the TER of each pesticide as a ratio of the pesticide with the highest TER across all sites/catchments.

**Field Study**

A catchment was selected for the purpose of monitoring of pesticide levels at selected sites and application of the risk indicator methodology. The main aim of this exercise was to attempt to validate the output of the risk indicator methodology through field based sampling of pesticide levels in water and sediment. Due to the transient nature of pesticide contamination, it is often difficult to detect pesticides using a routine (i.e. monthly) sampling routine. Thus in order to maximise the potential for detecting pesticides more intensive sampling took during the spraying (to account for spray drift contamination) and rainfall (to account for drainage and runoff) seasons.

The field study took place in the Lourens River catchment, Western Cape. This catchment has been intensively studied and numerous publications on these studies are available in the

scientific literature. A significant amount of data is therefore available for input into the proposed risk indicator. Data on pesticide application per crop type (apples, grapes, pears and plums) was obtained from farmers records. The total amount of pesticide applied in each sub-catchment and for the whole of the catchment was estimated based on these records (Table 1).

**Table 1:** Summarised pesticide application data for selected sites (BB&, C, LG4, VW and LR) included in the Lourens River study area (NA – Not Applied).

| Pesticide | BB7 | C | LG4 | VW | LR |
|---|---|---|---|---|---|
| Azinphos-methyl | 169.9 | 108.6 | 36.3 | 169.9 | 664.8 |
| Beta-cyfluthrin | 0.6 | 0.6 | 0.2 | 0.6 | 3 |
| Carbaryl | 101.9 | 20.5 | 15.8 | 101.9 | 176.6 |
| Carbendazim | 58.4 | 94.4 | 20.1 | 58.4 | 459 |
| Chlorpyrifos | 149 | 102.4 | 40.4 | 149 | 598.7 |
| Cypermethrin | NA | NA | NA | NA | 0.4 |
| Dimethomorph | NA | 135.5 | 57.8 | NA | 382.5 |
| Endosulfan | 79.2 | 15.9 | 12.3 | 79.2 | 137.3 |
| Flufenoxuron | 1.9 | 3.1 | 0.7 | 1.9 | 15.3 |
| Flusiazole | 50.9 | 10.2 | 7.9 | 50.9 | 88.3 |
| Methyl parathion | 70.2 | 50.9 | 15.8 | 70.2 | 280.8 |
| Propiconazole | NA | NA | NA | NA | 17.7 |
| Prothifos | 88.7 | 81.6 | 27.4 | 88.7 | 469.6 |
| Thiacloprid | 26.5 | 25.5 | 6.8 | 26.5 | 133.3 |
| Trifloxystrobin | NA | 2 | 0.9 | NA | 5.7 |

Sites were chosen so as to determine contamination at the catchment and sub-catchment scale. One site in the Lourens River main stem (LR) was chosen as the site representative of the entire catchment. This site is immediately downstream of both farms and therefore receives discharge from the Lourens River upstream as well as the tributaries flowing through each of the farms. Four additional sampling sites, (BB7, LG4, C and VW) were located within four tributaries so as to determine contamination at smaller spatial scales. Each of the four tributaries are characterised by different crops, buffer zone distances and slope conditions. Pesticide concentrations measured in water and sediment samples collected during the course of the study are listed in Tables 2 and 3.

**Table 2:** Summary of pesticide concentrations (µg/ℓ) detected in water samples collected in the Lourens River

| Active Ingredient | BB7 | | | C | | | LG4 | | | VW | | | LR | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max |
| α-CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| AZP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAR | **1** | **<0.05** | **0.03** | nd | nd | nd | **2** | **<0.05** | **0.5** | nd | nd | nd | **1** | **0.3** | **0.3** |
| CBZ | nd | nd | nd | **3** | **<0.05** | **<0.05** | **2** | **<0.05** | **0.06** | **1** | **<0.05** | **<0.05** | **3** | **<0.05** | **<0.05** |
| CPF | nd | nd | nd | nd | nd | nd | **1** | **<0.05** | **<0.05** | **1** | **0.1** | **0.1** | nd | nd | nd |
| CYF | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| DIM | **1** | **<0.05** | **<0.05** | **1** | **0.3** | **0.3** | **1** | **<0.05** | **<0.05** | nd | nd | nd | **2** | **0.3** | **0.3** |
| α-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| β-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| FLZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PAR | nd | nd | nd | nd | nd | nd | **1** | **<0.05** | **<0.05** | nd | nd | nd | nd | nd | nd |
| PCZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PTF | nd | nd | nd | nd | nd | nd | **1** | **<0.05** | **<0.05** | nd | nd | nd | nd | nd | nd |
| TCP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| TXB | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 3:** Summary of pesticide concentrations (µg/kg) detected in sediment samples collected in the Lourens River.

| Active Ingredient | BB7 | | | C | | | LG4 | | | VW | | | LR | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max |
| α-CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| AZP | **4** | **<10** | **<10** | **6** | **<10** | **<10** | **6** | **<10** | **10** | **1** | **<10** | **<10** | **3** | **5** | **10** |
| CAP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAR | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CBZ | nd | nd | nd | **2** | **<10** | **<10** | **1** | **<10** | **<10** | **2** | **<10** | **10** | **3** | **<10** | **10** |
| CPF | nd | nd | nd | **2** | **<10** | **<10** | nd | nd | nd | **3** | **<10** | **<10** | **1** | **10** | **10** |
| CYF | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| DIM | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| α-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| β-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| FLZ | **1** | **<10** | **<10** | nd | nd | nd | nd | nd | nd | **1** | **<10** | **<10** | nd | nd | nd |
| PAR | **1** | **20** | **20** | nd | nd | nd | **7** | **<10** | **20** | nd | nd | nd | **6** | **<10** | **20** |
| PCZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PTF | **2** | **<10** | **10** | **13** | **<10** | **10** | **10** | **<10** | **10** | **1** | **<10** | **<10** | **2** | **<10** | **<10** |
| TCP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| TXB | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

## Risk Indicator Application

The developed risk indicator methodology was applied to the Lourens River catchment with the objective being to calculate a PUI, PeXI and PeRI for each sub-catchment site (BB7, C, LG4 and VW) and for the entire catchment (LR). As detailed pesticide application data were available, the most detailed level of each index was calculated (i.e. PUI_3, PeXI_3 and PeRI_3).

*PUI*

A PUI_3 was calculated for all sites in the catchment (Figure 1). The total amount of applied active ingredient was calculated per crop per sub-catchment (PEU). Azinphos-methyl application in sub-catchment BB7 was the highest of all applied active ingredients across all sub-catchments (169.9 kg). Thus, the PUI for each active ingredient was calculated by expressing its respective PEU a ratio of 169.9. For the catchment site (LR), which is a far greater spatial scale and therefore not directly comparable to the smaller sub-catchments, the PEU for each pesticide was expressed as a ratio of 665 (the total quantity of azinphos-methyl applied in the catchment).

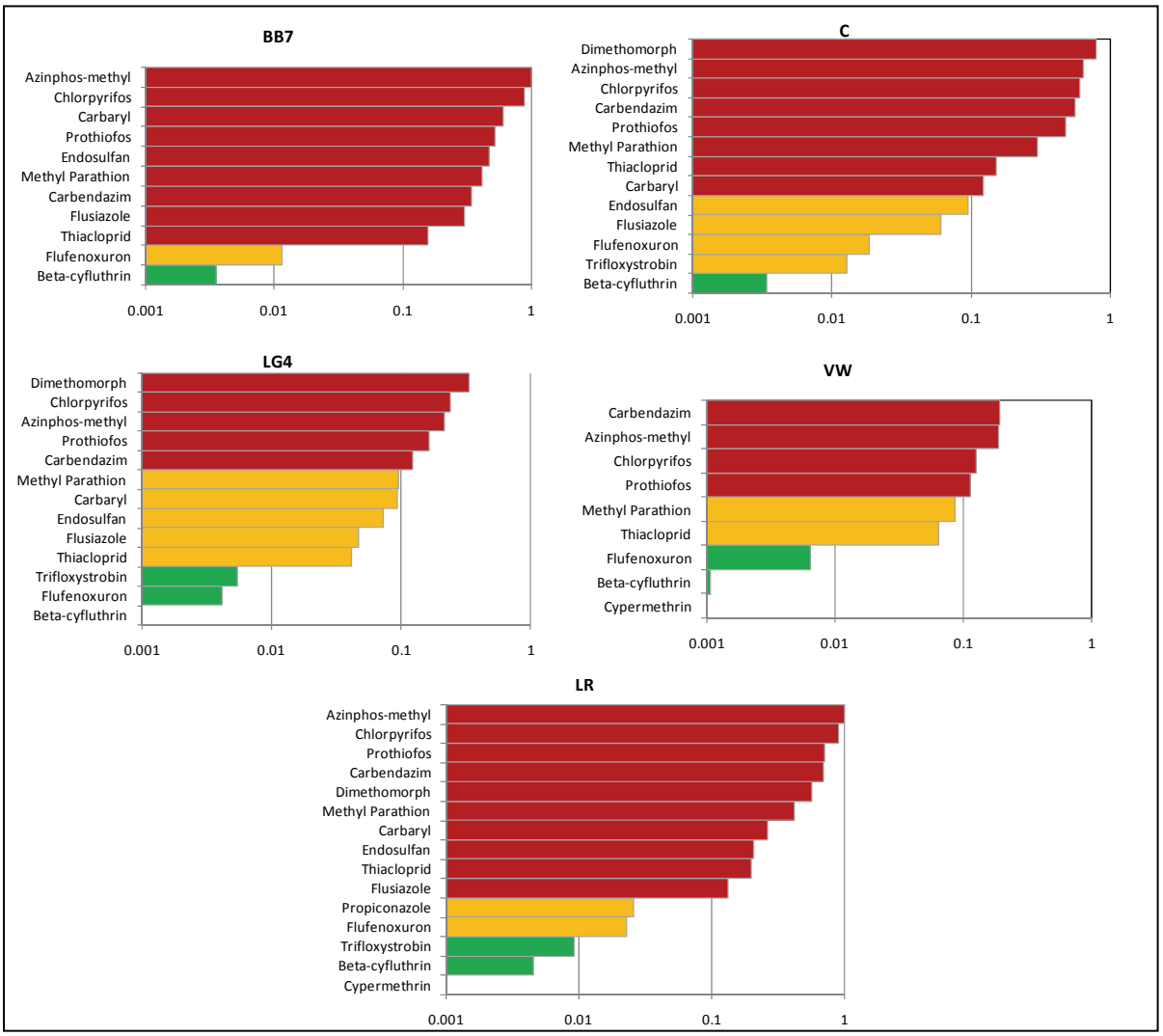



**Figure 1:** Graphs illustrating the output of the PUI for pesticides applied upstream of each site included in the study

*PeXI*

A Geographical Information System (GIS) was used to identify those orchards adjacent to tributaries that fell within defined distance classes from the tributaries (5, 7.5, 10, 15, 20, 30 and 40 m). For each field adjacent to the tributary in question, the total loss of applied

pesticide was calculated using the spray drift model identified in the risk indicator methodology. This was performed for each pesticide applied in each tributary. For runoff input data, a digital elevation model (DEM) for the catchment area was transformed into slope categories using GIS. Only orchards directly adjacent to river reaches were included for analysis in the calculation of the runoff component of the PeXI. For each field, the orchard area was over-layed with the slope profile, so as to generate a shapefile containing a description of crop type and slope (percentage). As some fields would cover more than one slope category, these fields were sub-divided into smaller field segments, each with its own unique slope category. Runoff losses were calculated assuming a 20 mm rainfall event (the average rainfall for the catchment for rainfall events above 10 mm) and a 10-day time period between application and the rainfall event. Physicochemical data for input into the runoff model was obtained from the EU Footprint Database. For each field segment (i.e. field with a specific slope category), the total loss of active ingredient per crop type was calculated using the runoff model identified in the risk indicator methodology. For each sub-catchment the total loss of each active ingredient was calculated by summing the loss per crop type. For each crop type, the total loss of each active ingredient was multiplied by the water index to obtain a final loss (kg) per crop type. The total loss of each active ingredient was then calculated by summing the total loss across each crop type (i.e. for those active ingredients applied to more than one crop type). Results of the PeXI are displayed in Figure 2.

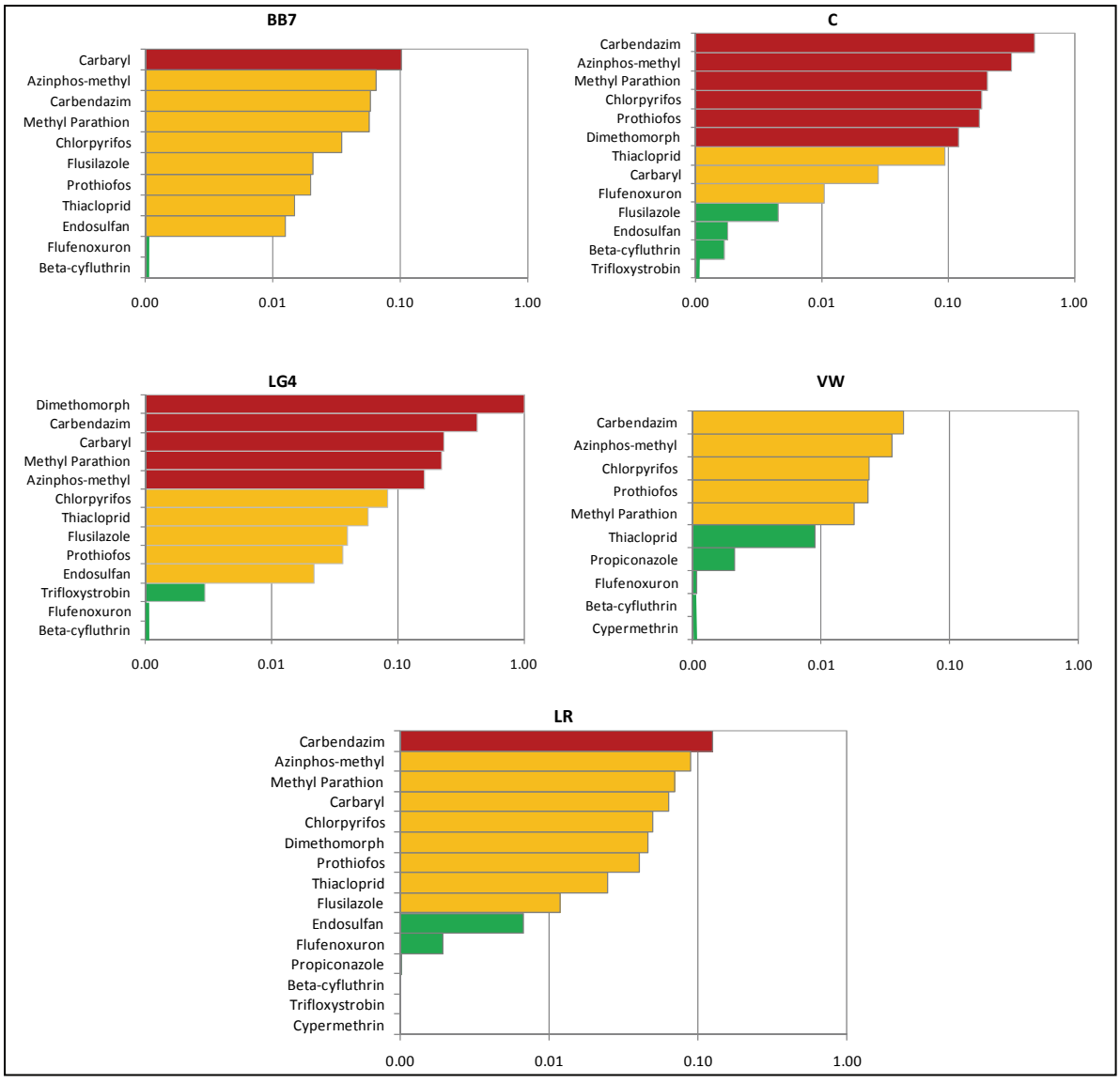



**Figure 2:** Graphs illustrating the output of the PeXI for sites BB7, C, LG4, VW and LR in the Lourens River catchment

Sites C and LG4 were predicted to be more contaminated, with a greater number of pesticides being identified as having high potential exposure. In contrast, sites BB7 and VW in particular, were predicated to have lower pesticide exposure potential with most pesticides falling in the Medium and Low PeXI score categories. The estimated contribution of runoff and spray drift to total preside loss from each of the catchments is displayed in Figure 3. Runoff would appear to be the major route of pesticide loss at LG4, while spray drift is the main transport route at VW. Both runoff and spray drift are important transport routes at site BB7 and VW.

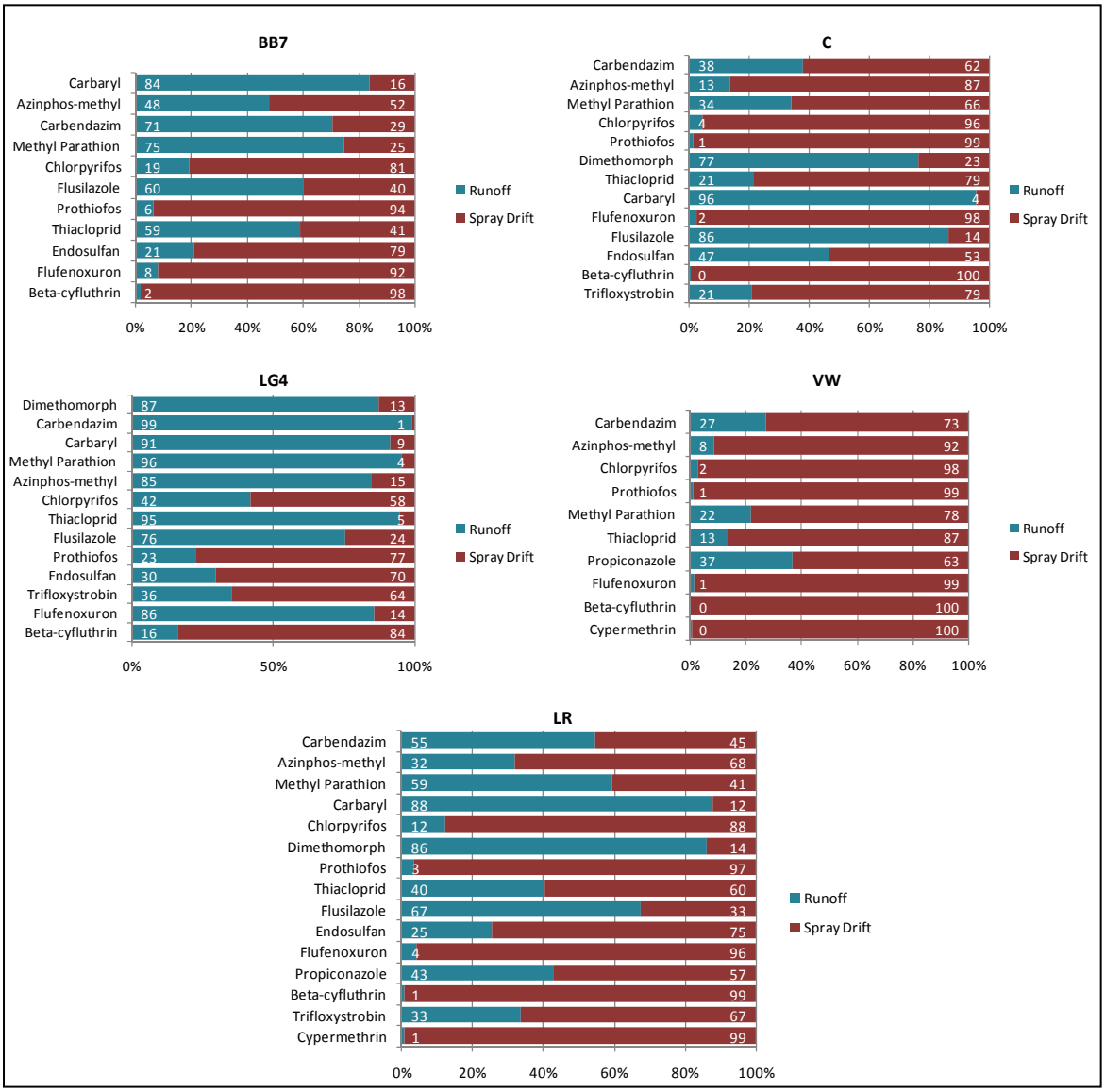



**Figure 3:** Graphs illustrating the relative contribution of runoff and spray drift to the PEL for sites BB7, C, LG4, VW and LR in the Lourens River catchment.

*PeRI*

Toxicity data was obtained from the USEPA EcoTox database. SSDs were derived using BurrliOz software and the concentration at which 95% of species would be protected was used as the toxicity value for each active ingredient. The PEC for each pesticide in each sub-catchment was divided by the relevant toxicity value to obtain the TER (Toxicity to Exposure Ratio). Chlorpyrifos at site C had the highest TER (190.45) and all TERs for all pesticides in each sub-catchment were divided by this value to obtain the final PeRI score (Figure 5).

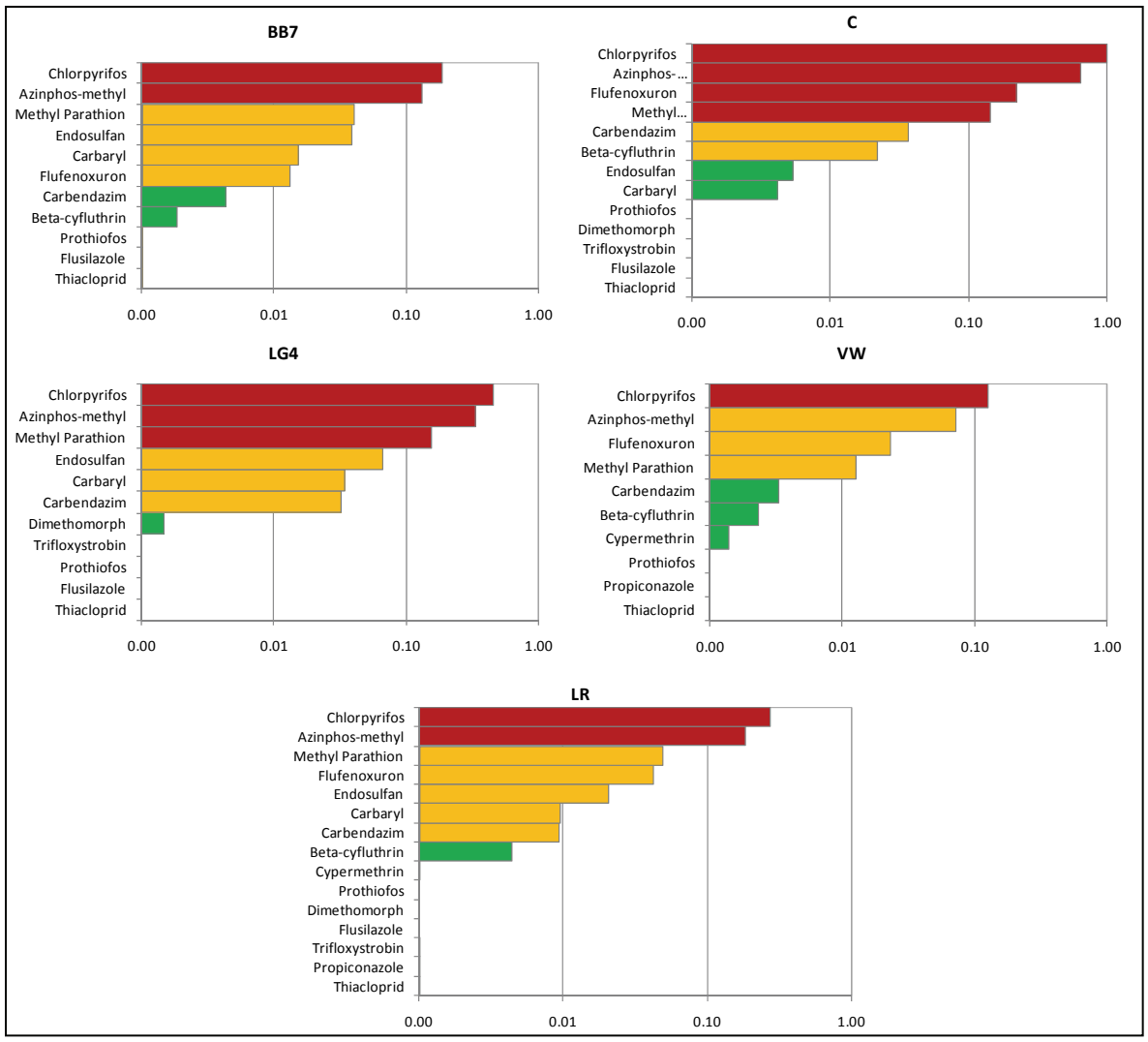



**Figure 4:** Graphs illustrating the output of the PeRI for sites BB7, C, LG4, VW and LR in the Lourens River catchment.

Whilst there was quite a marked difference in the level of contamination across sites as predicted by the PeXI, from a risk perspective, all sites have pesticides that fall into the high risk category. These pesticides are azinphos-methyl, chlorpyrifos, methyl parathion and to a lesser extent flufenoxuron. The high risk of these pesticides is as a result of their relatively high likelihood of transport into surface water (as indicated by their relatively high PeXI scores) and their comparatively high toxicity values. Other pesticides such as carbendazim, dimethomorph and carbaryl, whilst having relatively high PeXI scores, had medium to low PeRI scores, primarily as a result of the low toxicity of these pesticides towards the aquatic ecosystem.

## Index Validation

While the PeRI relies on inputs from the PUI and PeXI, the index itself cannot be validated through field based monitoring of pesticide levels as it provides an indication of ecological risk to the aquatic ecosystem. The PeRI could therefore only be validated by means of conducting laboratory or field-based bioassays using aquatic organisms as test species. Thus only outputs of the PUI and PeXI were compared to field based monitoring data.

In general, the PUI over-estimated pesticide contamination at all sites. Furthermore it did not accurately identify the relative difference in exposure potential across sites (i.e. BB7 was identified as the most highly contaminated site, whilst monitoring data indicates it was one of the least impacted sites). It was however, slightly more successful at predicting the relative

exposure potential of pesticides within a site. This is particularly true for site VW, where spray drift was identified as being the major route of entry of pesticides into the tributary, thus indicating that highly-applied pesticides are more likely to enter adjacent water bodies than pesticides applied in lower total quantities. This relationship was less distinct at sites where runoff played a major role in transport (i.e. LG4), indicating that other physiochemical and geographical parameters play a more important role in determining pesticide transport in runoff.

The PeXI provides a more refined estimate of exposure than the PUI. The PeXI categorises fewer pesticides with high potential for exposure. Given the patterns of contamination observed during the field monitoring, it is clear that the PeXI is better supported by field monitoring data than the PUI. The PeXI clearly identifies sites C and LG4 as the highest contaminated sites, with six and five active ingredients respectively, having a PeXI score falling in the High category. In contrast, only carbaryl at site BB7 was classified as having high exposure potential, whilst all pesticides at VW were classified as having medium or low exposure potential.

A further validation exercise was done through comparison of runoff samples collected on the 15$^{th}$ of November. For all sites pesticides that were predicted to move off target primarily by runoff were generally found in samples collected on this day. For site VW, which is predominantly influenced by spray drift, no pesticides were detected. These results provide a good indication that that the models used in PeXI are able to integrate catchment information and provide a very good indication of the main route of transport for different pesticides in different catchments.

**Sensitivity Analysis**

A sensitivity analysis was performed to determine the relative importance of input variables in the runoff and spray drift models used to calculate the PeXI. The method of analysis is a simple approach and is referred to as one-at-a-time sensitivity analysis. This involves varying input parameters independently, one at a time, all other parameters being constant and observing the influence on model predictions. For this analysis, runoff and spray drift model input parameters were varied in increments within realistic minimum and maximum ranges. The sensitivity analysis revealed that $K_{OC}$ has the greatest influence on the model output for runoff, with low $K_{OC}$ values greatly increasing the likelihood for pesticides to be lost in runoff. For spray drift, the buffer zone distance has the greatest influence on the model output, with decreasing distance resulting in large increases in the loss of pesticide.

**Conclusion & Recommendations**

The pesticide risk indicator developed in this project is based on realistic transport runoff and spray drift processes. The assessments of these processes are based on sound scientific principles and are used in a manner that the results are not entirely qualitative but semi-quantitative. The input data required for the indices is readily available or can be easily calculated. The risk indicator takes the pesticide use, pesticide properties, pesticide toxicity and geographical characteristics into account. The outputs of the PeXI and PeRI do not represent the absolute exposure and risk but a relative exposure and risk rating among pesticides or land uses in a catchment. It does not take any pesticide interactions or degradation beyond the point of its entry in waterways, (i.e. it provides the “edge of field” scenario). The PeXI and PeRI can be highly beneficial in customising monitoring programmes or to identify pesticides that required relatively greater attention in terms of their potential behaviour in environment. With respect to the Lourens River, the indicator was successful in the following:

- PeXI scores were able to differentiate between highly contaminated and less contaminated sites.

- PeXI scores were fairly reliable in predicting the relative exposure potential of specific pesticides across and within sites.
- Expressing the PEL as percentage of contribution by runoff and spray drift enabled the identification of the most important exposure route for pesticides at all sites.

The outputs provided by the indicator could therefore clearly lead to improved utilisation of limited resources for monitoring and management. The output of the indicator, as described in the sections above, show that the PeXI score for the different pesticides applied in the Lourens River catchment are generally consistent with monitoring results. The indicator can therefore prove to be a useful screening and decision-making tool. The indicator is not a simulation model and therefore not designed to predict accurate environmental concentrations of pesticide likely to reach surface water, but merely assesses an indicative risk factor with individual pesticides at different sites within a catchment. It is therefore appropriate that results from the indicator are used for first-tier assessment and screening purposes. An additional advantage of the indicator is that it can help with regards to identifying appropriate mitigation measures aimed at minimising the transport of pesticides associated with specific transport routes (i.e. runoff or spray drift).

Recommendations for future work include:

- Development of a national pesticide use database for regulatory and policy decision making and environmental modelling and monitoring.
- Using the methodology developed in this project an online decision support tool utilising freely available pesticide physicochemical and toxicity data should be developed aimed at providing farmers and water resource managers an indicator of pesticide risks to the aquatic environment.
- Validation of the risk component of the indicator (i.e. PeRI) by linking outputs of the PeRI with aquatic ecosystem health indicators.
- Development of a similar indicator methodology aimed at identifying exposure potential to groundwater resources (via leaching) and the potential risks to human and animal health.

**ACKNOWLEDGEMENTS**

The research in this report emanated from a project funded by the Water Research Commission and entitled: *Development of a risk indicator methodology to estimate the relative risk of pesticide contamination in South African water resources.*

The financing of the project by the Water Research Commission and the contribution of the members of the Reference Group is acknowledged gratefully. The Reference Group responsible for this project consisted of the following persons:

- Mr C Moseki (WRC)
- Ms A Moolman (WRC)
- Dr K Murray (WRC)
- Mr B Pletschke (Rhodes University)
- Dr S Jooste (DWA)
- Mr E van der Walt (ARC)
- Prof H Bouwman (North-West University)
- Mr M Claassen (CSIR)
- Dr R Heath (Golder Associates)
- Prof JH van Wyk (University of Stellenbosch)
- Dr J Meyer (University of Pretoria)
- Prof Okonkwo (Tshwane University of Technology)
- Dr Brent Newman (CSIR)
- Ms Bettina Genthe (CSIR)

The following organisations are also acknowledged for their assistance in the compiling of this report. The authors would like to thank:

**Mr Ben De Villiers** and **Lourensford Estates** for pesticide use data and permission to access their farm to conduct field work.

**Mr Gerald Wright** and **Vergelen Wine Estate** for pesticide use data and permission to access their property to conduct field work.

# TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

# 1. LITERATURE REVIEW

## 1.1 Background

As the demand for food has increased throughout the world, farmers have had to expand their food output twofold to help meet this ever-rising demand. The largest increase in food demands have occurred in the non-industrial or developing countries, where rapid population growth in these countries is chiefly responsible. Most developing countries produce barely enough food to meet their present needs and therefore must expand their food production greatly or face a severe food shortage in the near future. In the past the quickest way to expand food outputs was to increase the area of land under cultivation, but scientific improvements in agriculture during the 1900's enabled farmers to produce relatively higher yields. Almost since the advent of agriculture, farmers have used various substances to enrich the soil and to eradicate insect pests and diseases, but modern pesticides were, however, only introduced into South Africa during the 1900's. A growing dependency on agrochemicals means that they are now produced in large quantities and arranged into several groups and subgroups with insecticides, herbicides and fungicides being the three most important groups. They can further be subdivided into different classes such as organophosphates, organochlorines, carbamates and pyrethroids. A pesticide is generally defined as any substances or mixture of substances deliberately released into the crop environment, intended for preventing, destroying, repelling or mitigating any pests that harm crops or used as a plant regulator, defoliant or desiccant. Each of these different agricultural processes requires a specific class of chemical intended for a particular function. Agrochemicals also occur is different physical states, such as a solid, liquid or gaseous form. This will accordingly determine the way in which a pesticide is applied, though the most common methods of application are to spray them as liquids manually using a backpack or hand spray, mechanically using equipment attached to a tractor or by means of aerial spraying (Yousefi, 1999).

Presently, the use of agrochemicals has become almost standard in agricultural practice due to the increasing demand of quality and quantity of food products. Although these agricultural chemicals have had their benefits to society they have, however, also been overused or used indiscriminately and have thus contributed to environmental pollution (Naidoo and Buckley, 2003), especially in aquatic ecosystems (Sereda and Meinhardt, 2003). Non-point source pesticide pollution from agricultural activities (including storage, transport and irresponsible handling), conducted adjacent to water bodies, such as canals, dams, ponds, pans and streams, is widely regarded as one of the greatest causes of contamination of surface waters (Loague *et al.*, 1998; Moore *et al.*, 2002; Naidoo and Buckley, 2003; Schulz, 2004).

Major users of pesticides are concentrated in industrialised nations, especially Europe and North America, which collectively make up about 60% of the market (Bouwman, 2003; Naidoo and Buckley, 2003). Africa makes up for 3% of the pesticide volume purchased throughout the world. The management mechanisms controlling pesticide use in African countries in many instances differ or lack drastically in comparison to the countries in which they have been developed, where management of the use of pesticides is a high priority (Bouwman, 2003) and as a consequence, has lead to contamination of the environment. These mechanisms include control of use, funding, enforcement frameworks and disposal facilities (which has led to the accumulation of obsolete pesticides; [Naidoo and Buckley, 2003]). The contamination of surface waters is especially a cause of recent public concern (Heath and Claassen, 1999).

It is well known that residues of persistent pesticides (especially those of organochlorine insecticides) are found to be extremely harmful to non target aquatic organisms because of

their ecotoxicological effects, their potential to bioaccumulate and their hormone disrupting effects on wildlife and/or humans (Awofulu and Fatoki, 2003; Cuppen *et al.*, 2000; Capri *et al.*, 2003; Heath and Claassen, 1999; van den Brink *et al.*, 2000). Some persistent organochlorine pesticides were banned or restricted in many developed countries during the 1970's and 80's, although some are still in use due to their effectiveness and lack of suitably effective alternative products, e.g. the spraying of DDT still remains the most widely used malaria prevention strategy in South Africa (Awofolu and Fatoki, 2003; Bouwman, 2003; Sereda and Meinhardt, 2003; Tanabe *et al.*, 1994). Other pesticides still widely used in developing countries include chlorpyrifos, dimethoate, gamma-BHC and dichlorprop (Maharaj, 2005). Even though many of these pesticides have been recently replaced with more easily biodegradable, less toxic (to non-target organisms) substances characterised by lower application doses, the evidence of contamination of groundwater and surface waters still occur (Capri *et al.*, 2003).

A large portion of agrochemicals does not reach the intended target organism (e.g. 10-30% of pesticides applied on the ground, and 50-75% of sprayed pesticides [WWF, 1999]). Instead, this portion is carried away, where it may, for example enter the aquatic environment.

The potential sources of pesticide contamination of surface waters as given in Heath and Claassen, (1999) are:

(a) Direct application of pesticides to water bodies (dams and rivers) in order to control undesirable fauna and flora (viz. fish, biting black fly, aquatic weeds, mosquitoes, aquatic snails, etc.).
(b) Aerial spraying against terrestrial pests causes underlying water bodies to be contaminated by such spraying operations.
(c) Contamination by accidental, spillage or careless disposal of surpluses is liable to occur anywhere where pesticides are used on a regular basis.
(d) Contamination by pesticides from industrial sources is well exemplified by the incorporation of insecticides in the textile and wood industries.
(e) Contamination by drainage from agricultural or Forest Land is probably the major contribution in countries where aerial spraying is not well developed.
(f) Contamination by aerial spraying by means of natural forms of transport such as wind or rain.

### 1.2 Pesticides in South Africa

The African continent's highest produce-producing country and therefore the largest pesticide market in sub-Saharan Africa is South Africa, which forms 60% of the pesticide market in Africa (Dinham, 1993; Naidoo and Buckley, 2003). Of the 122,341,000 ha area that South Africa covers, more than 85% is used for agriculture and forestry (Yousefi, 1999). Agricultural practice in South Africa is becoming increasingly dependent on the widespread use of toxic pesticide chemicals for crop protection, growth regulation and seed treatments to enhance productivity (London and Myers, 1995a, b), which inevitably leads to contamination of non-target environments (London and Myers, 1995a; London, 1998; Naidoo and Buckley, 2003).

In addition, the scarcity of water adds additional stress to the ecological integrity of our aquatic systems. Unlike most other sub-Saharan African countries, South Africa has a low average annual rainfall as well as relatively infertile soils. Between 11 and 15% of its land is arable and serious climatic constraints, such as periodic droughts, hinder agricultural production even further. Despite these circumstances, productivity needs to increase to meet the food demands of its growing population. (South African Year Book 2002/2003).

Agriculture has changed from mainly subsistence farming to a mixture of small-scale, subsistence, emerging and large scale commercial farming giving rise to a broader use of insecticides (Bouwman *et al.*, 2006; Naidoo and Buckley, 2003). Commercial farmers in South Africa are major producers of poultry, cattle, sheep, citrus fruits, deciduous fruits, maize, wheat, sugar cane, sunflowers and many other crops. Subsistence farmers and small-scale farmers also play an important role within South Africa's social and economic structure focusing more on cash crops. The use of agricultural chemicals and pesticides for crop protection has also increased amongst the various emergent farming sectors in South Africa (Sereda and Meinhardt, 2003), which potentially poses additional risks both to human health and non-target agro-ecosystems due to a lack of education in pest management.

Yousefi (1999) indicated that from 1978 to 1979, wood preservatives were the highest volume sold agrochemical in South Africa followed by insecticides, herbicides and fungicides. The use of herbicides and fungicides has, however, noticeably increased in recent years. An overall increase from 1994 to 2000, in sales of pesticides was noted, with the highest values recorded for triazines, organometallic compounds, carbamates/thiocarbamates, organophosphates, hydrocarbons, anilines/ acetanilides, and organochlorines and this rise was expected to increase even further (Maharaj, 2005).

Currently, approximately 180 pesticide active ingredients are commercially available in South Africa, formulated as approximately 400 registered trade names (Meinhardt, 2003, 2008; Nel *et al.*, 2000) of which the herbicides form the largest market in product volume sold, followed by fungicides and then insecticides (Meinhardt, 2008; London *et al.*, 2000). However, the actual quantities of different pesticides applied per crop remain unknown as no effective monitoring or surveillance mechanism currently exists for this purpose (London, 1995).

Until recently the list of pesticides included the use of those substances that have now been banned, expired or discarded, including several of the POPs (Persistent Organic Pollutants) and other pesticide products that have been since superseded, which pose a threat to the environment. Examples of some of these are aldrin (registration withdrawn in 1992), BHC (registration withdrawn as pesticide in 1983), chlordane (registration withdrawn in 2001), dieldrin (all sales banned in 1984), DDT (banned in 1983 except for malaria control), endrin (withdrawn in 1980) and heptachlor (registration withdrawn 1976) (Dalvie and London, 2001; Naidoo and Buckley, 2003; Vermeulen *et al.*, 1998). Despite this, some pesticides that are banned in other countries are still in use in South Africa due to their effectiveness and for different social and economic reasons and are therefore deemed irreplaceable by newer products. For example, substances like DDT are still used by governmental organizations (National Department of Health) to control malaria (Awofolu and Fatoki, 2003; Bouwman, 2003; Bouwman *et al.*, 2006; Sereda and Meinhardt, 2003; Tanabe *et al.*, 1994). It is noteworthy that prothiofos is only registered in three counties with South Africa being one of them (Bollmohr *et al.*, 2007). Bouwman *et al.*, (2008) recently detected the presence of the mirex compound in aquatic bird's eggs. This was unexpected as this compound was never registered for use in South Africa. South Africa, Mozambique and Botswana have the highest amount of obsolete pesticide stocks in the southern Africa region but were relatively clean compared to the rest of Africa (Naidoo and Buckley, 2003). During 1999, the ASP (African Stockpile Programme) initiated a clean-up project of which 1,050 tons of obsolete pesticides was embarked upon in South Africa by AVCASA (Agricultural and Veterinary Chemical Association of South Africa) and this supposedly led to a technically cleaner and safer environment. It was later realised that not all obsolete pesticides had been collected, and it was estimated that at least 50 tons had not been retrieved due to the campaign drive not reaching all farmers (Dalvie and London, 2001; Naidoo and Buckley, 2003).

There are four major sectors within the South African community that use pesticides, namely, governmental, agricultural, industrial and domestic users. The agricultural sector is the primary user of pesticides and is thus the main source of pesticide contamination in non-

target environments (Meinhardt, 2003). Usage patterns of agrochemicals are extremely variable across agricultural sectors as well as in different regions (London and Meyers, 1995a). Locations within South Africa that have been shown to represent agricultural areas of intensive pesticide usage include: Hartbeespoort Dam (Brits area); Springbok Flats (Nylsvlei; Marble Hall, Groblersdal, Roedtan, Bronkhorstspruit); the Mpumalanga lowveld; northern KwaZulu-Natal and the Western Cape (per. comm. Verdoorn, 2004[1]). An area that has been extensively researched with regards to pesticides in aquatic ecosystems is the Western Cape particularly the Lourens River and its tributaries associated with fruit orchards.

It was indicated by London and Meyers (1995a) that in general, use patterns show that insecticides, herbicides, fungicides and growth regulators are mainly used by deciduous farming. Vineyards, wheat and vegetable production use primarily fungicides, herbicides and nematicides, respectively. The three main organophosphate insecticides used are azinphos-methyl, chlorpyrifos and dimethoate. Fungicides include phthalic acid derivatives, copper salts (especially copper oxychloride), sulphur and specifically dithiocarbamates. Dominant herbicides include dipyridyls (particularly paraquat), chlorphenoxyacetic acids (particularly 2,4D), and triazines, particularly simazine, which was the pesticide with the highest sales in South Africa from 1994 to 2000. Ethylene dibromide and aldicarb are two widely used nematicides (Maharaj, 2005; Snyman *et al.*, 2003).

As stated previously, the increased use of pesticide exposure not only affects animals but may cause adverse chronic human health effects (Savage *et al.*, 1988). Studies conducted in South Africa concerning human exposure to pesticides include (to name a few):

- Bouwman *et al.* (2006) (DDT in human breast milk from KwaZulu-Natal);
- London *et al.* (1997) (neurologic and neurobehavioral effects of organophosphates in farm workers in the Western Cape);
- London and Bailie (2001) (pesticide poisonings);
- Claassen (1996), Du Preez et al. (2003a); Heath (1999), Heath and Claassen (1999), (risk based approach to assess possible health risks to humans when consuming fish from selected rivers in South Africa);
- Dalvie *et al.* (2004) (rural water sources and community awareness in Slanghoek Valley, Hex River Valley and Grabouw in Western Cape);
- Barnes (1999) (organophosphate pesticides in fruit orchard farm workers from the Western Cape);
- Richter *et al.* (1986) (organophosphate absorption in field workers exposed to pesticide spray drift in the Western Cape).

### 1.3 Fate and Effect Considerations

The relative importance of each route of entry into water is governed by many properties of both the pesticides and the environmental as well as the interactions between them (Health and Claassen, 1999). These include the physical and chemical properties of the pesticide, site-specific conditions (including spatial and temporal variability) and characteristics of the pesticide application method or management practice involved (Ansara-Ross *et al.*, 2008a; Dabrowski and Schulz, 2003; Maharaj, 2005; Tesfamichael and Kaluarachchi, 2006; Vermeulen *et al.*, 1990). Environmental factors include climatic condition, temperature, light intensity, evaporation rate and type of surface, which all influence the rate of uptake, environmental transport and decomposition of a pesticide. The extent to which a pesticide will affect aquatic organisms also depends on these factors, but mainly on the physicochemical properties of the pesticide. These physicochemical variables include water solubility, half-life for degradation in water and soil, sorption coefficient for organic carbon or

[1]Prof. G. Verdoorn, EWT Poison Working Group, Johannesburg

organic matter, octanol-water coefficient, molecular weight, saturated vapour pressure and Henry's Law constant. The organism's susceptibility to a pesticide is also a factor to consider and may be affected differently from species to species or within a species during breeding or low food availability. A pesticide's degree of toxicity also depends on how it is exposed to the organism (dietary, dermal or breathing for example). Secondary exposure occurs from scavenging on contaminated food, such as exposed carcasses, or feeding upon insects. Other factors such as dose, time and duration of application also play an important role in pesticide toxicity.

As pesticides constitute a very important group of compounds, they have to be controlled due to their high level of toxicity and their widespread use in agricultural practice. It is often difficult to achieve this due to the time, costs and logistics necessary and is also difficult to determine the persistence, fate and effects on non-target organisms. One approach is by using risk assessments in the form of cost-effective and easy-to-use models that identify potential risks associated with exposure and can estimate the fate and effect of pesticides posed to aquatic ecosystems (Rother and London, 2003; Wade, 2003). These models have proven to be effective predictive tools for the management of agrichemical usage and have been used internationally for the screening of new pesticides for registration and management of agrochemicals within the environment (Levitan *et al.*, 1995; Maharaj, 2005; Meinhardt, 2008; Reus *et al.*, 2002; van der Werf, 1996). In order to use these models, it is necessary to have a background of the physicochemical properties of the pesticide, which is easily obtained from existing data but more importantly to identify the processes involved in a specific environment to which the pesticide is exposed. Thus, it is necessary to have a good knowledge of the occurrence and application of agrochemicals under local conditions before applying these tools.

### 1.4 Regulation of Pesticides in South Africa

Development of South African pesticide legislation has become relatively advanced within recent years (Rother and London, 2003; Dalvie *et al.*, 2004) and has superseded the rest of Africa. It is generally aimed at monitoring microbiological, physical and chemical water quality (London *et al.*, 2004). The infrastructure to monitor and control pesticide contamination, however, especially in water resources, is poorly developed in South Africa (Cairncross *et al.*, 2003). Similar to many countries throughout the world, South Africa experiences pesticide poisoning, chronic health effects, suicides with pesticides, under-reporting of poisonings, wildlife poisonings, water contamination, stockpiling of pesticides, pest resistance, and non-target contamination or poisoning (Rother and London, 1998; 2003). Despite these occurrences, minimal monitoring of pesticides pollution in the environment actually takes place (London *et al.*, 2000) especially at a local Government level. Limitations imposed on this monitoring include the fact that that relatively few accredited laboratories in South Africa undertake pesticide analysis and those that do are also generally unable to do so on a large scale; there is a prohibitive cost of analysis and a high level of expertise and equipment sophistication that are required, leading to technical constraints. The inability to interpret and manage any results that might be obtained is also a shortcoming (London *et al.*, 2004, 2005; Schulz *et al.*, 1998; Schulz, 2001a).

Another problem is that South Africa's legislation on pesticides is extremely complex and fragmented with laws and regulations being spread across fourteen Acts and administered by seven different government departments as well as a non-statutory committee (Rother & London, 1998). Examples of these are the National Water Act No. 36 of 1998, the Atmospheric Pollution Prevention Act No. 45 of 1965, the Environment Conservation Act No. 73 of 1989 and the Fertilizers, Farm Feeds, Agricultural Remedies and Stock Remedies Act of 1947, and more recently, the National Environmental Management Act of 1998. The latter controls the sale and registration of veterinary and agricultural remedies and sets certain

standards for pesticide residues on the export of fruit. These Acts collectively attempt to cover the following (Rother and London, 2003):

- registration of pesticides,
- establishing maximum residue limits,
- government spraying of pests,
- monitoring of water pollution from agricultural activities,
- classification of hazardous substances,
- pesticides poisoning as a medical notifying condition,
- registering pesticides used on the human body,
- worker rights,
- control of discharges into water sources,
- transport of pesticides,
- waste management; and so forth.

It is important to monitor the presence of pesticides in the aquatic environment but while South African laws strongly suggest the need for monitoring, this is currently not a high priority. A number of key changes have recently been addressed within the legislative framework, dealing with the environment that could substantially improve on the Act's capacity to obviate adverse environmental impacts on water sources (London *et al.*, 2000). Although currently Act 36 of 1947 provides for the establishment of a Registrar's Office to deal with registration of pesticides and regulates their toxicity classification, requirements for labelling, advertising, disposal, sale, importation and use of pesticides, it does not address environmental consequences of pesticide pollution in water. The Act can take action over end-users from disregard or inappropriate application as stipulated on the label in accordance with the Regulation stipulated in Act 36 of 1947 that may consequently lead to pollution of aquatic ecosystems (Naidoo and Buckley 2003). There are, however, deficiencies and gaps in this legislation leading to the inadequate enforcement of existing legislation.

Although South Africa has the necessary laws governing pesticide use in the country, enforcing its legislation and monitoring of pesticides is lacking (Rother and London 1998). This is mainly due to the expense involved. Also current pesticide registration in South Africa is based largely on international standards as most pesticides are imported into South Africa (London *et al.*, 2005). A need for impact assessments to be carried out under local conditions is thus necessary (Maharaj 2005).

Of the 165 chemical companies in South Africa (Rother and London, 1998), most of the large ones are represented by umbrella organizations such as AVCASA (Agricultural and Veterinary Chemical Association of South Africa) and CAIA (Chemical and Allied Industries Association) that co-ordinate and monitor these companies. The smaller companies are not represented by an association. It is these small companies that are blamed for the illegal importation and sale of pesticide due to them being difficult to regulate (Naidoo and Buckley, 2003; Rother and London, 1998). In 1976, the Department of Agriculture discontinued its practice of requiring agrochemical companies to submit returns on agrochemical production (Barlin-Brinck, 1986). Under the current Act, chemical manufacturers are obliged to register their agrochemicals with the Department of Agriculture, but this is not enforced (Yousefi 1999). Strict moratoriums have been put in place for some pesticides as mentioned previously. In addition restrictions on the type of application of several pesticides have been enforced by the Registrar, such as prohibiting aerial applications of 2,4-D, dicamba, MCPA and trichlopyr, and the restricted use of certain pesticides to specific agricultural problems such as parathion and endosulfan. Even so, many banned, restricted or unregistered chemicals are still being acquired and used (Yousefi 1999). In general many laws and acts applicable to the management and regulation of pesticides exist, however enforcement of these legislative tools is lacking.

### *1.4.1 Pesticide registration*

All agricultural remedies offered for sale in South Africa need to be registered under the control of the Agricultural and Veterinary Remedies act, Act 36 of 1947 and subsequent revisions. This is administered and implemented by the Directorate Agricultural Input Productions through the Registrar of Agricultural and Veterinary chemicals under the National Department of Agriculture.

Current South African legislation requires that testing be done under local conditions for residue decline, efficacy and phytotoxicity of a new pesticide (Meinhardt, 2003; 2008). MRL (maximum residue limits) are required by performing pesticide residue trials and are set using toxicity data generated by the compound's mother company. Environmental and toxicity data required for registration do not, however, have to be generated under South African conditions and as long as the local testing requirements are met, data generated from international sources are accepted (Meinhardt, 2003). The general impression is that the registration process does not place much emphasis on the potential environmental variations that are experienced within South Africa. It would appear as if aspects such as prevention of contamination of water sources are not considered in sufficient detail, and that local authorities rely heavily on international data (Meinhardt, 2003). Current registration procedures also rely almost exclusively on data on acute toxicity which do not account of long-term toxicity (London, 1995). Despite this, the potential impact of pesticides in South Africa surface waters has generally been of low priority and as such, has generally not been considered in aspects of water resource management.

### *1.4.2 The National Toxicity Monitoring Programme*

Water legislation in South Africa was comprehensively revised in the National Water Act (No. 36 of 1998). This Act, which provides the legal framework for the implementation of the National Water Policy (DWAF, 1997), is founded on the Constitution, and sustainability and equity are central guiding principles. The Act defines the National Government, and therefore the Department of Water Affairs and Forestry, as the public trustee of the nation's water resources, with a mandate that includes ensuring water resource protection so as to allow sustainable resource us.

The first edition of the South Africa Water Quality Guidelines was presented in 1996 by the Department of Water Affairs and Forestry. This served as the primary source of information for determining the water quality requirements of different water users and for the protection and maintenance of the health of aquatic ecosystems. The listed constituents are, however, limited within the guidelines, with this being especially true for organic compounds and were based on the availability of the required cause-effect data and/or local knowledge as well as the limitations associated with chemical-specific criteria for certain constituents. The pesticide constituents given include atrazine and endosulfan (DWAF, 1996). According to Schultz (2001b) hardly any permissible maximum levels for pesticides in South African surface waters have been established.

The South Africa water standards to protect aquatic ecosystems are given as: aldrin (0.01 mg/ℓ), atrazine (0.01 mg/ℓ), chlordane (0.025 mg/ℓ), DDT (0.0015 mg/ℓ), dieldrin (0.005 mg/ℓ), endosulfan (0.00001 mg/ℓ), endrin (2 ng/L/0.002 mg/ℓ) and heptachlor (0.005 mg/ℓ), lindane (0.015 mg/ℓ), malathion (0.1 mg/ℓ), methoxychlor (0.02 mg/ℓ), mirex (0.001 mg/ℓ), parathion (0.008 mg/ℓ) and 2,4 dichlorophenol (4.0 mg/ℓ) (Dallas & Day, 1993; DWAF, 1996) (Table 4).

Recently, the Department of Water Affairs and Forestry designed and implemented the National Toxicity Monitoring Programme (NTMP). However, only atrazine and endosulfan are monitored to date. The National Toxicity Monitoring Programme (NTMP) was designed to measure, assess and report on a regular basis on the status and trends of the nature and

extent of (1) the potential for toxic effects to selected organisms, and (2) selected potentially toxic substances in South African inland surface water resources. There was a need for the NTMP, since DWAF has various international and national obligations:

a) South Africa is signatory to various international agreements and conventions, e.g. The Stockholm Convention.
b) Participation in global monitoring programmes like Global Environmental Monitoring Programme (GEMS).
c) A responsibility in following international trends in emerging problems like “Persistent Organic Pollutants (POPs)” or “Endocrine Disrupting Chemicals (EDCs)”

The Stockholm Convention, targeting twelve persistent organic pollutants (POPs), was ratified in 2002 by South Africa and became legally binding in 2004 (Bouwman, 2004). The restriction of the use and production or banning of the chemicals will reduce the hazards posed by these pollutants towards human health and the environment and only monitoring of the POP’s will prove the effectiveness of the Convention. The NTMP has preliminarily selected sixteen priority toxicants for monitoring within the programme (Table 1). These include the POPs, as identified by the Stockholm Convention (with the exception of dioxins and furans) and other chemicals identified by national stakeholders (including Department of Agriculture and Department of Health)

**Table 1:** List of toxicants included in the National Toxicity Monitoring Programme.

| **POPs relating to the Stockholm Convention** |
|---|
| Aldrin |
| Chlordane |
| DDT (DDD, DDE) |
| Dieldrin |
| Endrin |
| Heptachlor |
| Hexachlorbenzene |
| Mirex |
| PCBs (Arochlors) |
| Toxaphene |
| **Other current-use toxicants** |
| Endosulfan isomers (α- and β-) and the sulfate breakdown product |
| Lindane γ-BHC and the isomers (α-, β- and δ-BHC) |
| Monocrotophos |
| Atrazine |
| Simazine |
| Terbutylazine |

Guideline values were assigned to these toxicants according to the methods described in Warne *et al.* (2005). The guidelines have been developed so as to align with the concepts of the water resources classification system and the ecological reserve as advocated by Chapter 3 of the National Water Act (Act No.36 of 1998).

The Pilot Phase of the NTMP ran from 2006 to present at selected sites in the Gauteng region and the following challenges were identified the NTMP can be implemented:

- Within the NTMP, only water analysis and toxicity testing is performed. However many POPs and other currently used pesticides are associated with particles and will not be monitored via the programme.
- The NTMP only included immediate response toxicity testing. However many POPs and current-use pesticides result in chronic effects at concentrations being detected in the water. Therefore other tests (e.g. biomarker tests) need to be included.

- Many of the toxicants being monitored are endocrine disrupting chemicals (EDCs) and their effect is currently not monitored with the current toxicity testing methodologies.
- The list of toxicants (Table 1) does not reflect the toxicant profile for South African inland waters and more relevant toxicants need to be identified and included in the NTMP. Bollmohr *et al.* (2008) detected 15 additional pesticides (including various organophosphate insecticides, e.g. chlorpyrifos, fenamiphos, metamidophos) on a regular basis at various sites within the upper Olifants River).

## 1.5 Exposure

### *1.5.1 Non-point Source Exposure Pathways*

In order to assess the environmental impacts of pesticides, it is essential to understand the routes by which pesticides are transported from the point of application to the aquatic ecosystem (or other non-target environments of interest). Non-point source agricultural pollution is generally considered one of the major threats to surface water quality in rural areas (Loague *et al.*, 1998). Of all non-point source pollutants, insecticides are among the most crucial chemical stressors, simply because of their extremely high toxicity to many non-target aquatic organisms (Baier *et al.*, 1985).

In comparison to point sources, our knowledge of the extent of non-point source pollution is still quite restricted (Line *et al.*, 1997). The main factors contributing to this situation are presumably the number and characteristics of variables (e.g. land use, meteorology, soil types) that must be taken into account to understand and predict the occurrence and extent of non-point source pollution (Walklate, 1992; Wauchope, 1996). Non-point source pesticide pollution can enter streams and rivers via three main routes; leaching, spray drift and runoff. Since many insecticides have relatively low water solubility, their transport into surface waters via leaching is negligible (Flury, 1996). Leaching would contribute preferentially to contamination of groundwater and thus might affect surface waters only under specific geological conditions (Squillace *et al.*, 1996).

Spray drift and edge-of-field runoff are the most important routes of entry for agricultural non-point source insecticide pollution into surface waters (Groenendijk *et al.*, 1994) and may result in considerably different exposure scenarios (Erstfeld, 1999). Whereas spray drift leads to input of pesticides dissolved in the water phase, the contamination during runoff is sometimes largely as a result of pesticides associated with suspended particles (Mian and Mulla, 1992). Although pesticides dissolved in the water phase pose more of an immediate toxicological threat, sediment associated pesticides have also been shown to adversely affect macroinvertebrate communities (Schulz and Liess, 2001).

### *1.5.2 Runoff*

Surface runoff is the lateral movement of water from agricultural fields into adjacent water bodies and occurs when the precipitation rate exceeds the infiltration rate of the soil or when the precipitation volume exceeds the infiltration capacity of a soil. A complex interaction of multiple variables ultimately influences the quantity of pesticide that can be expected to be present in surface runoff (Table 2), the most important of which include; the time interval between the application of pesticides and the first heavy rainfall event; the slope and soil types of the catchment; the quantity of applied pesticide and the size and characteristics of vegetated buffer strips (Cole *et al.* 1997). Furthermore, runoff is highly dependent on the physico-chemical properties of the pesticides themselves, which ultimately determine the amount of pesticide physically available to surface runoff (Blanchard & Lerch 2000; Capel &

Larson 2001). Pesticides can be found in two forms in surface runoff; in the soluble form (dissolved in runoff water) and adsorbed to suspended solids). The proportion and quantity of a chemical in each form at a given site depends upon the extent of sorption with the associated soil matrix, partitioning between runoff water and the suspended eroded material in transit and the degradation rate in the soil. Thus, important physico-chemical properties to consider include the water solubility, half-life and $K_{OC}$ (soil sorption coefficient; the tendency of a chemical to bind to organic carbon in the soil). Pesticides with low water solubility tend to be more associated with suspended sediments as opposed to being dissolved in the water phase of the surface runoff. Soil properties also play an important role in terms of the amount of surface runoff and the quantity of transported pesticide that occurs during an event. Soils with higher organic carbon content will tend to bind pesticides more than soils with low organic carbon content (Flury 1996), while for any given precipitation amount, loamy and clay soils will give rise to a greater quantity of surface runoff (and hence pesticide loss) than a sandy soil, which will promote infiltration and leaching (Reus *et al.*, 1999). Furthermore, pesticides with long half-lives (i.e. organochlorines such as endosulfan and DDT) can be measured in surface runoff events many months after the last application (Dabrowski *et al.*, 2002a).

Slope has been shown to be the most important factor influencing runoff but can be greatly modified by the presence of vegetation (Wilcox & Wood, 1989). The timing of rainfall events in relation to the application date and half-life time of pesticides also plays a significant role in determining the amount of pesticide available in surface runoff. Studies have shown that the first heavy rainfall after application results in the highest quantity of pesticides in surface waters (Domagalski *et al.*, 1997; Dabrowski *et al.*, 2002a). Large rainfall events occurring a few days after the application of pesticides have resulted in very high concentrations of pesticides being detected in the Lourens River (Schulz, 2001a).

**Table 2:** Important variables influencing the risk of surface water contamination via surface runoff.

| | Low Risk | High Risk |
|---|---|---|
| **Slope characteristics** | | |
| Slope | Low | High |
| **Pesticide characteristics** | | |
| Water solubility | Low | High |
| Soil adsorption | High | Low |
| Persistence | Low | High |
| **Soil characteristics** | | |
| Texture | Coarse sand | Fine clay |
| Organic matter | High | Low |
| Macropores | Few, small | Many, large |
| **Weather characteristics** | | |
| Rainfall | Small volumes, infrequently | Large volumes, frequently |

### *1.5.3 Spray Drift*

Spray drift is the offset movement of airborne pesticides at the time of application (or soon thereafter) to any site other than that intended for application and can include spray droplets, vapours, or dust particles moving away from a target area. Spray drift is one of the most important sources of non-point source pesticide pollution in edge-of-field surface waters, such as ditches, streams and ponds (Groenendijk *et al.*, 1994; Holvoet *et al.*, 2008). Due to the direct input of contamination, pesticide levels detected in adjacent water bodies are often high, posing a significant risk to aquatic fauna (Gilbert & Bell, 1988).

Pesticide drift can be difficult to manage because the full range of drift cannot be readily observed. Pesticides are most susceptible to spray drift when solutions are applied by ground spray equipment (i.e. tractors or portable handheld) but more so by aerial application. Many of the droplets produced by the nozzles during aerial application can be so

small that they remain suspended in air and are carried by air currents until they contact a surface (i.e. target crop or the ground). Applicator error can also cause drift but, even when pesticides are applied correctly, drift can still occur. As much as 30% of spray applications can move greater than 15 m from the intended site.

The tendency of a chemical to drift is influenced by a number of factors (Table 3). These include the physicochemical properties of the individual pesticide, especially vapour pressure and boiling point as well as by droplet size and environmental parameters such as weather conditions (including wind speed and direction), topography, the crop area being sprayed and application characteristics. A further influencing factor is the application equipment and methods (Dabrowski and Schulz, 2003; Dabrowski *et al.*, 2006). In some instances, the decisions made by the applicator may also have an influence of the risk of pesticide pollution to aquatic ecosystems (e.g. spraying during high winds). The proximity of water bodies from the pesticide application, the amounts of pesticide drift, and toxicity of the pesticide are important factors in determining the potential impacts from drift. Pesticides with high vapour pressures are more difficult to keep on the application site and will almost always drift. Higher application rates (grams per ha) also contribute to higher levels of drift.

**Table 3:** Important variables influencing the risk of surface water contamination via spray drift.

| | Low Risk | High Risk |
|---|---|---|
| **Weather characteristics** | | |
| Wind speed | Low | High |
| Wind direction | Away from water resource | Towards water resource |
| **Pesticide characteristics** | | |
| Water solubility | Low | High |
| Soil adsorption | High | Low |
| Persistence | Low | High |
| **Buffer zone characteristics** | | |
| Buffer zone width | Wide | Narrow |
| Vegetation | Well vegetated, wind breaks | Poorly vegetated, no wind breaks. |
| | Few, small | Many, large |
| **Application characteristics** | | |
| Equipment | Ground | Aerial |

The environmental impacts of spray drift can be minimised by the use of buffer zones between water bodies and crops (De Snoo and De Wit, 1998). There is no buffer zone specified under South African regulations. Other mitigation strategies include vegetated buffer strips (Patty *et al.*, 1997) and wind-breaks (Ucar and Hall, 2001), and in-stream mitigation factors such as vegetated ditches and wetlands (Rodgers and Dunn, 1992).

Because of the direct input and bioavailability of pollutants introduced by spray drift, it is commonly regarded as the worst case scenario for pesticide exposure in aquatic risk assessment (Schulz 2001b; Ganzelmeier et al., 1995; Gilbert and Bell, 1988). Therefore the current regulatory risk assessment in Europe largely focuses on spray drift. This is not the case in South Africa, as very few studies on spray-drift borne contaminants compared to runoff have been done (Schulz 2004). As indicated by Schulz (2004) there is a lack of data with respect to surface water contamination by insecticides due to spray drift, which is of particular importance with regard to the role of spray drift in regulatory risk assessment. It is therefore clear that further research is needed to determine the effects of spray drift as a source of pesticide contamination in the aquatic environment more accurately.

There are simple risk models available internationally that estimate the probability of risks of pesticides to aquatic ecosystems. One such model that focuses specifically on spray drift as the route of pesticide exposure is the PRIMET (Pesticide Risks in the tropics to Man,

Environment and Trade) model. Non-point source pollution models such as PRIMET incorporate various variables in an attempt to predict contamination levels. One such variable is the percentage of spray drift, calculated using the IMAG Drift Calculator (Holterman and van der Zande, 2003). Basic drift values are also obtained from Ganzelmeier *et al.* (1995), the Spray Drift Task Force (US EPA, 1999) and Rautmann *et al.* (2001).

The PRIMET model is a simple predictive risk based model of aquatic, groundwater, terrestrial and human dietary impact of pesticides (van den Brink *et al.*, 2005). The model requires input of pesticide characteristics, environmental parameters as well as pesticide use incorporating application data. The model output provides an ETR (exposure toxicity ratio) of the pesticide indicating either that there is no risk to the environment; a risk may be present or a risk is certain based on worst case assumptions. The strength of this model is that it is user friendly, requires a minimum of input data and it is freely available. Its shortfall is that it focuses specifically on spray drift and does not take into consideration sediment data. This model was developed by van den Brink *et al.*, 2005) as a first tier assessment of the risks of pesticides.

PERPEST is another model that Predicts the Ecological Risks of PESTicides in freshwater ecosystems (van Nes and van den Brink, 2003). The model is based on Case-Based Reasoning (CBR) and simultaneously predicts the effects of a particular concentration of a pesticide (herbicides, insecticides and more recently fungicides) on various community endpoints. When information is required on the potential risks in a situation, this model retrieves similar experiences or cases about similar situations from the memory or database. It then reuses this experience in the context of a new situation for a prediction and gives a potential risk in accordance to the most similar cases. Data is generated into the case base database using empirical data such as toxicity, and thereby has the potential in renewing and updating cases continuously. In this way the model enables sustained learning since new experiences are retained, making it available for future cases. PERPEST results in a prediction showing the probability of classes of effects (i.e. none, slight, or clear effects, with an optional indication of recovery) on the various grouped endpoints. These two models are currently being assessed for suitability under South African aquatic conditions (Ansara-Ross, 2008)

## 1.6 Occurrence of pesticides in SA surface waters

In general, research on the occurrence of pesticides in surface and groundwater has received relatively little attention in South Africa. A factor that has contributed to the lack of research is the shortage of laboratories with the equipment and expertise to carry out complex analyses (Dallas and Day, 1993). Of the studies that have been carried out, very few have attempted to establish a direct link between agricultural chemical use, transport pathways and pesticide concentrations detected in the environment. The majority of studies have involved a once-off broad survey approach (i.e. once off sampling across a study area) as opposed to a targeted, detailed approach.

### *1.6.1 Once-off Monitoring Studies*

The detection of atrazine in groundwater during the late 1980's was the first South African evidence of pesticides reaching groundwater. Subsequently, this had led to the banning of industrial applications of atrazine in South Africa in 1990 (Vermeulen *et al.*, 1998; Meinhardt, 2008). Atrazine is still, however, used in agriculture and frequently detected in surface and groundwater (Bouwman *et al.*, 2003; Du Preez *et al.*, 2003a; Grange *et al.*, 2003; Meintjies *et al.*, 2000; van Vuren *et al.*, 2003; Weaver, 1993). Monitoring of organochlorine pesticides in South African waters showed widespread occurrences of some banned pesticide residues still present in the environmental (Grobler, 1994; Naude *et al.*, 1998; London *et al.*, 2000)

and are believed to be still in use under unknown trade names due to their low cost (Awofulu and Fatoki, 2003). DDT is, however, still used officially and under strict control by the Department of Health and Welfare and remains the most widely used malaria prevention strategy by controlling the vector, the *Anopheles* mosquito, in malarial areas in South Africa as well as dieldrin use for the control of the Tsetse fly. The presence of DDT found in rivers of the Kruger National Park and northern KwaZulu-Natal areas can be explained by this activity (Bouwman *et al.*, 2003; Heath 1992; Maharaj, 2005). However, there is still a paucity of data on organochlorine pesticide residues in the South African aquatic environment (Awofulu and Fatoki, 2003; Maharaj, 2005).

Awofulu and Fatoki (2003), evaluated different methods for selective determination of pesticides and determined levels of aldrin α- β- δ- BHC, γ-chlordane, ∑DDT, dieldrin, endosulfan, endrin, hexachlorobenzene (HCB), and heptachlor in water and sediment samples from freshwater systems in the Eastern Cape (Buffalo, Keiskamma, Tyume and Swartkops rivers and the Sandile Dam) that receive runoff from agricultural lands and effluents from industries. β-BHC and heptachlor were the highest residue concentration detected in river water and sediment from the Buffalo River. Some of the pesticide values in this study were found to be much higher than the studies of Grobler *et al.* (1994) for the Olifants River and Weaver (1993) for the Hex River (where no organochlorines were detected) but were much lower than DDT (and metabolites) values found by Naude *et al.* (1998) in sediment.

Other studies conducted in the Western Cape on other river systems included the analyses of selected pesticides in groundwater from the Hex River Valley (Weaver, 1993). The results showed that none of the selected pesticides were detected at quantities above the detection limits in any of the water samples tested. The Hex River Valley investigation was the first study to provide data for pesticides in groundwater in South Africa. A study initiated by the Department of Water Affairs and Forestry (HRI-DWAF) investigated atrazine as well as several other pesticides in surface and groundwater in the Vaalharts Irrigation Scheme. Weaver (1993) followed up on this study but found no traces of atrazine in soil or borehole water samples from this location. Relatively low concentrations, however, were detected in the incoming water to the Vaalharts Irrigation Scheme samples.

There are few studies conducted in other areas in South Africa. Greichus *et al.* (1977) determined DDD, DDE, DDT, and dieldrin were insecticides most commonly found in both the Hartbeespoort and Voëlvlei dams, with lindane found in trace amounts and aldrin, heptachlor epoxide and chlordane found in very low concentrations. Hartbeespoort Dam had higher levels than Voëlvlei Dam of insecticides and PCBs in all types of samples studied (water, bottom sediment, aquatic plants, aquatic insects, fish, fish-eating birds and their eggs). Roux *et al.* (1994) studied various pesticides (DDR, DDD, DDE, dieldrin, heptachlor, lindane and endosulfan) and PCBs (arochlor 1254 and 1260) in water, sediment and biota from the Crocodile (east) River, and other sites from the Eastern Transvaal, however only p,p-DDE was found in muscle tissue of fish. Grobler (*et al.*, 1991; 1994) investigates pesticide levels in water, sediment and fish samples collected from the Olifants River, Eastern Transvaal, South Africa as well as from the Loskop and Phalaborwa Dams. Ten chlorinated pesticides and two polychlorinated biphenyls were analysed during December 1990, but were either not detected in the water phase or concentrations in sediment samples were too low for detection. However, residues of DDT were found in all fish specimens collected. The levels were lower than those reported in literature and were within international criteria for the protection of aquatic life. Grange *et al.* (2003) identified atrazine, anthracene, camphor, 1,2-dichlorobenzene and 1,4-dichlorobenzene in surface water samples collected near Johannesburg. Studies done by van Dyk (1978), Coetzee and Vahrmeijer (1986) and Hassett *et al.* (1987) show widespread contamination of surface water with α-, β-endosulfan, atrazine and chlorinated pesticides in the crop-growing regions of South Africa. Meinhardt *et al.* (1998) indicated herbicides sprayed for clearing areas moved into the Limpopo River and polluted the water. Barlin-Brinck (1991) found

organochlorine pesticides and atrazine in surface waters and fish in the Free State and Eastern Transvaal, respectively. Heath (1992) studied organochlorine pesticides in fish from the Letaba and Crocodile Rivers and found dieldrin, endosulfan, DDT, DDE and DDD in some fish from the Crocodile River in particular. In 1999 a study was undertaken again by Heath on various fish species from the Crocodile River, Mpumalanga, and correlated these values to estimates from a GIS model. Noteworthy pesticides included BHC, lindane, dieldrin, heptachlor and DDE (Heath *et al.*, 2003). Meintjies *et al.* (2000) studied the widespread contamination of estrogen and estrogen-mimicking substances including agricultural pesticides of surface water and groundwater at low concentrations. Pesticides analysed from the Vaal River, Johannesburg, Windhoek (Namibia), Vereeniging and Pretoria areas included DDT and metabolites, methoxychlor, endosulfan, chlordane and dicofol. Atrazine was detected in dam and river water but was not found in drinking water of Johannesburg, Windhoek, Vereeniging or Pretoria. Most substances detected were of agricultural and industrial origin.

### *1.6.2 Repeated Monitoring Studies*

While once-off surveys have shown that pesticides do occur in water resources it is difficult to determine the extent of the problem due to lack of repeated sampling in the study locations. Studies conducted in the Western Cape, including the Hex, Palmiet, Berg (London *et al.*, 2000) and Lourens rivers (Schulz, 2001a,b; Schulz and Peall, 2001; Schulz *et al.* 2001a,b; Dabrowski *et al.*, 2002a; Dabrowski and Schulz, 2003; Schulz *et al.* 2003; Dabrowski *et al.*, 2006) and in northern KwaZulu-Natal (Sereda and Meinhardt, 2003) are the most extensive in terms of routine, repetitive monitoring and are summarised in Table 4. Physicochemical properties of the most frequently detected pesticides are displayed in Table 6. The studies conducted in the Western Cape showed that azinphos-methyl, chlorpyrifos and endosulfan were frequently detected in water samples (77, 44 and 68% frequency of detection, respectively). Endosulfan in particular has been detected at relatively high concentrations in all of the rivers sampled. These high concentrations could be attributable to the fact that endosulfan is highly persistent and remains in the environment for a long period of time. Both endosulfan and chlorpyrifos were detected more frequently in sediment samples as opposed to water samples, which is most likely attributable to the comparatively lower water solubility of these compounds (Table 6). In contrast, azinphos-methyl was detected mostly in water samples. Furthermore there is quite a high variation in the Western Cape rivers with chlorpyrifos being detected at highest frequencies in the Berg and Hex rivers and comparatively lower frequencies in the Lourens and Palmiet rivers. Endosulfan is however detected at highest frequencies in the Hex and Lourens rivers. This variation is likely to be caused by catchment specific factors, including crop type (and therefore pesticide application) as well as geographic factors that may lead to contamination being particularly high for example in the Hex River (i.e. soil and climatic conditions).

Sereda and Meinhardt (2003) investigated the widespread contamination of pesticides of surface- and ground-water at low concentration in the Ubombo and Ingwavuma districts of KwaZulu-Natal in 2000 and 2001 (Table 4). Residues were attributed to the high usage of insecticides in the area, for both agricultural and anti-malarial spraying activities. The most frequently-detected pesticides included the pyrethroids (cypermethrin, λ-cyhalothrin and cyfluthrin, with deltamethrin and permethrin detected below quantifiable levels), organophosphates (fenthion and fenitrothion) organochloines (DDT and its metabolites (pp-DDD and pp-DDE)) and carbamates, (carbosulfan and carbofuran). This sampling campaign revealed clear trends in the frequency of detection which could be attributable to the physicochemical properties of the pesticides. The pyrethroids were more commonly detected in sediment samples as opposed to water samples which are most likely as a result of their very low water solubility and high $K_{OC}$. Fenitrothion was most frequently detected in water samples at very low concentrations (below detection limit). This can be explained by its relatively high water solubility and very short half-life. In contrast, fenthion which has a

comparatively lower water solubility was detected more often in sediment samples. It was also found that the selected reference sites situated in game parks also had traces of insecticides and could not be used for the purpose for which it was intended as they did not meet the requirements set for control sites. A similar pattern can be observed when comparing carbofuran and carbosulfan (Table 4 and Table 6).

These detailed studies demonstrate how knowledge and interpretation of physicochemical properties can play an important role in estimating or predicting the phase (i.e. dissolved in water or adsorbed to sediment) a pesticide is likely to occur in.

**Table 4:** A summary of commonly detected pesticides in four rivers in the Western Cape (Berg, Hex, Lourens and Palmiet rivers) and in the Ubombo and Ingwavuma districts of northern KwaZulu-Natal (DL – concentrations at the detection limit).

| | | Water Samples | | | Sediment Samples | | |
|---|---|---|---|---|---|---|---|
| **Pesticide** | **River** | **Detections** | **Frequency** | **Concentration** | **Detections** | **Frequency** | **Concentration** |
| Azinphos-methyl | Lourens | **30 (39)** | **77%** | **0.02-1.5** | **11 (21)** | **52%** | **1.2-1247** |
| Chlorpyrifos | Berg | 8 (13) | 62% | 0.01-0.31 | | - | - |
| | Hex | 16 (22) | 73% | 0.3-3.38 | - | - | - |
| | Lourens | 3 (18) | 17% | 0.03-0.2 | 14 (20) | 70% | 0.2-924 |
| | Palmiet | 4 (15) | 27% | 0.01-0.66 | - | - | - |
| | **Summary** | **31 (70)** | **44%** | **0.01-3.38** | **11 (14)** | **79%** | **6.7-924** |
| Endosulfan | Berg | 6 (13) | 46% | 0.01-0.36 | - | - | - |
| | Hex | 18 (22) | 82% | 0.03-1.56 | - | - | - |
| | Lourens | 19 (24) | 79% | 0.006-2.9 | 10 (12) | 83% | 11.3-12 082 |
| | Palmiet | 7 (15) | 47% | 0.03-1.38 | - | - | - |
| | **Summary** | **50 (74)** | **68%** | **0.006-2.9** | **10 (12)** | **83%** | **11.3-12 082** |
| Cypermethrin | N. KZN | **7 (83)** | **4%** | **DL - 40.74** | **14 (127)** | **11%** | **0.04-1651** |
| Cyfluthrin | | **4 (83)** | **5%** | **DL** | **32 (127)** | **25%** | **0.01-467** |
| Fenitrothion | | **32 (83)** | **63%** | **DL** | **5 (127)** | **4%** | **DL** |
| Fenthion | | **9 (83)** | **12%** | **DL** | **22 (127)** | **17%** | **0.28-1.38** |
| Carbofuran | | **15 (83)** | **22%** | **0.12-2.08** | **28 (127)** | **22%** | **3.71-10** |
| Carbosulfan | | **1 (83)** | **1%** | **0.61** | **20 (127)** | **16%** | **0.36-85.31** |

**Table 5:** A summary of the detection of three major pesticides detected in several studies conducted in the Lourens River catchment.

| | | Water Samples | | | Sediment Samples | | |
|---|---|---|---|---|---|---|---|
| **Pesticide** | **Sampling** | **Detections** | **Frequency** | **Concentration** | **Detections** | **Frequency** | **Concentration** |
| **Azinphos-methyl** | Routine | 1 (6) | 17% | nd-0.07 | 4 (6) | 67% | 1.2-22.5 |
| | Runoff | 17 (21) | 81% | 0.02-1.5 | 7 (15) | 47% | 7-1247 |
| | Spray drift | 12 (12) | 100% | 0.041-0.51 | - | - | - |
| **Chlorpyrifos** | Routine | 0 (5) | 0% | nd | 3 (6) | 50% | 0.2-0.6 |
| | Runoff | 3 (15) | 20% | 0.03-0.2 | 11 (14) | 79% | 6.7-924 |
| **Endosulfan** | Routine | 6 (6) | 100% | 0.006-0.06 | - | - | - |
| | Runoff | 11 (16) | 69% | 0.06-2.9 | 10 (12) | 83% | 11.3-12 082 |
| | Spray drift | 2 (2) | 100% | 0.067-0.9 | - | - | - |

**Table 6:** Physiochemical properties of pesticides frequently detected in studies conducted in the Western Cape and KwaZulu-Natal, South Africa.

| Pesticide | Class | Water Solubility (mg/l) | Half-life (days) | KOC (ml/g) |
|---|---|---|---|---|
| Azinphos-methyl | Organophosphate | 28 | 10 | 1 000 |
| Carbofuran | Carbamate | 319 | 29 | 22 |
| Carbosulfan | Carbamate | 0.11 | 21 | 9 489 |
| Chlorpyrifos | Organophosphate | 1.05 | 50 | 8 151 |
| Cyfluthrin | Pyrethroid | 0.0066 | 33 | 64 300 |
| Cypermethrin | Pyrethroid | 0.009 | 60 | 85 572 |
| Endosulfan | Organochlorine | 0.32 | 50 | 11 500 |
| Fenitrothion | Organophosphate | 19 | 2.7 | 322 |
| Fenthion | Organophosphate | 4.2 | 22 | 1 500 |

## 1.7 Linking Pesticide Concentrations to Routes of Exposure

Given the detrimental effects of pesticides in the aquatic environment it is important to establish links between pesticide levels detected in water resources and the possible transport pathways resulting in contamination. Such information can benefit long-term implementation of proper management and mitigation initiatives and also provide guidance with respect to routine monitoring of pesticides. In this respect, research performed in the Lourens River catchment is the most extensive in South Africa and has linked detected pesticide levels with runoff and spray drift events occurring in the catchment (Table 5).

As mentioned previously, spray drift is commonly regarded as the worst-case scenario for pesticide exposure in aquatic risk assessment. However, only a few studies have directly compared these routes of entry in the same catchment, two of which have been performed in the Lourens River catchment (Schulz, 2001b; Dabrowski and Schulz, 2003). These and other studies (Kreuger, 1998) have shown runoff to be the most important source of non-point source pesticide pollution at the catchment scale and it is therefore regarded as the most important factor in terms of contamination of surface waters in arid areas (Everts, 1997). One potential reason is related to land use factors and the fact that the spatial and temporal scale of runoff contamination is far greater than spray drift. Many pesticides have long half-life times and previous studies (Kreuger, 1998; Williams *et al.*, 1995) have shown that runoff-induced pesticide loading can occur long after the previous application, indicating that runoff integrates chemical input over a large time span. Runoff can also influence an entire catchment simultaneously and as such, a river can collect surface runoff from a large geographical area. Furthermore, rainfall is non-directional and does not restrict the number of orchards prone to runoff. In comparison spray drift is instantaneous and contamination can only occur during application, in combination with specific meteorological requirements (downwind orientation of surface waters to the point of application), which further restricts the potential for contamination. Thus, the land use and the meteorological conditions restrict the number and length of tributaries that can possibly be affected by spray drift. Finally, runoff results in input of pesticides that are both dissolved in the water phase and associated with suspended sediment, therefore resulting in a dual contamination potential.

### *1.7.1 Runoff*

The importance of runoff as a source of pesticide contamination can be illustrated by studies performed in the Lourens River catchment (Western Cape). Studies showed that concentrations of azinphos-methyl, chlorpyrifos and endosulfan in both water and sediment phases were higher in samples collected during runoff conditions than those measured in routine sampling prior to the beginning of the rainy season (Table 5). Furthermore, only 20%

of water samples taken during runoff events had detectable concentrations of chlorpyrifos (an organophosphate pesticide with low water solubility and a high $K_{OC}$ (Table 6) while frequency of detection in sediment samples was 79%, revealing high concentrations of particle associated chlorpyrifos (up to 924 µg/kg). In contrast, another organophosphate, azinphos-methyl, (high water solubility and low $K_{OC}$) was detected more frequently in water samples (81%), with comparatively fewer sediment samples having any measurable levels (47%). Thus the water solubility and $K_{OC}$ of a compound is very important in terms of the fate of the pesticide and its partitioning in the water body. Furthermore azinphos-methyl was detected in 17% (1 out of 6 samples) of water samples taken during routine sampling, yet was detected in 81% (17 out of 21 samples) in samples taken during runoff conditions. In contrast, endosulfan a pesticide with a long half life was detected in 100% of samples taken during routine sampling and 68% of samples taken during runoff conditions. These results indicate a) that runoff leads to increased levels of pesticide levels, b) that routine sampling may not detect problematic pesticides particularly in the case of pesticides with relatively short half-lives (i.e. azinphos-methyl) and c) that the behaviour of pesticides in the environment is strongly related to their physicochemical properties.

A study performed in the Lourens River also showed the importance of strong rainfall events directly after pesticide application. Schulz (2001a) reported levels of 1.5 and 2.9 ug/l of azinphos-methyl and endosulfan, respectively while sediment concentrations were as high as 1247 and 12082 ug/kg, respectively. This study also highlights the importance of the influence of prevailing climatic conditions in an area. The rainfall event monitored in this study is uncharacteristic of the Western Cape as this is a winter rainfall area. Most parts of South Africa experience summer rainfall and surface runoff following high intensity thunderstorms could lead to very high concentrations of pesticides entering surface waters, similar to those reported from the Lourens River. Furthermore, pesticide application on fruit orchards takes place during the dry, windy summer months, which in combination with low base flows could lead to high levels of spray drift derived pesticide input. These climatic differences in regions are important in terms of the vulnerability of ecosystems to different exposure pathways.

### *1.7.2 Spray Drift*

As has been previously noted, very few studies have been conducted on contamination of water resources as a result of spray drift. Again, research conducted in the Lourens River has investigated this route of entry through sampling and modelling techniques. Those studies that have incorporated spray drift include studies by Schulz (2001b), Schulz *et al.* (2001d), Schulz *et al.* (2003a), Dabrowski and Schulz (2003) and Dabrowski *et al.* (2005a; 2006).

Dabrowski and Schulz (2003) used basic drift values (95th percentiles) by Ganzelmeier *et al.* (2005) to predict spray drift related to azinphos-methyl loads in the sub-catchments of the Lourens River, Western Cape. Dabrowski and Schulz (2003) also compared runoff and spray drift of predicted and measured levels of azinphos-methyl. Basic drift values were integrated into geographical information system (GIS) to predict spray drift related loading of azinphos-methyl in the Lourens River. Based on long-term meteorological data and average application regimes, they concluded that runoff led to a higher annual load than spray drift in the Lourens River. Runoff was found to be a clearly more important source of non-point pollution in this study. The basic drift values (Ganzelmeier *et al.* 2005) were found to be applicable for use in South African orchard areas as well as the values given by the Spray Drift Task Force, however further validation of drift values was recommended for use under South African conditions.

## 1.8 Effects

### *1.8.1 Ecological*

Amongst the limited number of studies that have been undertaken nationally to determine effects of pesticides in water resources most have focused on the Lourens River catchment in the Western Cape. During these studies a link between mainly azinphos-methyl, chlorpyrifos and total endosulfan exposure and various endpoints were established (mortality, community structure, biomarkers).

The first studies on effect of pesticides focused on bioaccumulation in various fish species (Greichus *et al.* 1977; Heath and Claassen, 1999; Bouwman *et al.*, 1990), followed by a range of in situ bioassays (Schulz and Peall, 2001; Schulz *et al.*, 2001c; Schulz, 2003), microcosms (Schulz *et al.*, 2002) and field studies (Schulz *et al.*, 2003; Thiere and Schulz, 2004; Bollmohr *et al.*, 2007; Bollmohr and Schulz, 2008; Bollmohr *et al.*, 2008). Recently research has increasingly focussed on biomarkers (Sturm *et al.*, 2008) and the effect of endocrine disrupting activities (Aneck-Hahn, 2005; Bornman *et al.*, 2007; Mahomed *et al.*, 2008).

### *1.8.2 Bioaccumulation*

Bouwman *et al.* (2008) studied the effect of organochlorine on possible eggshell thinning of water-associated birds. The African darter showed the highest levels of pollutants including p,p-DDT, DDE and chlordane and it was the only species which showed a negative association of eggshell thickness and pollution levels. However for individual compounds, the strongest negative association was with p,p'-DDE, sum chlordanes and beta-HCH identified the reduction in eggshell thickness of the African darter in relation to pollution levels as a cause of concern. Greichus *et al.*, (1977), detected bioaccumulation of pp-DDT (500-1200 µg/kg), pp-DDD (100-1900 µg/kg), pp-DDE (600-4200 µg/kg) and dieldrin (300-1300 µg/kg) in various fish species (whole fish species) in the Crocodile River and Berg River. Heath and Claassen (1999) investigated the bioaccumulation of 14 different pesticides in 14 different fish species inhabiting six different river catchments. Furthermore they were able to link the tissue levels of lindane, endosulfan, mercapthion and pirimiphos with the pesticide usage in the catchment.

### *1.8.3 Mortality*

Several studies have successfully linked survival of in situ exposed organisms (*Chironomus sp.* and indigenous amphipod) to measured aqueous and particle-associated insecticide contamination (azinphos-methyl, chlorpyrifos and endosulfan) in three orchard rivers in the Western Cape (Bollmohr, 1999; Schulz and Peall, 2001; Schulz *et al.*, 2001c; Schulz, 2003). The mortality of *Chironomus sp*. was significantly increased by 41-46% during a 24h azinphos-methyl exposure (0.36-0.87 µg/l) in the Lourens River (Schulz *et al.*, 2001d). A similar study by Schulz and Peall (2001) established a link between azinphos-methyl and endosulfan exposure (0.85 and 0.2 µg/l, respectively) and the mortality of *Chironomus* (43%). Remarkably, the results of the two latter studies are very similar. In situ exposed bioassays with amphipods (*Paramelita nigroculus*) in the Berg and Franschhoek rivers indicated that mortality was caused by runoff-related insecticide pollution (0.26 µg/l azinphos-methyl, prothiofos and endosulfan; 870 µg/kg endosulfan and chlorpyrifos) (Schulz, 2003). Results of a sediment toxicity test by Bollmohr *et al.* (2008a) indicate that a chlorpyrifos exposure of 5.89-6.38 µg/kg, poses a detrimental effect to the survival rate of an

estuarine copepod *(Mesochra parva).* This range of concentrations was exceeded in 37% of samples taken in the Lourens River estuary.

### *1.8.4 Microcoms*

Schulz *et al.*, (2002) established a link between survival in multispecies microcosm experiments exposed to azinphos-methyl and the abundance dynamics of macroinvertebrate species at various sites in the Lourens River. Microcosms were contaminated for 1 h (so as to simulate realistic field exposure length) with azinphos-methyl (control, 0.2, 1, 5, and 20 µg/L; three replicates each), and acute effects on survival were evaluated 6 days following exposure. The two highest treatments resulted in a significantly reduced invertebrate density for eight taxa. Furthermore five of the eight taxa being affected by azinphos-methyl exposure in the microcosm experiment (*Simuliidae, Demoreptus sp., Aphanicerca sp, Castanophlebia sp., Chironomidae*) showed significantly lower densities at a contaminated site in the Lourens River than at the control site. Similarly, four species that we were not affected in the microcosm experiments were found at significantly higher densities at the contaminated site compared to the control. The microcosm experiment employed a field relevant design, linked well with field studies and suggests that transient pesticide contamination affects the aquatic communities of the Lourens River.

### *1.8.5 Field studies*

Bollmohr *et al.*, (2007) investigated the risk of pesticides in South Africa and measured suspended particle concentrations of chlorpyrifos, prothiofos, cypermethrin, fenvalerate, endosulfan and p,p- DDE in the Lourens River estuary. This study indicated based on the use of species sensitivity distributions that chlorpyrifos and endosulfan posed the highest risk towards aquatic life, including freshwater and marine communities. Schulz *et al.* (2003) established a link between azinphos-methyl exposure to 0.73 µg/l and a significant decrease in density of zooplankton (cladocera and copepoda) in an artificial wetland within the Lourens River catchment. Results of a study by Thiere and Schulz (2004) using SASS5 showed a significant decrease in the number of taxa and the average score per taxon (ASPT) along the Lourens River probably due to azinphos-methyl (0.05 µg/l and 49 µg/kg in water and sediment, respectively), chlorpyrifos (94 µg/l) and endosulfan (122 µg/kg) exposure. Statistical analysis of the macroinvertebrate community (Principal Response Curve) at three different sites along the Lourens River indicated a possible impact to the community dynamic as a result of organophosphate exposure (azinphos-methyl and chlorpyrifos) (Bollmohr and Schulz, 2008). The authors suggested that particle associated organophophates > 30 µg/kg affected the community structure, while levels <10 µg/kg will not yield any significant effect. Bollmohr *et al.* (2008b) identified endosulfan and chlorpyrifos as one of the variables influencing meiofauna community structures in the Lourens River estuary by comparing tow runoff events, differing in pesticide exposure.

### *1.8.6 Biomarker*

Sturm *et al.* (2008) suggested a link between the inhibition of rainbow trout acetylcholinesterase (brain) and detected organophosphate concentrations in the Lourens River. After a seven day exposure of rainbow trout to chlorpyrifos (0.01 µg/l; 74.4 µg/kg ) and azinphos-methyl (0.14 µg/l; 57.9 µg/kg) the enzyme was inhibited by 40%. However, the measured concentrations are far below the NOEC levels for chlorpyrifos (0.33 µg/l ; 200 µg/kg) and azinphos-methyl (>3.3 µg/l; 20 µg/kg), determined within this study via microcosm experiments.

### *1.8.7 Endocrine Disrupting Activity*

Over the past two decades, increasing concern and public debate have developed over the potential adverse effects of exposure to a group of chemicals that have the potential to alter the normal functioning of the endocrine system in wildlife and human (NIEHS, 2006). These chemicals are known as endocrine disrupting chemicals (EDCs) since they may act as oestrogen and androgen agonist and antagonists, aromatase inhibitors and thyroid modulators (Hutchinson *et al.*, 2006). EDCs are found in many everyday products including plastics, metal food cans, flame retardants, toys, cosmetics, pesticides and detergents. A list of 127 pesticides with endocrine disrupting mode of actions has been identified in developed countries (McKinlay *et al.*, 2008). Recently Burger and Nel (2008) mentioned at least 15 pesticides with the potential of endocrine disrupting activity. However in South Africa there is very little information on the EDC levels in water and currently only limited screening methods are in place (Aneck-Hahn, 2005). Most chemical analytical methods are expensive and are not sufficient to identify all the environmental chemicals and to predict a combination of toxicity and bioavailability. One of the pesticides with a high oestrogenicity is the organochlorine DDT, which is still used as malaria control in South Africa. Therefore a lot of research focused on the occurrence in water systems and the effect on human and wildlife (Bornman *et al.*, 2007). It is particularly interesting since p,p-DDT shows oestrogenic activity, whereas the breakdown product p,p-DDE shows androgenic activity (McKinlay *et al.*, 2008). Mahomed *et al.* (2008) indicated a possible link between atrazine, terbuthylazine, chlorpyrifos and lindane exposure and oestrogenicity found in the Apies River, South Africa. Bornman *et al.* (2007) suggested a link between pesticide concentrations found in an urban nature reserve (α-BHC, lindane, heptachlor-epoxide, endrin, methoxychlor, p,p-DDT, p,p-DDD) and histological evidence of intersex in sharptooth catfish as well as oestrogenic activity of the water (established by YES assay).

### *1.8.8 Human Health*

A study by Bouwman *et al.* (1990), determined the risk of human health due to consumption of DDT-contaminated fish in the Pongola flood plain in KwaZulu-Natal. Another study by Bouwman *et al.* (2006) assessed the bioaccumulation of pyrethroids in breast milk and found permethrin (186-1343 µg/l), cyfluthrin (26-1308 µg/l), cypermethrin (33-127 µg/l) and deltamethrin (60-258 µg/l). Whereas the latter is probably related to exposure during malaria control, the other's route of exposure could be spraydrift, contaminated drinking water and/ or food. For pp-DDT it was found that the concentration was higher within the milk fat of women using river water as drinking water (2220 µg/kg) compared to women using piped water (1324 µg/kg). The sources are still unclear but could include directly the river water or indirectly the consumption of fish out of the same river.

## 1.9 Risk Mitigation

Constructed wetlands and vegetated canals along a tributary of the Lourens River (Western Cape) were used to ascertain the retention of runoff-related agricultural pollution and the effects of spray drift. The initial studies tried to quantify retention of wetlands by taking input and output measurements using various current-use insecticides in South Africa. Schulz and Peall (2001b) investigated the retention, particularly of azinphos-methyl, chlorpyrifos and endosulfan in suspended particles and water into a wetland. They found that aqueous phase insecticide concentrations retention rates were between 77 and 99% and particle-associated insecticide load was retained at almost 100% for those pesticides studied. Schulz *et al.* (2001d, 2003a) investigated the effects of airborne azinphos-methyl from spray drift on vegetated wetlands. Concentration levels of pesticides in water and sediment cores were measured and included chlorpyrifos, prothiofos, α- β-endosulfan and endosulfan-sulphate.

Indigenous amphipods and midge (*Chironomus* sp.) were used in in-situ bioassays at the inlet and outlet of this wetland to determine the azinphos-methyl, chlorpyrifos and endosulfan exposure (Schulz and Peall 2001b, Moore *et al.*, 2002; Schulz *et al.*, 2001d; Schulz, 2003).

Additional studies focused on the effectiveness of in-stream vegetation in tributaries of the Lourens River in reducing transport of pesticides to the main stem river. The physical interception of spray-drift derived azinphos-methyl by emergent aquatic macrophytes was investigated by Dabrowski *et al.* (2005) and results showed that deposition in the tributary is potentially reduced by up to 88% by emergent vegetation. Monitoring of in-stream azinphos-methyl concentrations during runoff and spray drift events, showed that those concentrations derived from spray drift induced input were more effectively mitigated than those induced by runoff (Dabrowski *et al.* 2006). The effectiveness in retaining agricultural non-point source pesticide pollution due to spray drift events in constructed wetlands in the Lourens River, Western Cape as well as fate and effects of spray drift-borne azinphos-methyl was investigated by Schulz *et al.* (2003b). Macrophytes proved to facilitate the reduction of the loading of azinphos-methyl into nearby waterway following a spray-drift event in the wetland (Schulz *et al.*, 2003a). Schulz (2001b) compared runoff and spray-drift input of azinphos-methyl and endosulfan into Lourens River, while Schulz *et al.*, (2001d) focused on contracted wetlands along a tributary of the Lourens River to ascertain retention of spray drift-borne azinphos-methyl at the inlet and outlet of a vegetated pond.

## 1.10 Pesticide Risk Indicators

The literature clearly shows that pesticides are frequently detected in South African surface waters, potentially posing a risk to various components of the aquatic ecosystem. Despite this evidence, the potential impact of pesticides in South African surface waters has generally been a low priority and has generally not been considered in water resource management.

Although intensive monitoring and sampling can identify pesticide impacts, the cost of sampling and analysis makes this a highly costly exercise (particularly in the context of less developed countries). Risk indicators can be regarded as lower-tier risk assessment tools that provide a relative assessment of the environmental impact of pesticides through integration of ecotoxicological, environmental fate and pesticide use data. Risk indicators are regarded as useful tools in minimising off-site impacts of pesticides and can assist in decision making and policy formulation. Pesticide environmental risk indicators vary greatly in terms of their purpose, compartments, methodology (Reus *et al.*; 2002) and are often very broad in scope covering, for example, the impact on aquatic organisms, soil organisms, bees, occupational exposure and human health effects.

Ideally, an indicator needs to deal not just with the inherent hazard of a pesticide but also with the potential risk it poses. This involves taking into account the rate and method of application of the pesticide as well as environmental and site conditions (Reus *et al.*, 2002) and taking into consideration the asset threatened by use of that pesticide. Relative risk is assessed using site conditions (i.e. soil type, soil organic matter content, water input, slope of land, soil loss, recharge rate, depth of water table, etc.) and environmental conditions (i.e. rainfall and temperature). For each pesticide, the rate and method of application, its sorption and persistence properties, its toxicity to a range of receptor organisms (chosen to represent different trophic levels, e.g. algae, daphnia and fish) is assessed. For example patterns in the detection of pesticides in the Western Cape and northern KwaZulu-Natal (Table 4 and Table 5) could largely be described by the physicochemical properties of the respective pesticides (Table 6). In addition catchment specific factors unique to each catchment may also play a role in the magnitude of contamination of each of the detected pesticides (i.e. crop type, soil type and climatic conditions). Risk indictors attempt to integrate this

information using simple modelling techniques and other applications (e.g. geographical information systems) to provide a relative indication of the potential of contamination of surface waters by a number of pesticides used in the catchment such that results displayed in Table 4 and Table 5 can essentially be predicted.

On a first level of assessment, risk indicators may be designed as instruments for predictive risk management approaches to offer preliminary insights into the status quo of pesticide risks. They may be developed to obtain baseline information about pesticide use and risks, focusing on one or more realistic hazardous scenarios, and they may guide the identification of potential trouble spots and vulnerable areas where risk reduction might be requisite. In this respect risk indicators may be particularly beneficial to developing countries, where the costs of monitoring are prohibitive and data requirements are relatively easily obtainable. Furthermore, risk indicators can potentially highlight the most important route of contamination of surface waters (i.e. via runoff during rainfall or spray drift during pesticide application) and therefore provide valuable insight with respect to risk mitigation strategies for certain pesticides.

## 1.11 References

ANECK-HAHN NH, DE JAGER C, BORNMAN MS and DU TOIT D (2005) Oestrogenic activity using a recombinant yeast screen assay (RCBA) in South African laboratory water resources. *Water SA* **31**: 253-256.

ANSARA-ROSS TM, WEPENER V, VAN DEN BRINK PJ. and ROSS, MJ. (2008) A probabilistic risk assessment of the environmental impacts of pesticides in the Crocodile (west) Marico catchment, North West province. SUBMITTED TO WATER SA MARCH 2008.

ANSARA-ROSS TM, WEPENER V., VAN DEN BRINK PJ. and ROSS MJ. (2008b) Toxicity of three selected pesticides on indigenous species to South Africa and their comparative toxicity to standard test species. Unpublished data.

AWOFOLU RO and FATOKI OS (2003) Persistent organochlorine pesticide residues in freshwater systems and sediment from the Easter Cape, South Africa. *Water SA* **29**(3):323-330.

BAIER C, HURLE K and KIRCHHOFF J (1985) Datensammlung zur Abschätzung des Gefährdungspotentials von Pflanzenschutzmittel-Wirkstoffen für Gewässer. Parey Verlag, Hammburg.

BARNES JM (1999) Problems in monitoring overexposure among spray workers in fruit orchards chronically exposed to diluted organophosphate pesticides. *Int. Arch. Occup. Environ. Health* **72**(Suppl 3):M68-M74.

BARLIN-BRINCK M (1991) Pesticides in South Africa: An assessment of their use and environmental impact. The Wildlife Society of South Africa, Durban.

BENNETT ER, HAHN C, DABROWSKI JM, THIERE G, PEALL SKC and SCHULZ R (2003) Fate of aqueous-phase azinphos-methyl in a flow-through wetland in South Africa following a spraydrift event. Joint European-Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

BLANCHARD PE and LERCH RN (2000) Watershed vulnerability to losses of agricultural chemicals: interactions of chemistry, hydrology and land-use. *Environ. Sci. Technol.* **34**: 3315-3322.

BOLLMOHR S, DAY JA and SCHULZ R (2007) Temporal variability in particle-associated pesticide exposure in a temporarily open estuary, Western Cape, South Africa. *Chemosphere* **68**: 479-488.

BOLLMOHR S, and SCHULZ R (2008) Seasonal changes of macroinvertebrate communities in a Western Cape River receiving nonpoint-source pollution. *Environ. Toxicol. Chem*. (accepted).

BOLLMOHR S, SCHULZ R and HAHN T (2008) Interactive effect of salinity decrease, salinity adaptation and chlorpyrifos exposure on an estuarine harpacticoid copepod, Mesochra parva, in South Africa. *Ecotoxicol. Environ. Saf.* (accepted).

BORNMAN R, VAN VUUREN HJ, BOUWMAN H, DE JAGER C, GENTHE B, BARNHOORN EJ (2007) Endocrine disrupting activity and the potential health risk in the Rietvlei Nature Reserve. WRC Report 1505/1/07, Pretoria.

BOUWMAN H, COETZEE, A and SCHUTTE CHJ (1990). Environmental and health implications of DDT-contaminated fish from the Pongolo Flood Plain. *J. Afr. Zool.* **104**: 275-286.

BOUWMAN H, COOPPAN RM, BECKER PJ and NGXONGO S (1991) Malaria control and levels of DDT in serum of two populations in KwaZulu. *J. Toxicol. Environ. Health* **33**(3): 141-155.

BOUWMAN H, VOSLOO R, MABOETA M and BESTER B (2003b) An assessment of 30 years of environmental organochlorine residue data from Southern Africa. Joint European-Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

BOUWMAN H (2003) Pops, agriculture, malaria and pesticide exposure. Joint European-Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003, University of Cape Town, Cape Town, South Africa

BOUWMAN H (2004) South Africa and the Stockholm Convention on persistent organic pollutants. *S. Afr. J. Sci.* **100**: 323-328

BOUWMAN H, SEREDA B. and MEINHARDT HM (2006) Simultaneous presence of DDT and pyrethroid residues in human breast milk from a malaria endemic area in South Africa. *Environ. Poll.* **144**: 902-917.

BOUWMAN H, POLDER A, VENTER B and SKAARE JU (2008) Organochlorine contamination in cormorant, darter, egret, and ibis eggs from South Africa. *Chemosphere* **71**: 227-241.

BURGER AEC (2008) WRC Research programme on Endocrine Disrupting Compounds (EDCs): Volume 2. Implementation of a research programme for investigating EDCs in SA Water systems. WRC Report No 1402/1/08, Pretoria.

CAIRNCROSS EK, ADAM H, SOLOMON A, LONDON L and DALVIE A (2003) An evaluation of solid phase micro-extraction (SPME) for the analysis of water contamination with chlorpyrifos and endosulfan isomers. Joint European-Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

CAPEL PD and LARSON SJ (2001) Effect of scale on the behaviour of atrazine in surface waters. *Environ. Sci. Technol.* **35**: 648-656.

CAPRI E, PADOVANI E and TREVISAN M (2003) Modeling and measuring environmental concentration of pesticides in paddy rice. Joint European-Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

CLAASSEN M (1996) Assessment of selected metal and biocide bioaccumulation in fish from the Berg, Luvuvhu, Olifants, Sabie Rivers, South Africa. Unpublished MScThesis, Rand Afrikaans University, Johannesburg.

COCKROFT VG, DE KOCK AC, LORD DA and ROSS GJB (1989) Organochlorines in bottlenose dolphins *Tursiops truncates* from the east coast of South Africa. *South African. J. Marine Sci.* **8**(8): 207-217.

COETZEE JP and VAHRMEIJER JT (1986) The adsorption of atrazine by different clay minerals and its influence on the mobility of atrazine. Unpublished MSc dissertation, Potchefstroom University for Christian Higher Education, Potchefstroom, South Africa.

COLE JT, BAIRD JH, BASTA NT, HUHNKE RL, STORM DE, JOHNSON GV, PAYTON ME., SMOLEN MD, MARTIN DL and COLE JC (1997) Influence of buffers on pesticide and nutrient runoff from Bermudagrass turf. *J. Environ. Qual*. **26**: 1589-1598.

CSIR (1996) Overview of the pesticide and heavy metal levels present in the populations of the larger indigenous fish species of selected South African Rivers. Division of Water. Environment and forestry Technology, CSIR.

CUPPEN JGM, VAN DEN BRINK PJ, CAMPS E, UIL KF and BROCK TCM (2000) Impacts of the fungicide carbendazim in freshwater microcosms. I. Water quality, breakdown of particulate organic matter and response of macroinvertebrates. *Aqua. Toxicol.* **48**(2-3): 233-250.

DALLAS HF and DAY JA (1993) The effect of water quality variables on riverine ecosystems: a review. Water Research Commission, Pretoria.

DABROWSKI JM, PEALL SKC, REINECKE AJ, LIESS M and SCHULZ R (2002a) Runoff-related pesticide input into the Lourens River, South Africa: Basic data for exposure assessment and risk mitigation at the catchment scale. *Water, Air, Soil Poll.***135**: 265-283.

DABROWSKI JM, PEALL SKC, VAN NIEKERK A, REINECKE AJ, DAY JA and SCHULZ R (2002b) Predicting runoff-induced pesticide input in agricultural sub-catchment surface waters: Linking catchment variables and contamination. *Water Res.* **36**(20): 4975-4984.

DABROWSKI JM and SCHULZ R (2003) Predicted and measured levels of azinphosmethyl in the Lourens River, South Africa: Comparison of runoff and spray drift. *Environ. Toxicol. Chem.* **22**(3): 494-500.

DABROWSKI JM, BOLLEN A, BENETT ER and SCHULZ R (2005a) Pesticide interception by emergent aquatic macrophytes: potential to mitigate spray-drift input in agricultural streams. *Agric., Ecosys. Environ.* **111**: 340-348.

DABROWSKI, JM., BOLLEN, A., AND SCHULZ, R (2005b) Combined effects of discharge, turbidity and pesticide on mayfly behaviour: experimental evaluation of spray-drift and runoff scenarios. *Environ. Toxicol. Chem.* **24**(6):1395-1402.

DABROWSKI JM, BENETT ER, BOLLEN A and SCHULZ R (2006) Mitigation of azinphos-methyl in a vegetated stream: Comparison of runoff- and spray-drift. *Chemosphere* **62**(2):204-212.

DALLAS HF and DAY JA (1993) The effect of water quality variables on riverine ecosystems: A review. Report prepared for the Water Research Commission.

DALVIE MA and LONDON L (2001) Unwanted agricultural chemicals in Stellenbosch: need for public health intervention. *South African J. Sci.* **97**: 309-312.

DALVIE MA, CAIRNCROSS E, SOLOMON A and LONDON L (2003) Contamination of rural surface and groundwater by endosulfan in farming areas of the Western Cape, South Africa. Environmental Health: A Global Access Science Source 2(1) [electronic journal].

DALVIE MA, LONDON L, MBULI S and CAIRNCROSS E (2004) Knowledge and attitudes in rural Western Cape towards pesticides in water sources. *Water SA* **30**(1):43-50.

DAVIES HE and PEALL SKC (1997) A study of pesticide residue levels in farm dams in the Western Cape, South Africa. Report of the Fitz Patrick Institute, Cape Town.

DAVIES H (1997) An assessment of the suitability of a series of Western Cape farm dams as waterbird habitats. Unpublished MSc thesis. University of Cape Town.

DE KOCK AC (1985) Poly chlorinated biphenyls organochlorine compounds in marine and estuarine systems. Unpublished MSc dissertation, University of Port Elizabeth, South Africa.

DE KOCK AC and BOSHOFF AF (1987) PCBs and chlorinated hydrocarbon insecticide residues in birds and fish from the Wilderness Lakes system, South Africa. *Marine Poll. Bull.* **18**(7): 413-416.

DE KOCK AC and LORD DA (1989) Predicting the fate and effects of chlorinated hydrocarbons in a coastal marine system South-East Indian Ocean. *Int. J. Environ. Analytical Chem.* **36**(3): 133-138.

DE SNOO GR and DE WIT PJ (1998) Buffer zones for reducing pesticide drift to ditches and risks to aquatic organisms. *Ecotoxicol. Environ. Saf.* **41**(1): 112-118.

DOA (DEPARTMENT OF AGRICULTURE) (1947) Fertilizer, farm feeds and agricultural remedies Act, No. 36 of 1947, Government Printers, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY) (1996) South African Water Quality Guidelines. Vol. 7: Aquatic Ecosystems (1st edn.). Department of Water Affairs and Forestry, DWAF, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY) (1997) White Paper on a National Water Policy for South Africa. DWAF, Pretoria, South Africa.

DWAF (DEPARTMENT OF WATER AFFAIRS AND FORESTRY) (1998) National Water Act. Act 36/1998. DWAF, Pretoria, South Africa.

DINHAM B (1993) The Pesticide Hazard. A global health and environmental audit. Pesticides Trust, Zed press, London

DOMAGALSKI JL, DUBROVSKY NM and KRATZER CR (1997) Pesticides in the San Joaquin River, California: Inputs from the dormant sprayed orchards. *J. Environ. Qual.* **26**: 454-465.

DU PREEZ HH, HEATH RGM, SANDHAM LA and GENTHE B (2003a) Methodology for the assessment of human health risks associated with the consumption of chemical contaminated freshwater fish in South Africa. *Water SA* **29**(1): 69-90.

DU PREEZ LH, CARR JA, GIESY JP, HECKER MH, JOOSTE AM, KENDALL RJ, SMITH EE, SOLOMON KR and VAN DER KRAAK G (2003b) Exposure characteristics and responses to field exposures of *Xenopus laevis* to atrazine and related triazines in South African corn growing regions. *Joint European – Southern African International Conference on Pesticides in non-target agricultural environments – Environment and economic implications, 21-23 January 2003,* University of Cape Town, Cape Town, South Africa.

ERSTFELD KM (1999) Environmental fate of synthetic pyrethroids during spray drift and field runoff treatments in aquatic microcosms. *Chemosphere* **39**: 1737-1769.

EVERTS JW (1997) Ecotoxicology for risk assessment in arid zones: Some key issues. *Arch. Environ. Contam. Toxicol*. **32**: 1-10.

FLURY M (1996) Experimental evidence of transport of pesticides through feld soils – A review. *J. Environ. Qual*. **25**: 25-45.

GANZELMEIER H, RAUTMANN D, SPANGENBERG R, STRELOKE M, HERRMANN M, WENZELBURGER H-J, and WALTER H-F (1995) Studies of the spray drift of plant protection products. Mitteilungen aus der Biologischen Bundesanstalt für Land –und Forstwirtschaft, Blackwell Scientific, Berlin, Germany.

GILBERT AJ and BELL GJ (1988) Evaluation of the drift hazards arising from pesticide spray application. *Aspect. Appli. Biol.* **17**: 363-376.

GRANGE AH, PAPO MT, MATHEBULA S and SOVOCOOL GW (2003) Identification of compounds in South African stream samples using Ion Composition Elucidation (ICE). *Conference of the American Society of Masspectroscopy*. June 2003.

GREICHUS YA, GREICHUS A, AMMAN BD, CALL DJ, HAMMAN DCD and POTT RM (1977) Insecticides, polychlorinated biphenyls and metals in African lake ecosystems. I. Hartbeespoort Dam, Transvaal and Voëlvlei Dam, Cape Province, Republic of South Africa. *Arch. Environ. Contam. Toxicol.* **6**: 371-383.

GROENENDIJK P, VAN DER KOLK JWH and TRAVIS KZ (1994) Prediction of exposure concentration in surface waters. In: Hill, I.R., Heimbach, F., Leeuwangh, P., Matthiessen, P. (eds). Freshwater field tests for hazardous assessment of chemicals. Lewis Publisher, Baco Raton pp105-125.

GROBLER DF, VAN HEERDEN E, VAN VUREN JHJ and DU PREEZ HH (1991) Bioconcentration of atrazine, zinc and iron in the blood of Tilapia sparmanii (Cichlidae). *Comp. Biochemphysiol*. **100C**(3): 629-633.

GROBLER DF (1994) A note on PCBs and chlorinated hydrocarbon pesticide residues in water, fish and sediment from Olifants River, Eastern Transvaal, South Africa. *Water SA* **20**(3): 187-194.

GROBLER DF, BADENHORST JE and KEMPSTER P (1996) PCBs Chlorinated Hydrocarbons and Chlorophenols in the Isipingo Estuary, Natal, Republic of South Africa. *Marine Poll. Bull.* **32**(7): 572-575.

HASSETT AJ, VILJOEN PT and LIEBENBERG JJE (1987). An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1984 to September 1985. *Water SA* **13**(3): 133-136.

HEATH RG (1992) The levels of organochlorine pesticides in indigenous fish from two rivers that flow through the Kruger National Park, South Africa. *Water Supply* **10**: 177-185.

HEATH RG (1999) A catchment-based assessment of the metal and pesticide levels of fish from the Crocodile River, Mpumalanga Unpublished PhD Thesis, Rand Afrikaans University, Johannesburg, South Africa.

HEATH RG and CLAASSEN M (1999) An overview of the pesticide and metal levels present in populations of the larger indigenous fish species of selected South African Rivers. Water Research Commission Report No. 428/1/99.

HEATH RG, DU PREEZ HH and GENTHE B (2003) Human health risk assessment protocol development of consuming fish from a South African lowveld river. *Joint European – Southern African International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications.* 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

HOLVOETS K, VAN GRIENSVEN A, GEVAERT V, SEUNTJENS P and VANROLLEGHEM, PA (2008) Modifications to the SWAT code for modeling direct pesticide losses. *Environ. Modeling and Software* **23**: 72-81.

KEMPSTER PL, HATTINGH WHJ and VAN VLIET HR (1980) Summarised water quality criteria. Department of Environmental Affairs Technical Report TR 108, Pretoria, South Africa.

KREUGER J (1998) Pesticides in stream water within an agricultural catchment in southern Sweden, 1990-1996. *Sci. Total Environ*. **216**: 227-251.

LEVITAN L, MERWIN I and KOVACH J (1995) Assessing the relative environmental impacts of agricultural pesticides: the quest for a holistic method. *Agric., Ecosyst. Environ.* **55**: 153-168.

LINE DE, OSMOND DL, COFFEY SW, MCLAUGHLIN RA, JENNINGS GD, GALE JA and JS (1997) Nonpoint sources. *Wat. Environ. Res.* **69**: 844-860.

LOAGUE KL, CORWIN DL and ELLSWORTH TL (1998) The challenge of predicting nonpoint source pesticide pollution. *Environ. Sci. Technol.* **32**(15): 130.133/

LONDON L (1995) Biological monitoring of workers exposed to organophosphate pesticides: Guidelines for field application. *Occupational Health Southern Africa* **1**(4): 13-17.

LONDON L and MYERS J (1995a) General patters of agrichemical usage in the southern region of South Africa. *South African J. Sci*. **91**: 509-514.

LONDON L and MYERS J (1995b) Agrichemical usage patterns and workplace exposure in the major farming sectors in the southern region of South Africa. *South African J. Sci.* **91**: 515-522.

LONDON L, MYERS J, NELL V, TAYLOR T and THOMPSON ML (1997) An investigation into the neurologic and neurobehavioural effects of long-term agrichemical use among deciduous fruit farm workers in the Western Cape, South Africa. *Environ. Res.* **73**: 132-145.

LONDON L (1998) Occupational epidemiology in agriculture: A case study in the Southern African context. *Int. J. Environ. and Occupational Health* **4**: 245-256.

LONDON L, DALVIE MA, CAIRNCROSS E and SOLOMONS A (2000) The quality of surface and groundwater in the rural Western Cape with regard to pesticides. Water Research Commission Report No. 795/1/00, WRC, Pretoria.

LONDON L and BAILIE R (2001) Challenges for improving surveillance for pesticide poisoning: policy implications for developing countries. *Int. J. of Epidemiology* **30**: 564-570.

LONDON L, DALVIE MA, CAIRNCROSS E, SOLOMON A and ADAMS H (2004) Cost effective methods for monitoring pesticide pollution in water systems. WRC Report No. 1120/1/04, WRC Pretoria.

LONDON L, DALVIE MA, NOWICKI A and CAIRNCROSS E. (2005) Approaches for regulating water in South Africa for the presence of pesticides. *Water SA* **31**(1): 53-59

MCGREGOR F (1999) The mobility of endosulfan and chlorpyrifos in the soil of the Hex River Valley. Unpublished MSc thesis, Department of Geological Sciences, University of Cape Town.

MAHARAJ S (2005) Modeling the behaviour and fate of priority pesticides in South Africa. Unpublished MSc dissertation. Department of Earth Sciences. University of Western Cape, South Africa.

MCKINLAY R, PLANT JA, BELL JNB and VOULVOULIS N (2008) Endocrine disrupting pesticides: Implications for risk assessment. *Environ. Intern.* **34**(2): 168-183.

MEINHARDT HR, CLOETE MM, MYBURGH RM and BOUWMAN H (1998) Aspects of herbicide pollution in the Republic of South Africa. *International Conference on Pesticide Use in Developing Countries: Impact on Health and Environment.* Universidad Nacional, San Jose, Costa Rica.

MEINHARDT HR (2003) Evaluation of predictive models for pesticide behaviour in South-African soil. WRC Report No. 999/1/03. WRC, Pretoria.

MEINHARDT HR (2008) Evaluation of predictive models for pesticide behaviour in South African soils. Unpublished PhD Thesis, University of the North-West, Potchefstroom.

MEINTJIES E, VAN DER MERWE L. and DU PREEZ JL (2000) Qualitative and quantitative evaluation of estrogen-mimicking substances in the water environment. WRC Report No 742/1/00. WRC, Pretoria.

MIAN LS and MULLA MS (1992) Effects of pyrethroid insecticides on nontarget invertebrates in aquatic ecosystems. *J. Agric. Ent.* **9**: 73-98.

MOORE MT, SCHULZ R, COOPER CM, SMITH JR S and RODGERS JH (2002) Mitigation of chlorpyrifos runoff using constructed wetlands. *Chemosphere* **46**: 827-835.

NEL A, KRAUSE M, KHELAWANLALL N and VAN ZYL K (2000) A guide for the control of household and industrial pests in stored commodities, storage premises, timer, water, human and animal dwellings. National Department of Agriculture, Directorate Communications.

PATTY L, REAL B and GRILL JJ (1997) The use of grassed buffer strips to remove pesticides, nitrate and soluble phosphorus compounds from runoff water. *Pestic. Sci.* **49**: 243-251

PAPO T and MATHEBULA S (2003) Investigations of the occurrence of the Diazonin in the surface water of an urban river: Kaalspruit during the low flow periods with GC-MS. *Joint European – Southern African International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications*. 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

NAIDOO V and BUCKLEY CA (2003) Survey of pesticide wastes in South Africa and review of treatment options. Water Research Commission Report No. 1128/1/03, Pretoria, South Africa.

NAUDÉ Y, DE BEER WHJ, JOOSTE S, VAN DER MERWE L and VAN RENSBURG SJ (1998). Comparison of supercritical fluid extraction and Soxhlet extraction for the determination of DDT, DDD and DDE in sediment. *Water SA* **24**(3): 205-214.

PICK FE, DE BEER PR and VAN DYK LP (1981) Organochlorine insecticide residues in birds and fish from the Transvaal, South Africa. *Chemosphere* **10**(11-12): 1243-1251.

REUS J, LEENDERTSE P, BOCKSTALLER C, FOMSGAARD I, GUTSCHE V, LEWIS K, NILSSON C, PUSSEMIER L, TREVISAN M, VAN DER WERF H, ALFARROBA F, BLÜMEL S, ISART J, MCGRATH D and SEPPÄLÄ T (2002) Comparison and evaluation of eight pesticide environmental risk indicators developed in Europe and recommendations for future use. *Agric., Ecosyst. Environ*. **90**: 177-187.

RICHTER ED, ROSENVALD Z, KASPI L, LEVY S and GRUENER N (1986) Sequential cholinesterase tests and symptions for monitoring organophosphate adsorption in field workers and in persons exposed to pesticide spray drift. *Toxicol. Lett.* **33**: 25-35.

RELYEA R and HOVERMAN J (2006) Assessing the ecology in ecotoxicology: a review and synthesis in freshwater systems. *Ecol. Lett*. **9**: 1157-1171.

RODGERS JR JH and DUNN A (1992) Developing design guidelines for constructed wetlands to remove pesticides from agricultural runoff. *Ecol. Eng*. **1**: 85-95.

ROTHER HA and LONDON L (1998) Pesticide health and safety policy mechanisms in South Africa: The state of the debate. Occupational and Environmental Health Research Unit Working Paper 1. April 1998. Department of Community Health, University of Cape Town.

ROTHER HA and LONDON L (2003) Pesticide Policy in South Africa: Are non-target environments protected from pesticide toxic effects by legislated protective mechanisms? *Joint European – Southern African International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications.* 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

ROUX DJ, BADENHORST JE, DU PREEZ HH and STEYN GJ (1994) Note on the occurrence of selected trace metals and organic compounds in water, sediment and biota of the Crocodile River, Eastern Transvaal, South Africa. *Water SA* **20**(4): 333-340.

SAVAGE EP, KEEFE TJ, MOUNCE LM, LEWIS JA and BURCAR PJ (1988) Chronic neurological sequence of organophosphate pesticide poisoning. *Arch. Environ. Health* **43**: 38-45.

SCHULZ R, HAUSCHILD M, EBELING M, NANKO-DREES J, WOGRAM J and LIESS M (1998) A qualitative field method for monitoring pesticides in the edge-of-field runoff. *Chemosphere* **36**: 3071-3082.

SCHULZ R (2001a) Rainfall-induced sediment and pesticide input from orchards into the Lourens River, Western Cape, South Africa: importance of a single event. *Wat. Res.* **35**: 1869-1876.

SCHULZ R (2001b) Comparison of spray drift- and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa. *Chemosphere* **45**: 543-551.

SCHULZ R and LIESS M (2001) Toxicity of aqueous-phase and suspended particle-associated fenvalerate: chronic effects following pulse-dosed exposure of *Limnephilus lunatus* (Trichoptera). *Environ. Toxicol. Chem.* **20**: 185-190.

SCHULZ R and PEALL SKC (2001) Effectiveness of a constructed wetland for retention of nonpoint source pesticide pollution in the Lourens River catchment, South Africa. *Environ. Sci. Technol*. **35**(2): 422-426.

SCHULZ R, PEALL SKC, DABROWSKI, JM and REINECKE, AJ (2001a) Spray Deposition of two insecticides into surface waters in a South African orchard Area. *J. Environ. Qual*. **30**(3): 814-822.

SCHULZ R, PEALL SKC, DABROWSKI, JM and REINECKE, AJ (2001b) Current-use insecticides, phosphates and suspended solids in the Lourens River, Western Cape, during the first rainfall event of the wet season. *Water SA* 27(1):65-70.

SCHULZ R, PEALL SKC, HUGO C and KRAUSE V (2001c) Concentration, load and toxicity of spray drift-borne azinphos-methyl at the inlet and outlet of a constructed wetland. *Ecol. Eng*. 18:239-245.

SCHULZ R, THIERE G and DABROWSKI JM (2002) A combined mesocosm and field approach to evaluate the aquatic toxicity of azinphos-methyl to stream communities. *Environ. Toxicol. Chem.* **21**(10): 2172-2178.

SCHULZ R (2003) Using a freshwater amphipod in situ bioassay as a sensitive tool to detect pesticide effects in the field. *Environ. Toxicol. Chem*. **22**(5): 1172-1176.

SCHULZ R, HAHN C, BENNET ER, DABROWSKI, JM, THIERE G and PEALL SKC (2003) Fate and effects of azinphos-methyl in a flow-through wetland in South Africa. *Environ. Sci. Technol.* **37**: 2139-2144.

SCHULZ R (2004) Field studies on exposure effects and risk mitigation of aquatic nonpoint source insecticide pollution: a review. *J. of Environ. Qual*. **33**(2): 419-448.

SEREDA BL and MEINHARDT HR (2003) Insecticides contamination of the water environment in malaria endemic areas of KwaZulu-Natal (SA): The risk of insecticide resistance development in malaria vectors. WRC Report No. 1119/1/03. WRC, Pretoria.

SIBBALD RR, CONNELL AD, BUTHLER AL, NAIDOO P. and DUNN JD (1986) A limited collaborative investigation of the occurrence of dieldrin in selected biota in the Durban area. *South African J. Sci.* **82**(6): 319-321.

SQUILLACE PJ, CALDWELL JP, SCHULMEYER PM and HARVEY CA (1996) Movement of Agricultural Chemicals Between Surface Water and Groundwater, Lower Cedar River Basin, Iowa. United States Government Printing Office, Washington.

STURM A, RADAU TS, HAHN T and SCHULZ R (2007) Inhibition of rainbow trout acetylcholinesterase by aqueous and suspended particle associated organophosporous insecticides. *Chemosphere* **68**: 605-612.

TANABE S, IWATA H and TATSUKAWAR R (1994) Global contamination by persistent organochlorines and their ecotoxicological impacts on marine mammals. *Sci. Total Environ.* **154**: 163-177.

TESFAMICHAEL AA and KALUARACHCHI JJ (2006) A methodology to assess the risk of an existing pesticide and potential future pesticides for regulatory decision-making. *Environ. Sci. and Pol.* **9**: 275-290.

THIERE G and SCHULZ R (2004) Runoff-related agricultural impact in relation to macroinvertebrate communities of the Lourens River, South Africa. *Water Res.* **38**(13): 3092-3102.

UCAR T and HALL FR (2001) Windbreaks as a pesticide drift mitigation strategy: A review. *Pest Manage. Sci*. **57**(8): 663-675.

USEPA (U.S. ENVIRONMENTAL PROTECTION AGENCY) (1999) Background document for the Scientific Advisory Panel on orchard airblast: Downwind direction tolerance bounds for orchards. Technical Report. U.S. Environmental Protection Agency, Washington, D.C.

VAN DEN BRINK PJ, HATTINK J, BRANSEN F, VAN DONK E and BROCK TCM (2000) Impacts of the fungicide carbendazim in freshwater microcosms. II. Zooplankton, primary producers and final conclusions. *Aquatic Toxicol.* **48**(2-3): 251-264.

VAN DEN BRINK PJ, TER HORST MMS, BELTMAN WHJ, VLAMING J and VAN DEN BOSCH H (2005) PRIMET version 1.0, manual and technical description. Alterra PRIMET Rapport 3, Alterra, Green World Research, Wageningen.

VAN DER WERF HMG (1996) Assessing the impacts of pesticides on the environment. *Agric., Ecosyst. Environ*. **60**: 80-96.

VAN DYK LP (1978) Plaagdoders in die rivierwater van die Nasionale Krugerwildtuin. *Koedoe* **21**:77-80.

VAN DYK LP. and GREEFF CG (1977). Endosulfan pollution of rivers and streams in the Loskop dam cotton-growing area. *Agrochemophysica* **9**(3): 71-76.

VAN DYK LP, WIESE IH and MULLEN JEC (1982) Management and determination of pesticide residues in South Africa. *Residue. Rev.* **82**: 38-124.

VAN NES EH and VAN DEN BRINK PJ (2003) PERPEST version 1.0, manual and technical description. Alterra-rapport 787, Alterra, Green World Research, Wageningen.

VAN VUREN JHJ, DU PREEZ HH, VAN HEERDEN E and VAN RENSBERG E (2003) The relationship between atrazine bioaccumulation and physiological responses in *Tilapia sparmanii*. *Joint European – Southern African International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications*. 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

VERMEULEN JB, SWEET S, KRAUSE M, HOLLINGS N and NEL (1990) A guide to the Use of Pesticides and Fungicides in the Republic of South Africa. 34th Revised edition. Plant Protection Research Institute, Department of Agricultural Development, Pretoria.

VERMEULEN JB, GROBELER H and VAN ZYL K (1998) A guide to the use of herbicides, 15th edition. Plant Protection Research Institute, Published by the National Department of Agriculture of South Africa.

WADE P (2003) Modelling of the environmental fate and effects of organic pesticides – the state of the art. Joint *European – Southern African International Conference on Pesticides in non-target agricultural environments – Environmental and economic implications*. 21-23 January 2003, University of Cape Town, Cape Town, South Africa.

WALKLATE PJ (1992) A simulation study of pesticide drift from an air-assisted orchard sprayer. *J. Agric. Eng. Res*. **51**: 263-283.

WARE GW (1989) The pesticide book. 3rd Edition. Thomson Publications, USA.

WARNE MStJ, Palmer CG and Muller WJ (2005) Development of pilot guidelines for selected organic toxicants: 1. Protocol for aquatic ecosystem guideline development. Department of Water Affairs and Forestry, Pretoria, South Africa.

WAUCHOPE RD (1996) Pesticides in Runoff: Measurement, modelling and mitigation. *J. Environ. Sci. Health. Part B*. **31**: 337-344.

WEAVER JMC (1993) A preliminary survey of pesticide levels in groundwater from a selected area of intensive agriculture in Western Cape. Water Research Commission Report No. 268/1/93, Pretoria, South Africa.

WILCOX BP and WOOD MK (1989) Factors influencing interrill erosion from semiarid slopes in New Mexico (USA). *J. Range Manage.* **42**(1): 66-70.

WILLIAMS RJ, BROOKE D, MATTHIESEN P, MILLS M, TURNBULL A and HARRISON RM (1995) Pesticide transport to surface waters within an agricultural catchment. *J. Instit. Wat. Environ. Manage.* **9**: 72-81.

YOUSEFI VO (1999) Agrochemicals in South Africa. African Newsletter Occup*. Health Safety.* **1-99**: 537.

ZULLEI-SEIBERT N and SKARK C (1993) Verhalten von Pflanzenschutzmitteln auf dem Transportpfad "Oberflächenwasser-Uferfiltrat-Grundwasser". Berichte aus der Dortmunder Energie und Wasserversorgung 376.

# 2. PESTICIDE RISK INDICATOR DEVELOPMENT

## 2.1 Background

As described in Section 1, the negative environmental impacts associated with the use of pesticides, has necessitated the need to manage pesticides more effectively. Initially this took place primarily through monitoring. As evidence of the detrimental effects of pesticides in aquatic environments accumulates, so the need to predict areas of risk has become more and more urgent (Black *et al.* 2000). While extensive sampling in river catchments can identify 'hotspots' and areas of concern, the ability to predict problem areas is very valuable in implementing and prioritising mitigation strategies and in cutting costs associated with the analysis of samples. These high costs (analytical and manpower) associated with monitoring have gradually given rise to the development of modelling techniques aimed at predicting pesticide contamination, thereby helping to maximise sampling efficiency both in terms of location of sampling points and identification of pesticides that should be monitored or managed more carefully (thereby reducing analytical costs). Studies have linked agricultural land use to pesticide contamination in surface waters (Munn and Gruber 1997), and more recently a number of studies have attempted to predict pesticide impacts through use of modelling and risk assessment techniques. The risk a pesticide poses to the environment includes an estimation of exposure, which is usually based on predicted environmental concentrations (PEC). However, it has also been pointed out that modelling approaches in exposure assessment should also be validated through measurement of real contamination in the field (Solomon *et al.* 1996; Wauchope 1996). Combining an assessment of exposure with an assessment of effect (based on toxicity data) and estimation of risk can be performed. The risk a pesticide poses to the aquatic environment is dependent on a number of factors, including its toxicity and environmental fate properties and the influence of site-specific geographic and climatic conditions.

Because of the combination of land use, meteorological and physicochemical properties of pesticides, the prediction of non-point source pesticide pollution can require a great number of input variables, and complex models such as GLEAMS, PRZM and AGNPS have been developed for this purpose (FOCUS 1997). These models have been validated in the field with varying degrees of success (Donigian Jr. and Huber 1991; Solomon *et al.* 1996; Grunwald and Norton 2000), but have disadvantages in that they are complicated and normally require a large amount of input variables that may not be generally available (Adriaanse *et al.* 1997). Minimal data requirements and ease of application are the main advantages of simpler simulation methods such as risk indicators.

## 2.2 Relevance to South Africa

Based on the number of studies documenting the input and effects of pesticides in South African water resources, it is clear that there is a need to identify priority catchments at risk of pesticide impacts in a cost-effective manner. The Department of Water Affairs and Forestry (DWA) has recently designed and implemented the National Toxicity Monitoring Programme (NTMP), which monitors toxicity and a number of priority toxic chemicals, the majority of which are pesticides. While monitoring and sampling can contribute to the assessment of the impact of pesticides in aquatic ecosystems, this is a very expensive exercise. Furthermore, the NTMP currently only monitors two current use pesticides (atrazine and endosulfan), while the remainder are banned persistent organic pollutants (DWAF, 2005). Given the results of studies described above, the current monitoring design will not assess or identify risks of other, frequently used pesticides.

The National Water Act (Act 36 of 1998) requires rivers to be classified according to a specific class and establish resource quality objectives (RQOs), which are numeric or descriptive (narrative) goals for resource quality within which a water resource must be managed. RQOs are therefore designed to give effect to the desired class of a specific river. Given the highly toxic nature of pesticides and their risk towards ecological and human health, it is important that methodologies are developed to identify pesticides of concern as well as important areas of concern within agricultural catchments. Finally, the pesticide management policy (Government Gazette No. 28711), published by the Department of Agriculture (RSA, 2006), recommends the revision of the act that governs the registration of pesticides in South Africa (Act No. 36 of 1947) and recognises the need to develop tools capable of identifying and managing risks of pesticides in aquatic environments.

A validated risk indicator methodology can therefore potentially contribute towards the implementation of these initiatives through the identification of high risk pesticides (i.e. pesticides that frequently enter water resources) and catchment hotspots (i.e. areas within catchments where contamination is relatively high). Risk indicator methodologies may have direct implications for human health as similar methodologies could be used to assess risks to human health, particular in rural areas, where communities make direct use of untreated river and groundwater. Most risk indicators have been developed in developed countries, where, due to favourable socio-economic conditions, the emphasis is primarily on protecting the aquatic ecosystem. Developing countries differ fundamentally in this regard, in that many poor, rural, communities make use of untreated surface and groundwater and may therefore be vulnerable to pesticide risks. Risk indicators may therefore be highly beneficial in identifying rural communities at risk of exposure.

Application of risk indicators can include the following (Levitan 1997):

- Obtain baseline information about pesticide use and risks, and then track risk trends over time.
- Identify potential trouble spots and areas where action is needed to reduce risks.
- Monitor the impacts of agriculture and pesticide policies.
- Communicate the aims and results of risk reduction policies and programmes.
- Compare pesticide risks within an agricultural area.
- Obtain information about aggregated risks associated with use of multiple pesticides.
- Compare pesticide use in different situations (e.g. agricultural production systems using different levels of inputs).
- Provide information for other types of indicators, e.g. decision tools for farmers, green labels.

In designing and developing a risk indicator, the following should always be considered (OECD 2002):

- Indicators are useful as signposts and analytic tools, but should not be the sole basis for decision-making.
- Indicators are relative, qualitative measures of risk and not exact quantitative measures of risk. Whether or not it is important for an indicator to correspond closely to real risk depends upon the purpose of the indicator and how it is used.
- When designing an indicator, it is very important to be clear about the indicator's purpose. The purpose will help to determine how sophisticated a methodology is needed and how much and what types of data are needed.
- When interpreting and communicating indicator results, it is important to be clear about the indicator's purpose. Different purposes may require different ways of presenting results.

## 2.3 Data Requirements

As mentioned previously, one of the main advantages with respect to risk indicators is their utilisation of simple, readily available data. Risk indicators typically use simple modelling methods to estimate a relative risk of exposure and effects. In doing so, the intention is not to predict exact environmental concentrations and effects derived thereof, but rather to provide a relative indication of exposure risk (i.e. pesticide A is more likely to enter surface waters than pesticide B). Application information (i.e. the total amount of pesticide applied) and physicochemical data is generally sufficient to provide such a relative indication. This information can be incorporated into sub-models for spray drift, runoff and drainage to calculate risk indices that provide an indication of the PEC. This PEC is often divided by a derived effect concentration (e.g. a toxicity endpoint) to provide a ratio of risk. By applying this methodology to a number of pesticides used within an agricultural area, one can estimate the relative risk posed to the aquatic environment by a number of pesticides used within an agricultural area (i.e. pesticide B is more likely to pose a risk to the aquatic ecosystem than pesticide A). Once high risk pesticides have been identified, incorporating geographical and climatic information can then identify high risk areas or hotspots (i.e. catchments or sub-catchments where contamination would be expected to be higher or lower than others) where management or mitigation interventions may be required to minimise the impacts of the pesticide in question.

### *2.3.1 Exposure Data*

The ultimate objective of the exposure assessment is to determine a PEC. This assessment therefore estimates the quantity (or Predicted Environmental Load – PEL) of a certain pesticide that would be expected to enter an adjacent water resource and its resulting concentration (PEC) based on the hydrology of the system in question. The PEL is calculated by taking the main pathways for contamination of surface waters into account. For surface waters, these are runoff and spray drift. PELs for each exposure pathway are aggregated to provide an overall PEL value for a particular crop and its associated pesticides. A number of models have been developed, largely in the USA and Europe, in order to predict PECs. Some of these models are very complex and require a large amount of data input, much of which is not readily available (FOCUS 1997). The Organisation for Economic Co-operation and Development (OECD) as part of a risk indicator development for pesticide use in Europe developed a relatively simple runoff tool (OECD 1998). It was designed as a simple tool for prediction of pesticide loss in runoff and has been used in a risk indicator methodology used in Europe (HAIR 2004). The formula has a theoretical basis, but also comprises empirical and physical components; a hydrological model (based on a modified curve number method developed by Lutz (1984) and Maniak (1992)), catchment related factors which influence the extent of runoff (i.e. pesticide application, slope and the presence of buffer strips), a first-order kinetic for the fate of a pesticide and a term referring to the proportion of pesticide occurring in the water phase of runoff. Apart from a number European studies (Berenzen *et al.* 2005; Reus *et al.* 2002; Verro *et al.* 2002), this algorithm has been successfully applied and validated in a South African, (Dabrowski *et al.* 2002; Dabrowski and Schulz 2003) as well as in an Australia catchment (Kookana *et al.* 2005).

Similarly, for spray drift, a number of models exist ranging from highly complex to relatively simple. Spray drift tables developed by Ganzelmeier *et al.* (1995) and more recently updated by Rautmann *et al.* (2001) were also developed in Europe for the purposes of aquatic ecosystem risk assessments. These studies measured drift in a number of trials and developed standardised drift values for different crop types. These tables simply provide an indication of the percentage of an applied pesticide that would move from an area of application to non-target water bodies, depending on the distance of the water body from the point of application. These drift values have been used in South African studies to predict

spray deposition in tributaries adjacent to fruit orchards (Dabrowski *et al.* 2005; Dabrowski and Schulz 2003; Schulz *et al.* 2001). In all of these studies predicted deposition rates compared very well to actual measured deposition rates.

Typical data requirements can be broadly divided into three main categories; pesticide use data, physicochemical data and geographical data (Table 7). Pesticide use data provides an indication of the quantity of pesticide applied to a particular crop through its application rate and frequency. Physiochemical characteristics provide an indication of the environmental behaviour of the pesticide in the environment in terms of its affinity to bind to soil and its persistence in the environment. Geographical characteristics provide an indication of how the surrounding environment can influence the movement of pesticides from cropped areas into adjacent water bodies. Exposure models generally integrate this information and estimate the quantity (i.e. load) of pesticides leaving an agricultural area.

**Table 7:** Example of the type of data required to perform an exposure assessment for pesticides.

| | **Data Type** | **Description** |
|---|---|---|
| **Pesticide Use Data** | Application rate | The amount of active ingredient applied to a crop |
| | Frequency of application | The number of application and interval in between applications |
| | Pesticide type | |
| **Physicochemical Data** | Water Solubility | Highly water soluble pesticides are more mobile than insoluble ones |
| | Half-life (soil) | Pesticides with long-half lives are more persistent and therefore more likely to contaminate water bodies than pesticides with short half-lives. |
| | Koc | Tendency of a pesticide to bind to organic carbon. |
| **Geographical Data** | Rainfall | Frequency and intensity of rainfall influence the potential for pesticide to move as a result of runoff. |
| | Topography | Slope or gradient is an important factor in influencing the amount of runoff leaving a field. |
| | Wind | Wind direction and speed in relation to the position of adjacent water bodies are important with respect to contamination via spray drift. |
| | Soil | Soil texture (i.e. clay, loam and sand composition) and organic carbon content. |

### *2.3.2 Effect Data*

The effect assessment for the aquatic ecosystem is generally assessed through analysis of aquatic toxicity data. In general, the effect assessment is simply represented by an eco-toxicological endpoint, such as the 50% lethal concentration (i.e. LC50) of a reference species. For aquatic risk indicators these endpoints are normally algae, daphnia and a fish species (often rainbow trout). While these endpoints are simple and relatively easy to obtain, they are disadvantageous in that the risk of a pesticide is gauged by the sensitivity of a single organism at a single trophic level (i.e. risk is expressed for fish, macroinvertebrates and algae separately). In reality, aquatic ecosystems consist of multiple species, each with

varying degrees of sensitivity towards pollutants. More recently, species sensitivity distributions (SSDs) have been used to provide a more realistic, integrated effect assessment. The SSD approach allows environmental criteria to be assessed based on the effects of pollutants on biodiversity and multi-species communities. The SSD concept is frequently used in ecological risk assessments and has been used to derive water quality guidelines for pesticides included in the NTMP. The aim of SSDs is to determine the concentration of a toxicant that is protective of most species (usually 95%) in the environment. SSDs are constructed by fitting a cumulative distribution function to a plot of species toxicity data against rank-assigned percentiles (Wheeler *et al.* 2002). From the cumulative distribution, the PC95 (protective concentration 95%, i.e. concentration that is protective of 95% of species) value is extrapolated. The cumulative frequency distribution can be composed of species representing a particular trophic level or it can integrate species from all trophic levels so as to provide an integrated effect assessment.

The choice of data for input into deriving the SSD is important to consider. Aquatic toxicity data have historically focussed on a number of different endpoints, ranging from mortality (i.e. LC50 data) to reduced reproduction and behavioural changes on individual species (i.e. EC50), to microcosm experiments where entire communities are exposed to contaminants generating NOEC data. LC50 and EC50 data are far more common and given the purpose of the risk indicator (a relative comparison of pesticides in terms of their mobility and toxicity), it does not make too much difference which endpoint is used – as long as it is the same data (i.e. LC50 only) for all pesticides that are being compared.

### 2.4 Prediction of Risk

This step integrates the PEC with ecotoxicological data so as to derive a toxicity-exposure-ratio (TER). The TER essentially integrates exposure and effect data and expresses risk in numerical terms. If a TER is calculated for a number of pesticides used within a particular agricultural area it is possible to make a relative assessment of which of the pesticides poses the greatest risk to the aquatic environment.

### 2.5 Proposed Pesticide Risk Indicator Framework

This section describes the overall framework that will be adopted for the purposes of this study. The aim of the proposed pesticide risk indicator is to provide an indication of the relative exposure and subsequent risk that a number of pesticides used in an agricultural area (from field to catchment scale) may pose to the aquatic environment. Given that for any particular agricultural area the quantity and quality of information available may vary considerably, the risk indicator should be able to accommodate differences in data availability and should be applicable to different spatial scales. Furthermore, it should provide a best possible assessment with the information available. The extent of information available will determine the quality of and confidence in resulting predictions.

The proposed framework will calculate three indices. Each index results in an increase in complexity and provides more detailed and useful information. Within each index, the availability and quality of data determines the level of accuracy. The framework is designed such that, depending on data availability specific information can be obtained (at various levels of accuracy or confidence, here referred to as low, medium or high). Table 8 provides a framework of data requirements, outputs and the level of accuracy that can be expected. The following should be noted:

- The indicator does not predict exact risk – it is meant to either a) compare a number of pesticides and describe their relative risk within an agricultural area; or b) compare

a single pesticide across different geographical areas to describe the relative risk the pesticide poses within each of these geographical areas (i.e. identification of hotspots).
- The indicator is specific to surface water and considers spray drift and runoff as mechanisms of exposure.
- Final risk will be estimated for the water column only. This is because there is a lack of sediment toxicity data to estimate the effect risk of a pesticide associated with sediment.

The main purpose of the risk indicator designed in this project is to provide a qualitative indication of:

- the relative exposure potential of a number of different pesticides applied in a catchment and
- the relative risk posed by these different pesticides to the aquatic ecosystem.

In producing this output, the indicator should be able to be used to:

- identify high priority pesticides within a catchment based on their exposure and risk potential and
- identify hotspots where exposure and risk may be relatively high and
- identify the main route of entry of pesticides into surface waters (i.e. runoff or spray drift)

### *2.5.1 Description of Framework*

The framework comprises of three levels of indicator, each level (1 to 3) increasing in complexity and usefulness of information or outputs derived (Table 8). These levels include:

1. ***Pesticide Use Indicator (PUI):*** Provides an indication of which pesticides are likely to occur in a water resource based only on the **quantity** of pesticide used on/in a field or catchment (no exposure pathway is considered).

2. ***Pesticide Exposure Indicator (PeXI):*** Provides an indication of which pesticides are likely to occur in a water resource based on application data as well as physicochemical data of applied pesticides. This indicator relies on data collected for the PUI.

3. ***Pesticide Risk Indicator (PeRI):*** Provides an indication of the risk that previously identified pesticides pose to the aquatic environment based on the integration of exposure potential with toxicity data. This indicator relies on data collected for the PUI and PEXI.

Within each of the three indicators there are three levels of accuracy (or confidence) that can be derived; low, medium and high. The degree of accuracy is dependent on the manner in which pesticide use data and crop distribution data are derived. Estimated pesticide use and crop distribution data results in low confidence whilst actual data (i.e. data that includes accurate spray records) results in a higher level of confidence. Progressing to each level results in an integration of data that has been used in the previous levels (i.e. Level 3, results in an integration of data derived in Levels 1 and 2). The degree of confidence in outputs in levels 2 and 3 is dependent on the accuracy of data used in Level 1 (e.g. using actual pesticide data and estimated crop distribution data in Level 1, will result in a medium level of confidence in any of the subsequent levels for which outputs are derived).

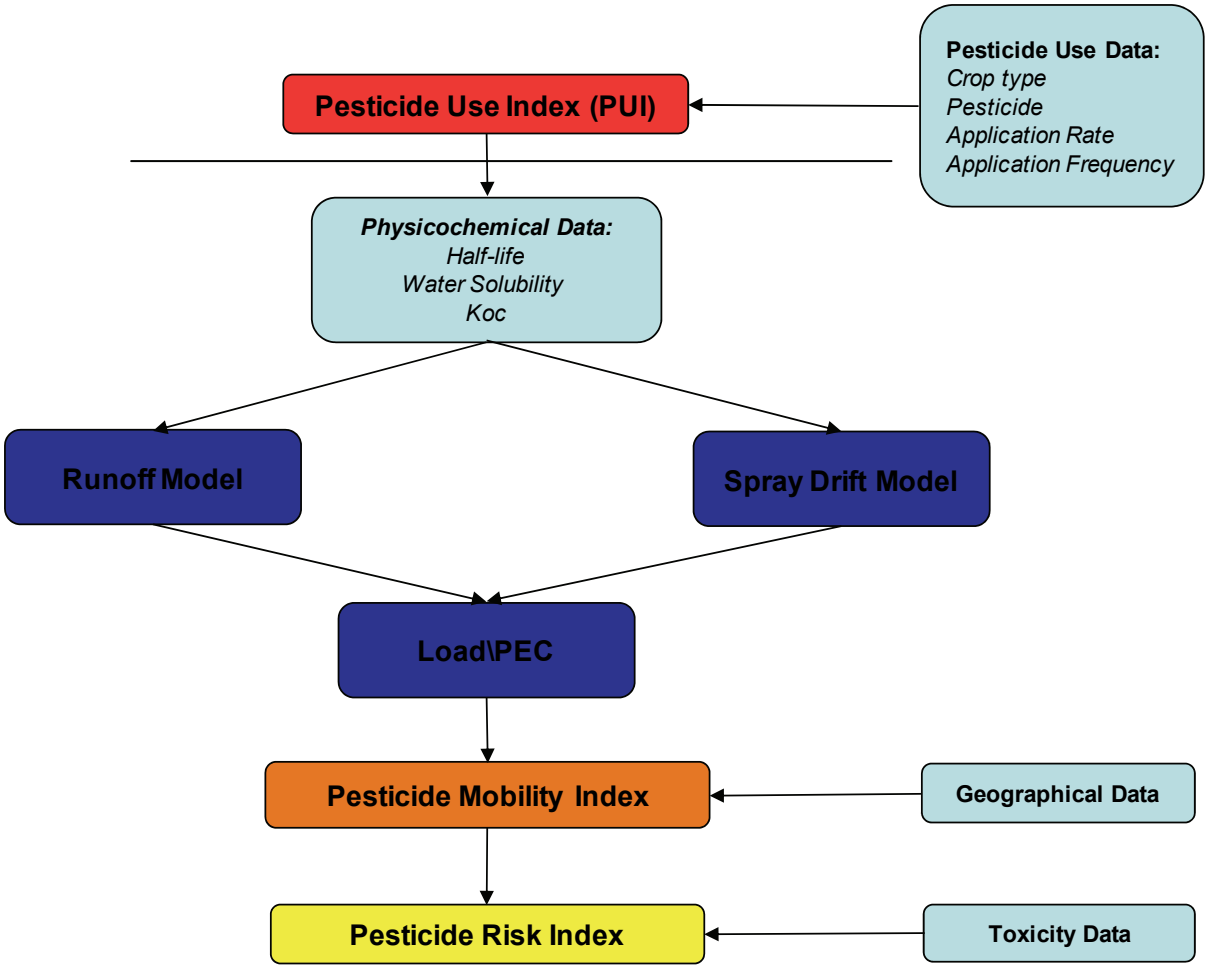



**Figure 1:** Schematic diagram of the proposed risk indicator framework. Light blue boxes indicate data input.

## 2.6 Pesticide Use Index (PUI)

This index simply uses pesticide application data as an indicator of the amount of pesticide that might be expected to enter non-target surface water environments. The assumption is that a pesticide that is applied in greater quantities is more likely to enter water resources in comparison to a pesticide that is used in smaller quantities. This index is dependent on the minimum amount of data input and is therefore the simplest and least accurate in terms of estimating pesticide exposure in surface waters. As it does not incorporate toxicity of pesticides, it does not provide an indication of effect risk. Rather it is a very rough assessment of exposure potential (i.e. which of a number of pesticides used in a catchment are more likely to enter water resources). The information collected for deriving this index is vital for determining increasingly complex (and realistic) indices in the framework. In general the PUI requires a low level of data complexity, and, using it as a standalone indicator, results in a low level of accuracy (Table 8). Of the two levels, PUI_1 is the least accurate while developing the PUI_3 is the most desirable. Data generated in this step (i.e. PEU or Predicted Environmental Use) is required to execute the subsequent, more detailed indices.

### *2.6.1 PUI_1*

The minimal information required is the estimated crop area and recommended pesticide application rate. This information could be obtained through interviews with farmers,

STATSSA census data or other applications such as Google Earth. Once crop information is available, pesticide application data can be estimated via sales data or recommended label application rates and frequency. It is therefore required to know what pesticides are generally applied to certain crops. This information results in a low level of accuracy and complexity.

### *2.6.2 PUI_2*

Requires a combination of actual crop area and estimated pesticide use, or vice versa (i.e. estimated crop area and actual pesticide use data). Actual data would generally be obtained through interviews with farmers (for application) or highly accurate ground-truthed GIS maps/remote sensing data (for crop area). This is the most likely level of accuracy that will be derived for this indicator.

### *2.6.3 PUI_3*

Requires actual crop area and pesticide application data. This combination is ideal and provides the most accurate indication of pesticide use for a field or catchment. At larger catchment scales that incorporate multiple farms this information may be very difficult to obtain (particularly for pesticide application information). It is likely that this information will only be available at a smaller field scale.

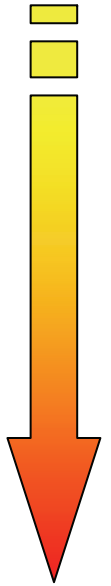
## 2.7 Pesticide Exposure Index (PeXI)

This step integrates the PEU (used to calculate the PUI) with more detailed geographic information (i.e. through use of GIS), physicochemical pesticide properties (e.g. half-life and water solubility) to provide an estimate of the Predicted Environmental Load (PEL). For example any two pesticides that are hypothetically applied in equal quantities, the one with a longer half-life is more likely to be present in surface waters as it takes longer to break down and is therefore more available for transport. The PEL is integrated with hydrological data (e.g. stream discharge) to provide an estimate of the Predicted Environmental Concentration (PEC). The PEC for all pesticides is used to calculate the PeXI. The level of accuracy of this indicator is dependent on the level of accuracy used to derive the PEU (i.e. a low accuracy PEU corresponds to a low accuracy PeXI, etc.). This information can therefore inform managers of pesticides that are most likely to enter water resources and where in the catchment this is likely to take place (i.e. hotspot identification).

## 2.8 Pesticide Risk Index (PeRI)

This step integrates outputs from the calculation of the PeXI (i.e. PECs) together with ecotoxicological data so as to derive a toxicity-exposure-ratio (TER). Ecotoxicological endpoints will be derived from species sensitivity distributions (SSDs). The TER values are then used to calculate the PeRI.

**Table 8:** Data requirements for each of the three indices (Pesticide Use Index [PUI], Pesticide Exposure Index [PeXI], Pesticide Risk Index [PeRI] included in the Pesticide Risk Indicator framework.

| Level | Output | Accuracy | Data Requirements | Source | Complexity |
|---|---|---|---|---|---|
| **1** | PUI_1 | Low | **PEU_1**: Estimated pesticide use and crop area. | Estimated: Sales data and recommended label application rates; Agricultural census data and GIS<br>Actual: Farm surveys of pesticide use and ground-truthed crop specific GIS data |  |
| | PUI_2 | Medium | **PEU_2**: Actual pesticide use and estimated crop area or vice versa | | |
| | PUI_3 | High | **PEU_3**: Actual pesticide use and crop area | | |
| **2** | PeXI_1 | Low | **PEL:** Physicochemical properties (KOC, half-life) and geographical data (slope, soil type, river network, crop coverage)<br>**PEC:** Hydrological data (discharge or average length, breadth and depth of water body) | Internet databases<br>GIS<br>Field measurements | |
| | PeXI_2 | Medium | | | |
| | PeXI_3 | High | | | |
| **3** | PeRI_1 | Low | **TER:** Toxicity data | Internet databases | |
| | PeRI_2 | Medium | | | |
| | PeRI_3 | High | | | |

**PEU:** Predicted Environmental Use (estimated total quantity of pesticide applied to a crop
**PEL:** Predicted Environmental Load (estimated load of pesticide moving off target as predicted by runoff and spray drift models)
**PEC:** Predicted Environmental Concentration (predicted concentration derived from a load of pesticide entering a water body with hydrological
**TER:** Toxicity to exposure ratio (the ratio of the PEC to the toxicity value for a specific pesticide).

## 2.9 References


ADRIAANSE P, ALLEN R, GOUY V, HOSANG J, JARVIS T, KLEIN M, LAYTON R, LINDERS J, SCHÄFER L, SMEETS L and YON D (1997) *Surface Water Models and EU Registration of Plant Protection Products – Doc. 6476/VI/96*.

BASCIETTO J, HINCKLEY D, PLAFKIN J and SLIMAK M (1990) Ecotoxicity and ecological risk assessment. *Environ. Sci. and Technol.* **24**: 10-15.

DOA (DEPARTMENT OF AGRICULTURE) (2007) A Gudie for the Control of Plant Pests. Pretoria, South Africa

BERENZEN N, LENTZEN-GODDING A, PROBST M, SCHULZ H, SCHULZ R and LIESS M. (2005) A comparison of predicted and measured levels of runoff-related pesticide concentrations in small lowland streams on a landscape level. *Chemosphere* **58**(5):683-691.

BLACK RW, HAGGLAND AL and VOSS FD (2000) Predicting the probability of detecting organochlorine pesticides and polychlorinated biphenyls in storm systems on the basis of land use in the Pacific Northwest, USA.. *Environ. Toxicol. Chem.* **19**(4):1044-1054.

DABROWSKI JM, BOLLEN A, BENNETT ER and SCHULZ R (2005) Pesticide mitigation by emergent aquatic macrophytes: potential to mitigate spray-drift input in agricultural streams. *Agric., Ecosys. Environ*. **111**: 340-348.

DABROWSKI JM, PEALL SKC, VAN NIEKERK A, REINECKE AJ, DAY JA and SCHULZ R (2002) Prediciting runoff-induced pesticide input in agricultural sub-catchment surface waters: linking catchment variables and contamination. *Water Res.* **36**:4975-4984.

DABROWSKI JM and SCHULZ R (2003) Predicted and measured levels of azinphos-methyl in the Lourens River, South Africa: comparison of runoff and spray drift. Environ. Toxico. and Chem. **22**(3):494-500.

DAFF (DEPARTMENT OF AGRICULTURE FISHERIES AND FORESTRY) (2010) List of Registered Products. http://www.nda.agric.za/doaDev/sideMenu/ActNo36_1947/AR/AR%20Lists.htm. Last Accessed: [February, 2010]

DOA (DEPARTMENT OF AGRICULTURE) (2007) A Guide for the Control of Plant Pests. Directorate: Food Safety and Quality Assurance. Department of Agriculture, Pretoria, South Africa

DONIGIAN JR. AS and HUBER WC (1991) Modeling of nonpoint source water quality in urban and non-urban areas. *United States Environmental Protection Agency, Environmental Research Laboratory, Office of Research and Development.* Athens, Georgia. EPA /600/3 -91/039.

DWAF (DEPARTMENT OF WATR AFFAIRS AND FORESTRY) (2005) *National Toxicity Monitoring Programme (NTMP) for Surface Waters Phase 2: Record of Decision Report. By K Murray, RGM Heath, JL Slabbert, B Haasbroek, C Strydom and PM Matji.* Report No.: N0000REQ0505 ISBN No.: 0-621-36404-5. Resource Quality Services, Department of Water Affairs and Forestry, Pretoria, South Africa.

FOCUS (1997) Surface Water Models and EU Registration of Plant Protection Products. Final report of the work of the Regulatory Modelling Working Group on Surface WaterModels of FOCUS (FOrum for the Co-ordination of pesticide fate models and their USe). European Commission.

GANZELMEIER H, RAUTMANN D, SPANGENBERG R, STRELOKE M, HERRMANN M, WENZELBURGER H-J, and WALTER H-F (1995) Studies of the spray drift of plant protection products. Mitteilungen aus der Biologischen Bundesanstalt für Land –und Forstwirtschaft, Blackwell Scientific, Berlin, Germany.

GRUNWALD S and NORTON LD (2000) Calibration and validation of a non-point source pollution model. *Agric. Wat. Manage*. **45**, 17-39.

HAIR (2004) Report of the workshop on pesticide risk indicators for man and the environment. Noordwijkerhout, The Netherlands.

KOOKANA RS, CORRELL RL and MILLER RB (2005) Pesticide Impact Rating Index – A pesticide risk indicator for water quality. *Water, Air Soil Poll.* **5**: 45-65.

LEVITAN L (1997) An overview of pesticide impact and risk assessment systems. OECD Workshop on Pesticide Risk Indicators. Copenhagen, 21-23 April, 1997. Copenhagen.

MUNN MD and GRUBER SJ (1997) The relationship between land use and organochlorine compounds in streambed sediment and fish in the Central Columbia Plateau, Washington and Idaho, USA. *Environ. Toxicol. Chem.* **16**(9):1877-1887.

OECD (1998) Pesticide Aquatic Risk Indicators Project: Annex 2: Report of Phase 1 of the Aquatic Risk Indicators Project. France: OECD Secretariat.

OECD (2002) Evaluating Progress in Pesticide Risk Reduction: Summary Report of the OECD Project on Pesticide Aquatic Risk Indicators.: Organisation for Economic Co-operation and Development.

RAUTMANN D, STRELOKE M, WINKLER R (2001)\ New basic drift values in the authorisation procedure for plant protection products. In: Workshop on Risk Assessment and Risk Mitigation Measures in the context of the Authorisation of Plant Protection Products (WORMM; Forster, R., Streloke, M. Eds.), 27-29 September, 1999, Heft 383, Biologischen Bundesanstalt für Land- und Fortwirtschaft, Berlin and Braunschweig, Germany

RELYEA R and HOVERMAN J (2006) Assessing ecology in ecotoxicology: a review and synthesis in freshwater systems. *Ecology Lett.* **9**: 1157-1171.

REUS J, LEENDERTSE P, BOCKSTALLER C, FOMSGAARD I, GUTSCHE V, LEWIS K, NILSSON C, PUSSEMIER L, TREVISAN M, VAN DER WERF H, ALFARROBA F, BLÜMEL S, ISART J, MCGRATH D and SEPPÄLÄ T (2002) Comparison and evaluation of eight pesticide environmental risk indicators developed in Europe and recommendations for future use. *Agric., Ecosys. Environ*. **90**: 177-187.

RSA (REPUBLIC OF SOUTH AFRICA) (2006) Government Gazette, 13 April 2006. Draft Pesticide Management Policy for South Africa. No. 28711.

SCHULZ R, PEALL SKC, DABROWSKI JM, REINECKE AJ (2001) Spray deposition of two insecticides into surface waters in a South African orchard area. *J. Environ. Qual*. **30**: 814-822.

SOLOMON KR, BAKER DB, RICHARDS RP, DIXON KR, KLAINE SJ, LA PONT TW, KENDALL RJ, WEISSKOPF CP, GIDDINGS JM, GIESY JP, HALL JR. LW and WILLIAMS JM (1996) Ecplogical risk assessment of atrazine in North American surface waters. *Environ. Toxicol. Chem.* **15**(1): 31-76.

VERRO R, CALLIERA M, MAFFIOLOI G, AUTERI D, SALA S, FINIZIO A and VIGHI M (2002) GIS-based system for surface water risk assessment of agricultural chemicals. 1. Methodological approach. *Environ. Sci. Technol.* **36**(7): 1532-1538.

WAUCHOPE RD (1996) Pesticides in Runoff: Measurement, modelling and mitigation. *J. Environ. Sci. Health. Part B*. **31**: 337-344.

WHEELER JR, GRIST EPM, LEUNG KMY, MORRITT D and CRANE M (2002) Species sensitivity distributions: data and model choice. *Marine Poll. Bull.* **45**: 192-202

# 3. RISK INDICATOR METHODOLOGY

## 3.1 Pesticide Use Index

Important input parameters for this index are pesticide use and crop area. Crop area can normally be determined by maps, GIS layers and/or Google Earth. As noted in the framework, exact crop area is preferable and the smaller the catchment size the easier this information is to obtain. GIS is the most useful application to calculate crop area. Most often GIS layers may depict agricultural land, without actually identifying the specific crop type. In this instance the only way to identify crop types is via ground-truthing (i.e. visual inspection of crops) or farmer interviews. At a more advanced level remote sensing and use of satellite images are capable of identifying crop types to varying degrees of success. Broadly speaking it is important for water resource and catchment managers to maintain up to date inventories of crops grown in agricultural catchments. The presence of pesticides in water resources is inherently linked to the type of crops grown and water resource management requires and integrated approach taking land use activities and their influence into account.

Pesticide application data is normally more difficult to obtain. In order to determine overall pesticide use, one needs to determine:

a.) which pesticides are applied to a specific crop and
b.) the rate at which this pesticide is applied and
c.) the frequency of application (i.e. how often the pesticide is applied).

For the purposes of this index the former is the minimum information that needs to be obtained. The simplest way to obtain this information is through interviews with farmers. However, a large catchment area may contain a number of farms each with a different land owner. To obtain this information from each farmer in a large catchment requires a large amount of time and effort and may not always be logistically possible. An added difficulty is that farmers are often reluctant to give out this information in lieu of the perception that they are responsible for pollution of water resources. A more indirect method is to obtain pesticide sales data for a particular region from agricultural extension networks and organisations such as CropLife and AVCASA. In general, there is a distinct lack of this information that is freely available. Given that this is the most important information for this indicator and for management of pesticides in general, it is important that further research is conducted on developing a database on pesticide use in South Africa. Generally a particular catchment will be suitable for certain crop types and will therefore determine the type of pesticides likely to be applied. However, even for one particular pest on one crop type, a number of different pesticides may be potentially used.

Once the applied pesticides have been identified, it is necessary to obtain the application rate (i.e. the amount of pesticide applied per hectare of crop). Again, the most desirable source of this information is from the farmers themselves. If this information is not available it can be estimated using recommended application rates as recommended by the pest control guide as published by the South African Department of Agriculture (DoA, 2007).

Finally, in order to determine the total amount of pesticide applied in a growing season, it is necessary to know how many times the pesticide is applied (frequency of application). Again, this information is often difficult to obtain, if one does not have access to farmers' spraying records. However, the pest control guide published by the Department of Agriculture (DoA, 2007) does provide some guidance on this aspect.

In general the size of the catchment will determine the source of the data. For small catchments, it may be relatively simple to obtain information directly for farmers. For large catchments, information will likely be collected from a combination of sources, including limited farms surveys, estimated data from agricultural surveys and available GIS layers (i.e. the National Land Cover data set). It is therefore implicit that the larger the catchment the more difficult it is to obtain detailed accurate data, which will ultimately affect the reliability of the pesticide risk indicator.

When calculating the total amount of pesticide applied it is important to remember that pesticide mixture is sold as a powder or an emulsifiable concentrate (from here on referred to as "pesticide concentrate"). Only a certain proportion of the mixture is comprised of the specific active ingredient responsible for the toxic mode of action of the pesticide, and this will vary from pesticide to pesticide. The pesticide concentrate is diluted in water and applied to crops. All registered pesticides in South Africa are listed in the pest control guide published by the Department of Agriculture (DoA, 2007, DAFF, 2010) and it is possible to obtain the amount of active ingredient per litre (in the case of a liquid) or kilogram (in the case of a powder). When calculating the application rate it is important to determine the amount of active ingredient applied per hectare, not the amount of emulsifiable concentrate/ active ingredient applied per hectare.

***Example: Calculation of the active ingredient applied to apples***

From spraying records, the following is applied to apples.

The pesticide concentrate Dursban is diluted at 100 mℓ (or 0.1 ℓ) per 100 litres of water and is applied at a rate of 2100 ℓ/ha (spray volume). The active ingredient of Dursban is chlorpyrifos at a concentration of 480 g/ℓ (or 0.48 kg/ℓ). The application rate (***AR***) of chlorpyrifos (in kg/ha) can be calculated as follows:

$AR = SV/100 \times PQ \times [a.i.]$

Where ***SV*** is litres of pesticide mixture applied per hectare (2100 ℓ/ha), ***PQ*** is the quantity of pesticide concentrate (in litres or kilograms) diluted per 100 litres of water (0.1 ℓ) and ***[a.i.]*** is the concentration of active ingredient (kg) per litre or kilogram of pesticide concentrate (0.48 kg/ℓ). In this case the AR of chlorpyrifos calculates to 1.008 kg/ha.

The total amount of active ingredient applied per single application (in kg) is calculated as follows:

$A.I._{kg} = CA \times AR$

where ***CA*** is the total crop area (ha) of the crop. Often a pesticide is applied more than once. Therefore the total amount of active ingredient applied per season can be calculated as follows:

$A.I._{season} = A.I._{kg} \times n$

where ***n*** is the number of applications per season.

### *3.1.1 Calculation of Predicted Environmental Use (PEU)*

The PEU is the estimated amount of pesticide applied to the catchment or crop of interest. The two different levels of the PEU can be calculated according to the equations in Table 9. Potential sources of information required for the calculation of the PEU are listed in Table 11.

**Table 9:** Details of calculation of the Pesticide Environmental Use (PEU).

| Index | Description of Terms |
|---|---|
| PEU = AR x CA x n | AR is the application rate<br>CA is the crop area<br>n is the total number of applications per season |

The level of accuracy of the PEU is determined by the accuracy of the data used to calculate the PEU

**Table 10:** PEU accuracy levels (i.e. _1, _2 or _3) associated with the level of accuracy of input data.

| | | Pesticide Application Rate | |
|---|---|---|---|
| | | **Estimated** | **Actual** |
| **Crop Area** | **Estimated** | PEU_1 | PEU_2 |
| | **Actual** | PEU_2 | PEU_3 |

**Table 11:** Data requirements for estimating pesticides use at field or catchment scale.

| Data Requirements | Source of Data |
|---|---|
| Crop Area | GIS layers (CSIR, ARC)<br>Google Earth<br>Remote Sensing<br>Agricultural Census (STATSSA)<br>Farm Surveys |
| Pesticide applied per crop | Farm surveys<br>Sales data (i.e. AVCASA, Ag extension networks) |
| Application rate | Farm surveys<br>Recommended application rates |
| Application frequency | Farm surveys<br>Recommended application frequency |

### *3.1.2 Calculation of the Pesticide Use Index (PUI)*

The PUI is calculated by expressing each of the pesticides as a ratio of the active ingredient with the highest PEU across all sites (i.e. the total amount of pesticide applied to orchards/crops upstream of the sampling site or within the catchment of interest). The total application for each active ingredient across all sites is expressed as a ratio of the active ingredient with the highest application across all the sites. Thus the active ingredient with the highest application would have a PUI of 1. The categories are classified according to Table 12.

**Table 12:** Pesticide Use Categories corresponding to the Pesticide Use Index (PUI) score.

| Use Category | PUI Score |
|---|---|
| High | 0.1-1 |
| Medium | 0.01-0.1 |
| Low | < 0.01 |

## 3.2 Pesticide Exposure Index (PeXI)

The PUI provides an estimate of the total load of pesticides applied to a field or catchment. The PeXI estimates the fraction of that applied load that moves from the field(s) to adjacent water bodies and expresses it as a concentration expected to occur in the water body. The PeXI therefore incorporates a number of physicochemical, spatial and geographical factors that ultimately influence the movement of pesticides into surface waters as well as hydrological characteristics that determine their concentration in the water body. For field scale assessments a visit to the particular field in question will be sufficient to determine the geographical and spatial factors. Once again, the larger the catchment and the more fields incorporated, the more complex the assessment becomes. In this respect the use of GIS is an essential tool to determine these more complex relationships. The PeXI integrates the physicochemical, spatial and geographical factors using simple transport models that take spray drift and runoff into account. All models and equations described below in the spray drift and runoff sections can be viewed in OECD (1998).

### *3.2.1 Spray Drift*

Spray drift is the airborne movement of pesticides from the point of application to a nearby water body. Contamination is therefore direct and occurs during the application process. The potential for pesticides to enter water bodies as a result of spray drift is closely correlated to the application rate and the frequency of application. Therefore information obtained for the PUI will largely satisfy the data requirements for contamination resulting from spray drift in the PeXI. Physicochemical properties of the pesticides themselves do not play a large role in determining their movement into water resources. They do however play a role in determining whether they are more likely to be associated with the water or sediment phase once they enter the water body. Additional factors that determine pesticide input are the distance of crops from the water body as well as the type of crop that is being sprayed.

Pesticide contamination of surface water via spray drift was calculated using drift values derived by Ganzelmeier *et al.* (1999). These values were developed based on extensive trials performed by the German BBA, which measured pesticide drift at different distances from the point of application on different crop types. Given that the percentage of spray drift over 50 m is very low (Table 13), for the purposes of the index, only fields adjacent to water bodies are assessed.

**Table 13:** Percentage of applied pesticide likely to drift to adjacent water bodies based on distance of water body from the crop and the type of crop being treated.

| Distance (meter) | Vine (early) | Vine (late) | Fruit (early) | Fruit (late) | Arable (early) | Arable (late) |
|---|---|---|---|---|---|---|
| 1 | 23.2 | 20 | 46.2 | 26.7 | 4 | 5 |
| 2 | 8 | 12 | 34.5 | 22.3 | 1.6 | 1.8 |
| 3 | 4.9 | 7.5 | 29.6 | 19.6 | 0.9 | 1.4 |
| 4 | 2.6 | 5.8 | 23.8 | 15.3 | 0.6 | 1.0 |
| 5 | 1.6 | 5.2 | 19.5 | 10.1 | 0.5 | 0.7 |
| 7.5 | 1 | 2.6 | 14.1 | 6.4 | 0.3 | 0.5 |
| 10 | 0.4 | 1.7 | 10.6 | 4.4 | 0.3 | 0.4 |
| 15 | 0.2 | 0.8 | 6.2 | 2.5 | 0.2 | 0.2 |
| 20 | 0.1 | 0.4 | 4.2 | 1.4 | 0.1 | 0.1 |
| 30 | 0.1 | 0.2 | 2.0 | 0.6 | 0.1 | 0.1 |
| 40 | 0.1 | 0.2 | 0.4 | 0.6 | 0.1 | 0.1 |
| 50 | 0.1 | 0.2 | 0.2 | 0.6 | 0.1 | 0.1 |

From these tables, using regression analysis, it is possible to generate equations describing the percentage drift likely to occur over a certain distance for a certain crop (Table 14).

**Table 14:** Drift equations for calculating the percentage of an applied pesticide lost due to spray drift (D%), where x is the distance between a field and water body (in meters) and "a" and "b" are constants (OECD, 1998).

| Crop Type | Formula | Constants |
|---|---|---|
| Fruit trees (early) | $L\%_{spray} = (a-b*\ln(x))^2$ | a=7.08298 b=1.68712 |
| Fruit tress (late) | $L\%_{spray} = 1/(a+bx^2)$ | a=0.03597 b=0.00179 |
| Arable (early) | $L\%_{spray} = (a+b/x)^2$ | a=0.32397 b=1.73651 |
| Arable (late) | $L\%_{spray} = EXP(a-b*\ln(x))$ | a=1.58074 b=1.17817 |

### *3.2.2 Runoff*

For runoff the physicochemical properties of pesticides will play a large role in determining their movement from land into the water resources. Therefore any indicator needs to take this into account when estimating pesticide losses. Runoff originates from all fields within a catchment, and therefore in contrast to the $L\%_{spray}$ calculations, all fields within a catchment area are considered for the runoff calculations.

$$L\%_{runoff} = \left(Q/P\right) \times f \times \exp\left(-3 \times \ln 2 / DT50_{soil}\right) \times 100/(1+Kd)$$

**While the formula looks relatively complex, it is in fact relatively simple and requires relatively easily obtainable input data. Terms for the equation and sources of data can be viewed in Table 15 and Table 16 respectively.**

**Table 15:** Explanation of terms required for calculating the percentage of an applied active ingredient lost in runoff (OECD, 1998).

| Term | Description |
|---|---|
| $L\%_{runoff}$ | Percentage of active ingredient being available in run-off water as dissolved substance |
| ***Q*** | Runoff amount (mm) calculated according the model of Lutz & Maniak (1984, 1992). See Table 2.11 (Appendix) for Q values corresponding to specific rainfall amounts (P). |
| ***P*** | Rainfall amount (mm) |
| $DT50_{soil}$ | Half-life of active ingredient in soil |
| ***f*** | Correction factor, with f = f1 x f2 x f3 |
| ***f1*** | Factor, that reflects the influence of field slope on L%:<br>if slope < 20%: f1 = (0.02153 x slope) + (0.001423 x slope$^2$)<br>if slope ≥ 20%: f1 = 1 |
| ***f2*** | Factor, that reflects the influence of plant interception PI (%) on L%:<br>$f2 = 1 - PI/100$ |
| ***f3*** | Factor, that reflects the influence of a densely covered buffer zone on L%:<br>f3 = 0.83$^{WBZ}$ with<br><br>WBZ = Width of the buffer zone (metres); if the buffer zone is not densely covered with plants, in which case the width is set to zero. |
| ***Kd*** | KOC •%OC / 100<br><br>KOC – Sorption coefficient of a.i. to organic carbon<br>%OC – Organic carbon content of soil |

**Table 16**: Data requirements and their sources for estimating losses of pesticides attributable to runoff.

| Data Required | Source of Data |
|---|---|
| Q | OECD Tables (see Table 2.11, Appendix 2.6) |
| P | Local weather stations, WeatherSA, ARC |
| DT50soil | Pesticide databases (e.g. Footprint Pesticide Properties Database) |
| Slope | Maps, GIS, Google Earth, Field Measurements |
| PI | |
| WBZ | Maps, GIS, Google Earth, Field Measurements |
| KOC | Pesticide databases (e.g. Footprint Pesticide Properties Database) |
| %OC | Soil Maps, Field Measurements |

### *3.2.3 Calculation of the PEL*

In order to derive a final PeXI value it is necessary to first calculate the PEL and then the PEC. The PEC essentially incorporates flow characteristics of the water body in question so as to derive a concentration from the PEL. The basic equation for calculating the PEL is described in Table 17.

**Table 17:** Calculation of the Predicted Environmental Load (PEL)

| Equation | Description of Terms |
|---|---|
| PEL = PEU x WI x ($L\%_{spray}$ + $L\%_{runoff}$) | WI is the Water Index which is in estimate of the proportion of an agricultural field bordered by an adjacent water body. |

The water index (WI) is the probability of surface water lying adjacent to a field and is expressed as a ratio of the length of the water body ($L_{WB}$) lying adjacent to the field to the perimeter ($P_{Field}$) of the field:

$$WI = \frac{L_{WB}}{P_{Field}}$$

The accuracy of the calculated PEL is determined by the accuracy of the PEU and the accuracy of the geographical data (i.e. slope, buffer zone width, soil type, etc.).

**Table 18:** PEL accuracy levels (i.e. _1, _2 or _3) associated with the level of accuracy of PEU and geographical data.

| | | Geographical data | |
|---|---|---|---|
| | | **Estimated** | **Actual** |
| **PEU** | **PEU_1** | PEL_1 | PEL_1 |
| | **PEU_2** | PEL_1 | PEL_2 |
| | **PEU_3** | PEL_2 | PEL_3 |

In the case of a larger catchment area, there will most likely be multiple fields containing different crops at varying slopes and potentially varying soil types. Estimation of $L\%_{spray}$ and $L\%_{runoff}$ is therefore slightly more complex and, in this respect, the use of GIS is an invaluable tool for extracting the necessary spatial data for input into the respective formulae. Using GIS and calculating the PEU, $L\%_{runoff}$ and $L\%_{spray}$ for each field in the catchment and deriving a PEL for each of the fields is the most accurate approach (Method 1, Table 19). This would imply that for each field, input data would be collected or assessed and a PEL would be calculated on a field by field basis. The final catchment PEL would be the sum of the PELs for each field in the catchment.

A less accurate method for deriving the PEL would be to estimate or obtain average or mean values for each of the geographical inputs (i.e. average values representative of all fields included in the sub-catchment, Method 2, Table 19).

**Table 19:** Explanation of two potential methods for calculating a catchment scale Predicted Environmental Load (PEL)

| Equation | | Explanation |
|---|---|---|
| *Method 1: Accurate* | | |
| PEL (Field 1)<br>PEL (Field 2)<br>PEL( Field 3) | = PEU(Field1) x WI ($L\%_{spray}$ + $L\%_{runoff}$)<br>= PEU(Field2) x WI ($L\%_{spray}$ + $L\%_{runoff}$)<br>= PEU(Field3) x WI ($L\%_{spray}$ + $L\%_{runoff}$) | Use data input variables per field in the catchment and sum the PEL for each field to derive a catchment PEL |
| PEL (Catchment) | = PEL(field1) + PEL(field2) +PEL(field3), etc. | |
| *Method 2: Estimated* | | |
| PEL (Catchment) | = PEL x WI ($L\%_{spray}$ + $L\%_{runoff}$) | Use average input variable for all fields in the entire catchment |

### *3.2.4 Calculation of PEC*

In this study, results of the PeXI will be validated through field monitoring of pesticide concentrations. The concentration of a pesticide in the surface water is the most environmentally relevant parameter, as concentration ultimately determines the level of toxicity that can be expected and thus the likely impact. For example a pesticide with a high PEL entering a stream with a very high discharge could potentially result in a considerably lower concentration than a comparatively smaller load entering a stream with a very low discharge. Therefore calculation of the PEC is the most important parameter with regards to comparing likely in-stream contamination amongst sites.

The calculated PEL, together with discharge data is used to calculate the respective PEC for a pesticide at a site. Basic hydrological data is required to estimate the volume of water in the receiving water body. This basic data is relatively easy to measure (through field based measurements) or to estimate. The PEC can be calculated as follows:

$$PEC\_n = \frac{PEL\_n}{(D \times 1000)}$$

Where *D* is the discharge of the stream in $m^3/s$. If discharge data is not available for the stream, an alternative method can be used to calculate the PEC:

$$PEC\_n = \frac{PEL\_n}{(l \times d \times w)}$$

where, *n* is the level of accuracy of the PEL, *l* is the length of the water body adjacent to all orchards analysed in the PEXI, *d* is the depth of this section of the water body and *w* is the width of the section of water body. PEC_1, _2 and _3 will correspond with PEL_1, _2 and _3 as input, respectively. There is one important aspect to consider when calculating the PEC. This calculation does not take temporal aspects of contamination into consideration and assumes that the concentration is derived from all pesticide losses occurring simultaneously and entering the water resource simultaneously. In reality the following occurs:

- Runoff and spray drift events take place over a prolonged period time (i.e. a number of hours). Losses associated with each of these transport routes therefore take place

over a similar period and the sum of pesticide losses for each of these activities will not enter a water body simultaneously.
- The receiving water body is often a flowing body and thus any pesticide entering the water body will thus be transient and the concentration will be a function of the amount entering at a specific time and the flow of the water body (i.e. pesticides are not contained within the stretch of water of interest – they move in and out of a stretch continuously).

This means that the calculated PEC will not be realistic and will most likely be significantly higher than actual concentrations measured during routine monitoring programmes. However, the indicator is designed to provide an estimate of the relative concentrations of a number of pesticides compared to one another and is not designed to give accurate pesticide concentrations as would be detected in the field. The calculation of the PeXI provides an index for comparison of pesticides.

### *3.2.5 Calculation of the PeXI*

The PEC is expressed as a ratio of the highest PEC for all pesticides included in the analysis. For example, assume that the PEC for three pesticides is 4, 2 and 1 µg/ℓ, respectively. The PECs for all three pesticides are divided by 4 (the highest PEC value) to derive PeXIs of 1, 0.5 and 0.25, respectively. This method of calculating the PeXI scores ensures that the transport and concentration of the different active ingredients is expressed relative to the active ingredient with the highest PEC. This ratio is the final PeXI score attributed to each pesticide. These scores enable a relative comparison of the likely transport of each pesticide at site included in the analysis, with the pesticide having a value of 1 being the one most likely to be detected at high concentrations. The PeXI scores are used to assign an exposure category to each pesticide, namely, High, Medium and Low (Table 20).

**Table 20:** Categories associated with Pesticide Exposure Index (PeXI) scores.

| Exposure Category | PeXI |
|---|---|
| High | 0.1-1 |
| Medium | 0.01-1 |
| Low | <0.01 |

## 3.3 Pesticide Risk Index

The pesticide risk index (PeRI) incorporates toxicity data to provide an indication of the likely toxic risks associated with a given exposure. In order to determine this it is necessary to integrate the PEC calculated previously with a toxicity value for each of the active ingredients included in the analysis.

### *3.3.1 Toxicity Data*

Toxicity data can be collected from freely available databases such as the USEPA EcoTox database, which allows users to obtain a wide range of toxicity data covering different endpoints (i.e. LC50, EC50, NOEC, etc.) for a number of different chemicals. In instances where a large amount of data is available for a specific active ingredient, it is recommended to use the Species Sensitivity Distribution approach to derive a final toxicity value for each chemical. When collecting and summarising data the following guidelines should be followed:

- When collecting data for derivation of the SSD it is important that the same toxicity endpoint data is obtained for each chemical (i.e. LC50 or EC50 data only). This will

allow for a relative comparison between chemicals using the same test endpoint for each chemical. As LC50 is the most commonly available.

- Ensure that the toxicity data is of suitable quality.
- When collecting data, only data for freshwater aquatic species should be collected (i.e. macroinvertebrates, fish, algae, crustaceans).
- In many instances, more than one LC50 toxicity value is available for a particular species. In these instances the geometric mean of the all the values for the particular species should be calculated to derive a single value. This reduces particularly high or low values from skewing the data.

SSDs can be derived using freely available BurrliOz software (CSIRO, 2010). This software selects the distribution that best fits the available toxicity data from a family of distributions (i.e. the Burr Type III family) rather than trying to apply a single pre-determined distribution (Figure 2). The software further allows the user to calculate the concentration at which a certain percentage of species would protected. For the purposes of this indicator the concentrations at which 95% of species would be protected was chosen as the final toxicity value for input into the PeRI.

For some active ingredients there is insufficient data to derive an SSD. As a guideline, data for at least five different species should be used for constructing an SSD. In cases where insufficient data is available the lowest toxicity value for the species should be used.

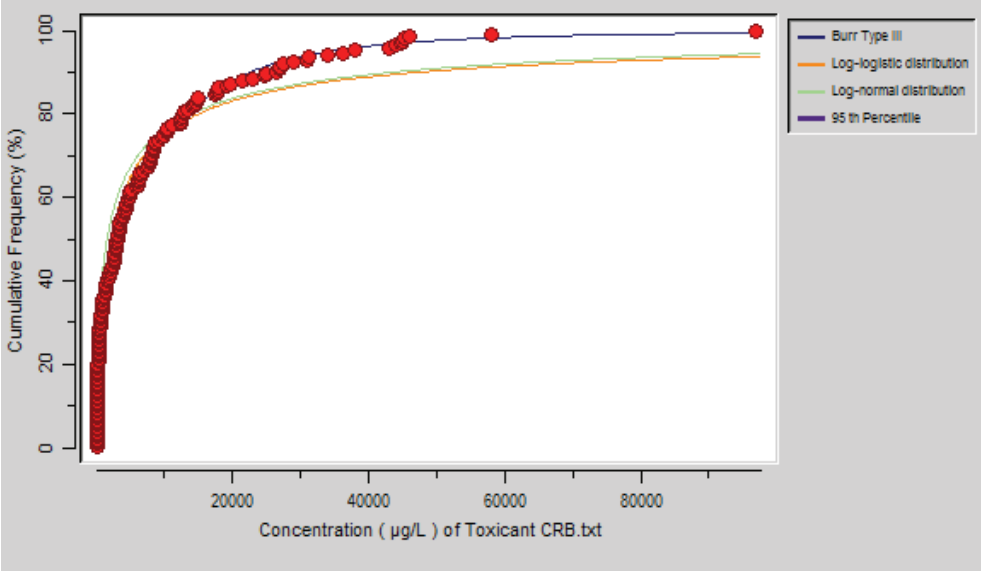



**Figure 2:** Example of an SSD curve produced in BurrliOZ with LC50 values for the pesticide carbaryl as input data.

### *3.3.2 Calculation of the TER*

The TER is calculated by simply dividing the PEC by the toxicity value for a specific pesticide (Table 21).

**Table 21:** Calculation of three levels of the TER (toxicity to exposure ratio).

| Equation | Explanation |
|---|---|
| TER =PEC/ToxV | ToxV is the toxicity value derived for the pesticide |

The level of accuracy of the TER is dependent on the accuracy of the PEC (i.e. _1, _2 or _3) and the method of determining the toxicity value. Using an SSD approach is regarded as being a more rigorous and realistic approach in comparison to using a single toxicity value.

**Table 22:** TER accuracy levels (i.e. _1, _2 or _3) associated with the level of accuracy of PEC and toxicity data.

| | | Toxicity Data | |
|---|---|---|---|
| | | **Single Value** | **SSD** |
| **PEC** | **PEC_1** | TER_1 | TER_1 |
| | **PEC_2** | TER_1 | TER_2 |
| | **PEC_3** | TER_2 | TER_3 |

### *3.3.3 Calculation of the PeRI*

The PeRI is calculated in a similar fashion to the PeTI. The highest calculated TER is used as the benchmark and all TER values for pesticides included in the analysis are divided by the highest TER value to derive the PeRI. The PeRI scores are categorised according to Table 20.

**Table 23:** Risk categories corresponding to calculated Pesticide Risk Index (PeRI) values.

| Risk Category | PeRI Value |
|---|---|
| High | 0.1-1 |
| Medium | 0.01-1 |
| Low | <0.01 |

## 3.4 References

CSIRO (2010) BurrliOz: A Flexible Approach to Species Protection. [Last Accessed October 2010: http://www.cmis.csiro.au/envir/burrlioz/]

DAFF (DEPARTMENT OF AGRICULTURE FISHERIES AND FORESTRY) (2010) List of Registered Products. http://www.nda.agric.za/doaDev/sideMenu/ActNo36_1947/AR/AR%20Lists.htm. Last Accessed: [February, 2010]

DOA (DEPARTMENT OF AGRICULTURE) (2007) A Guide for the Control of Plant Pests. Directorate: Food Safety and Quality Assurance. Department of Agriculture, Pretoria, South Africa

GANZELMEIER H, RAUTMANN D, SPANGENBERG R, STRELOKE M, HERRMANN M, WENZELBURGER H-J, and WALTER H-F (1995) Studies of the spray drift of plant protection products. Mitteilungen aus der Biologischen Bundesanstalt für Land –und Forstwirtschaft, Blackwell Scientific, Berlin, Germany.

OECD (1998) Pesticide Aquatic Risk Indicators Project: Annex 2: Report of Phase 1 of the Aquatic Risk Indicators Project. France: OECD Secretariat.

# 4. FIELD STUDY

A field sampling study was designed in order to attempt to validate the outcomes of the risk indicator methodology. This was done through sampling of water and sediment samples at critical periods during the year. Due to the transient nature of pesticide contamination, it is often difficult to detect pesticides using a routine (i.e. monthly) sampling routine. Therefore the sampling programme was designed so as to focus sampling during periods where pesticide contamination would most likely be expected to occur. Thus, more intensive sampling took place during the spraying (to account for spray drift contamination) and rainfall (to account for drainage and runoff) seasons. Water and sediment samples were collected so as to determine partitioning of analysed pesticides between the sediment and water phases.

The aim of the sampling was to determine whether the risk indicator methodology can predict differences in pesticide contamination. Accordingly, samples were analysed for pesticides so as to determine the following:

- Partitioning of pesticides between the water and sediment phases.
- Frequency of occurrence of different pesticides in collected samples.
- Magnitude of concentration of pesticides in collected samples.
- Spatial differences in the extent of contamination.

## 4.1 Lourens River Study Area

The Lourens River rises at an altitude of 1080 m in a naturally vegetated fynbos area and flows in a south-westerly direction for 20 km before discharging into False Bay at the Strand (S34°06´; E18°48´). The catchment region is characterised by intensive farming, with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of 92 $km^2$ and receives an annual mean rainfall of 915 mm. Roughly 87% of its 35 x $10^6$ $m^3$ mean annual discharge occurs during the autumn, winter and early spring months between April and October (Tharme *et al.*, 1997), as is characteristic of the region's Mediterranean climate. The main soil type is silty loam and the slopes in the catchment vary between <2% in the area near the river and <8% in the upstream stretches of the river and some of the tributaries. Apples, grapes (for wine production), pears and plums are grown in the area, to which a number of insecticides and fungicides are applied on an annual basis, mainly between August and February of the following year.

This catchment has been intensively studied and numerous publications on these studies are available in the scientific literature. A significant amount of data is therefore available for input into the proposed risk indicator. Of additional advantage is the fact that only two farms border the selected area; one on each side of the river. This provides for a more controlled study area and allows for relatively easy collection of data input variables. Few assumptions are therefore necessary for input into a risk indicator methodology.

### *4.1.1 Lourens River Study Sites*

Sites were chosen so as to determine contamination at the catchment scale as well as at the field scale. One site in the Lourens River main stem (LR) was chosen as the site representative of the entire catchment (Figure 3). This site is immediately downstream of both farms and therefore receives discharge from the Lourens River upstream as well as the tributaries flowing through each of the farms. Four additional sampling sites, named after the

orchard in closest proximity to the site (BB7, LG4, C and VW) were located within four tributaries so as to determine contamination at smaller spatial scales. Each of the four tributaries are characterised by different crops, buffer zone distances and slope conditions. Pesticide application in the catchment of each tributary was determined based on the type and total area of crop present and pesticide application records from the farmers. The sampling design therefore allows for the risk indicator to be tested at both the field and catchment scale. Additionally the sampling design will allow for the identification of hotspot areas within the catchment (i.e. tributaries with relatively high pesticide contamination).

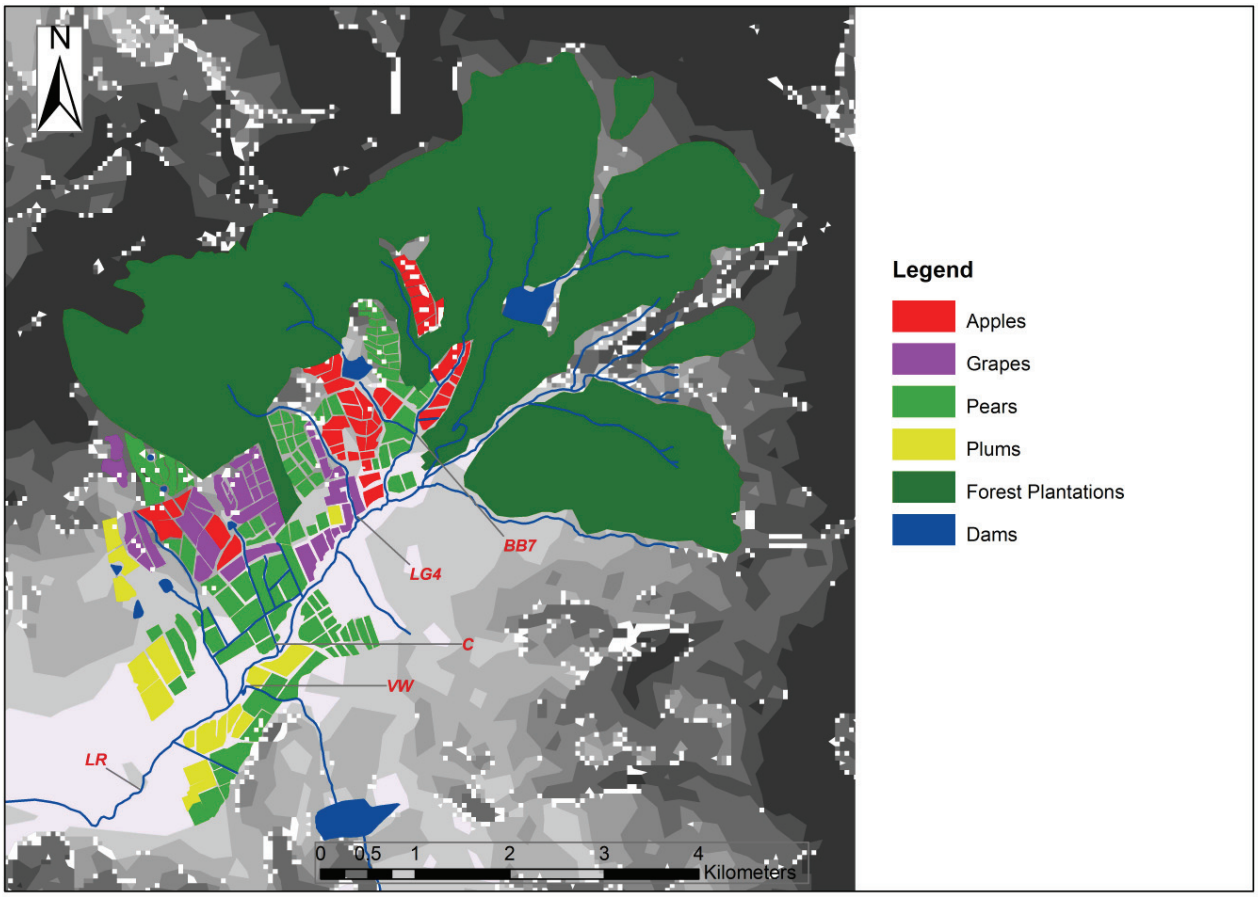



**Figure 3:** Land use and sampling sites for the Lourens River catchment, Western Cape.

## 4.2 Sampling Protocol

Given the high costs of pesticide analysis a sampling protocol was designed so as to maximise the potential quality and usefulness of data derived (Table 24). Consequently a targeted sampling exercise was adopted as opposed to a routine monitoring exercise. Within each catchment, more regular sampling will take place during the spray application and rainfall season so as to maximise the potential for detecting pesticide residues in samples.

**Table 24:** Periods of pesticide application, rainfall and pesticide monitoring in the Lourens River catchment.

| | 2009 | | | | 2010 | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Oct | Nov | Dec | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep |
| Application | | | | | | | | | | | | |
| Rainfall | | | | | | | | | | | | |
| Monitoring | | | | | | | | | | | | |

### *4.2.1 Sample Collection*

Water samples were collected in 1ℓ acetone washed glass containers with a screw cap lined with clean aluminium foil. Samples were immediately placed in a cool box containing ice and kept in dark conditions. Sediment samples were collected at deposition zones at each of the sites. These are locations in the stream/river where the energy regime is low and fine-grained particles accumulate in the stream bed. Depositional zones can cover large areas at some sites and small pockets at other sites. The stream velocities at these zones have decreased and the fine-grained particles have deposited in the stream bed, which are ideal for the purposes of sampling and analysing sorbed pesticides. Sediment samples were collected from approximately the top 1 cm of deposition zones at each site using a metal scoop and were stored in 250 mℓ glass containers. All samples were stored at 4 degrees or below from time of collection until extraction. All samples were extracted within 72 hours of collection.

### *4.2.2 Sampling Schedule*

Samples were collected so as to coincide with periods when pesticide contamination of the water bodies is expected to occur. The Lourens River falls within the Western Cape and therefore experiences a Mediterranean climate. The main application period is characterised by low rainfall and high winds, with spray drift being the most likely route of entry for pesticides into surface waters. The start of the rainy season (April/May) is also characterised by high pesticide input. Thus, sampling took place once every week starting the middle of October to the beginning of February. Sampling also took place again during the start of the rainfall season to account for pesticide input via runoff.

## 4.3 Pesticide Application Data

Pesticide application data were obtained from spray records provided by the farmers (Appendix 1). For each crop the application rate (kg/ha) and total amount of pesticide applied (kg) was determined. This was done for each of the four tributaries as well as for the entire catchment (Table 25, Table 26 and Table 27).

Overall, mancozeb is by far the most commonly applied pesticide. Additionally, azinphos-methyl, chlorpyrifos, carbendazim, prothifos and methyl parathion are applied in relatively high quantities (Table 26). Flufenoxuron, propiconazole, beta-cyfluthrin and cypermethrin are all applied in low quantities, largely due to the very low application rate and small number of applications (Table 26 and Table 27). The majority of pesticides are applied to apples and pears, with comparatively fewer pesticide applied to grapes and plums.

**Table 25:** Area of different crop types in each of the sub-catchments sampled for pesticide levels in water and sediment.

| Sampling Site | Apples | Grapes | Pears | Plums |
|---|---|---|---|---|
| | | (ha) | | |
| BB7 | 55.37 | 0 | 32.44 | 0 |
| C | 11.13 | 36.12 | 52.46 | 0 |
| LG4 | 8.6 | 15.4 | 11.17 | 0 |
| VW | 0 | 0 | 18.29 | 3.8 |
| Lourens Catchment (LR) | 96 | 102 | 255 | 82 |

**Table 26:** Total quantity of pesticides (kg) applied to four different fruit types grown in the Lourens River catchment during 2009/2010.

| Active Ingredient | Apples | Grapes | Pears | Plums | Total |
|---|---|---|---|---|---|
| Azinphos-methyl | 180.6 | 0 | 315.9 | 22.9 | 519.4 |
| Beta-cyfluthrin | 0.4 | 0 | 1.8 | 0 | 2.1 |
| Carbaryl | 157.9 | 0 | 0 | 31.4 | 189.3 |
| Carbendazim | 0 | 0 | 351.0 | 0 | 351.0 |
| Chlorpyrifos | 179.6 | 73.4 | 196.6 | 1.9 | 451.4 |
| Cyhexatin | 0 | 0 | 175.5 | 0 | 175.5 |
| Cypermethrin | 0 | 0 | 0 | 1.8 | 1.8 |
| Dimethomorph | 0 | 306.0 | 0 | 0 | 306.0 |
| Endosulfan | 122.6 | 0 | 0 | 0 | 122.6 |
| Flufenoxuron | 5.2 | 0 | 11.7 | 0 | 16.9 |
| Flusiazole | 84.2 | 0 | 0 | 0 | 84.2 |
| Mancozeb | 1190.0 | 693.6 | 1842.8 | 0 | 3726.4 |
| Methyl parathion | 69.4 | 0 | 157.2 | 31.4 | 258.0 |
| Propiconazole | 0 | 0 | 0 | 8.4 | 8.4 |
| Prothifos | 86.7 | 49.0 | 196.6 | 0 | 332.2 |
| Thiacloprid | 18.6 | 0 | 84.2 | 0 | 102.8 |
| Trifloxystrobin | 0 | 15.3 | 0 | 0 | 15.3 |

**Table 27:** Application rate, frequency of application and total amount of pesticide active ingredient applied to four crops in two sub-catchments (BB7 and C) of the Lourens River, Western Cape.

| Site | Active Ingredient | Apples | | | Pears | | | Plums | | | Grapes | | | All Crops |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | Total |
| | | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg) |
| **BB7** | Azinphos-methyl | 0.53 | 4 | 117.4 | 0.54 | 3 | 52.6 | | | | | | | ***169.9*** |
| | Beta-cyfluthrin | 0.005 | 1 | 0.3 | 0.005 | 2 | 0.3 | | | | | | | ***0.6*** |
| | Carbaryl | 1.84 | 1 | 101.9 | | | | | | | | | | ***101.9*** |
| | Carbendazim | | | | 0.6 | 3 | 58.4 | | | | | | | ***58.4*** |
| | Chlorpyrifos | 1.05 | 2 | 116.3 | 1.01 | 1 | 32.8 | | | | | | | ***149.0*** |
| | Endosulfan | 1.43 | 1 | 79.2 | | | | | | | | | | ***79.2*** |
| | Flufenoxuron | | | | 0.06 | 1 | 1.9 | | | | | | | ***1.9*** |
| | Flusiazole | 0.23 | 4 | 50.9 | | | | | | | | | | ***50.9*** |
| | Methyl Parathion | 0.4 | 2 | 44.3 | 0.4 | 2 | 26.0 | | | | | | | ***70.2*** |
| | Prothiofos | 1.01 | 1 | 55.9 | 1.01 | 1 | 32.8 | | | | | | | ***88.7*** |
| | Thiacloprid | 0.22 | 1 | 12.2 | 0.22 | 2 | 14.3 | | | | | | | ***26.5*** |
| **C** | Azinphos-methyl | 0.53 | 4 | 23.6 | 0.54 | 3 | 85.0 | | | | | | | ***108.6*** |
| | Beta-cyfluthrin | 0.005 | 1 | 0.1 | 0.005 | 2 | 0.5 | | | | | | | ***0.6*** |
| | Carbaryl | 1.84 | 1 | 20.5 | | | 0.0 | | | | | | | ***20.5*** |
| | Carbendazim | | | 0.0 | 0.6 | 3 | 94.4 | | | | | | | ***94.4*** |
| | Chlorpyrifos | 1.05 | 2 | 23.4 | 1.01 | 1 | 53.0 | | | | 0.72 | 1 | 26.01 | ***102.4*** |
| | Dimethomorph | | | | | | | | | | 1.25 | 3 | 135.45 | ***135.5*** |
| | Endosulfan | 1.43 | 1 | 15.9 | | | | | | | | | | ***15.9*** |
| | Flufenoxuron | | | | 0.06 | 1 | 3.1 | | | | | | | ***3.1*** |
| | Flusiazole | 0.23 | 4 | 10.2 | | | | | | | | | | ***10.2*** |
| | Methyl parathion | 0.4 | 2 | 8.9 | 0.4 | 2 | 42.0 | | | | | | | ***50.9*** |
| | Prothifos | 1.01 | 1 | 11.2 | 1.01 | 1 | 53.0 | | | | 0.48 | 1 | 17.34 | ***81.6*** |
| | Thiacloprid | 0.22 | 1 | 2.4 | 0.22 | 2 | 23.1 | | | | | | | ***25.5*** |
| | Trifloxystrobin | | | | | | | | | | 0.06 | 1 | 2.02 | ***2.0*** |

**Table 27 (continued):** Application rate, frequency of application and total amount of pesticide active ingredient applied to four crops in two sub-catchments (LG4 and VW) of the Lourens River, Western Cape.

| Site | Active Ingredient | Apples | | | Pears | | | Plums | | | Grapes | | | All Crops |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | Total |
| | | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg) |
| **LG4** | Azinphos-methyl | 0.53 | 4 | 18.2 | 0.54 | 3 | 18.1 | | | | | | | ***36.3*** |
| | Beta-cyfluthrin | 0.005 | 1 | 0.0 | 0.005 | 2 | 0.1 | | | | | | | ***0.2*** |
| | Carbaryl | 1.84 | 1 | 15.8 | | | 0.0 | | | | | | | ***15.8*** |
| | Carbendazim | | | 0.0 | 0.6 | 3 | 20.1 | | | | | | | ***20.1*** |
| | Chlorpyrifos | 1.05 | 2 | 18.1 | 1.01 | 1 | 11.3 | | | | 0.72 | 1 | 11.09 | ***40.4*** |
| | Dimethomorph | | | 0.0 | | | 0.0 | | | | 1.25 | 3 | 57.75 | ***57.8*** |
| | Endosulfan | 1.43 | 1 | 12.3 | | | 0.0 | | | | | | | ***12.3*** |
| | Flufenoxuron | | | 0.0 | 0.06 | 1 | 0.7 | | | | | | | ***0.7*** |
| | Flusiazole | 0.23 | 4 | 7.9 | | | 0.0 | | | | | | | ***7.9*** |
| | Methyl parathion | 0.4 | 2 | 6.9 | 0.4 | 2 | 8.9 | | | | | | | ***15.8*** |
| | Prothifos | 1.01 | 1 | 8.7 | 1.01 | 1 | 11.3 | | | | 0.48 | 1 | 7.39 | ***27.4*** |
| | Thiacloprid | 0.22 | 1 | 1.9 | 0.22 | 2 | 4.9 | | | | | | | ***6.8*** |
| | Trifloxystrobin | | | 0.0 | | | 0.0 | | | | 0.06 | 1 | 0.86 | ***0.9*** |
| **VW** | Azinphos-methyl | 0.53 | 4 | 117.4 | 0.54 | 3 | 52.6 | | | | | | | ***169.9*** |
| | Bet-cyfluthrin | 0.005 | 1 | 0.3 | 0.005 | 2 | 0.3 | | | | | | | ***0.6*** |
| | Captan | | | 0.0 | | 3 | 0.0 | | | | | | | ***0.0*** |
| | Carbaryl | 1.84 | 1 | 101.9 | | | 0.0 | | | | | | | ***101.9*** |
| | Carbendazim | | | 0.0 | 0.6 | 3 | 58.4 | | | | | | | ***58.4*** |
| | Chlorpyrifos | 1.05 | 2 | 116.3 | 1.01 | 1 | 32.8 | | | | | | | ***149.0*** |
| | Endosulfan | 1.43 | 1 | 79.2 | | | 0.0 | | | | | | | ***79.2*** |
| | Flufenoxuron | | | 0.0 | 0.06 | 1 | 1.9 | | | | | | | ***1.9*** |
| | Flusiazole | 0.23 | 4 | 50.9 | | | | | | | | | | ***50.9*** |
| | Methyl Parathion | 0.4 | 2 | 44.3 | 0.4 | 2 | 26.0 | | | | | | | ***70.2*** |
| | Prothiofos | 1.01 | 1 | 55.9 | 1.01 | 1 | 32.8 | | | | | | | ***88.7*** |
| | Thiacloprid | 0.22 | 1 | 12.2 | 0.22 | 2 | 14.3 | | | | | | | ***26.5*** |

**Table 27 (continued):** Application rate, frequency of application and total amount of pesticide active ingredient applied to four crops in the entire catchment (LR) of the Lourens River, Western Cape.

| Site | Active Ingredient | Apples | | | Pears | | | Plums | | | Grapes | | | All Crops |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | App. rate | Frequency | Total | Total |
| | | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg/ha) | (n) | (kg) | (kg) |
| **LR** | Azinphos-methyl | 0.53 | 4 | 203.5 | 0.54 | 3 | 413.1 | 0.59 | 1 | 48.2 | | | | ***664.8*** |
| | Beta-cyfluthrin | 0.005 | 1 | 0.5 | 0.005 | 2 | 2.6 | | | | | | | ***3.0*** |
| | Carbaryl | 1.84 | 1 | 176.6 | | | | | | | | | | ***176.6*** |
| | Carbendazim | | | | 0.6 | 3 | 459.0 | | | | | | | ***459.0*** |
| | Chlorpyrifos | 1.05 | 2 | 201.6 | 1.01 | 1 | 257.6 | 0.81 | 1 | 66.1 | 0.72 | 1 | 73.4 | ***598.7*** |
| | Cypermethrin | | | | | | | 0.001 | 2 | 0.4 | | | | ***0.4*** |
| | Dimethomorph | | | | | | | | | | 1.25 | 3 | 382.5 | ***382.5*** |
| | Endosulfan | 1.43 | 1 | 137.3 | | | | | | | | | | ***137.3*** |
| | Flufenoxuron | | | | 0.06 | 1 | 15.3 | | | | | | | ***15.3*** |
| | Flusiazole | 0.23 | 4 | 88.3 | | | | | | | | | | ***88.3*** |
| | Methyl parathion | 0.4 | 2 | 76.8 | 0.4 | 2 | 204.0 | | | | | | | ***280.8*** |
| | Propiconazole | | | | | | | 0.07 | 3 | 17.7 | | | | ***17.7*** |
| | Prothifos | 1.01 | 1 | 97.0 | 1.01 | 1 | 257.6 | 0.81 | 1 | 66.1 | 0.48 | 1 | 49.0 | ***469.6*** |
| | Thiacloprid | 0.22 | 1 | 21.1 | 0.22 | 2 | 112.2 | | | | | | | ***133.3*** |
| | Trifloxystrobin | | | | | | | | | | 0.06 | 1 | 5.7 | ***5.7*** |

## 4.4 Pesticide analysis

Pesticides were analysed by Hearshaw and Kinnes Analytical Laboratories in Cape Town. All pesticides listed in Table 27 were analysed for in both water and sediment samples obtained from each of the five sites. Pesticides were analysed by means of LC-MS/MS and limits of quantification are listed in Table 28.

**Table 28:** Limits of quantification for pesticides sampled in water and sediment samples collected from the Lourens River catchment.

| Active Ingredient | Limits of Quantification | |
|---|---|---|
| | Water (µg/ℓ) | Sediment (µg/kg) |
| α- Cypermethrin | 0.1 | 10 |
| Azinphos-methyl | 0.1 | 10 |
| Carbaryl | 0.5 | 10 |
| Carbendazim | 0.05 | 10 |
| Chlorpyrifos | 0.1 | 10 |
| Cyfluthrin | 0.1 | 10 |
| Cypermethrin | 0.1 | 10 |
| Dimethomorph | 0.5 | 10 |
| α- Endosulfan | 0.1 | 10 |
| β- Endosulfan | 0.1 | 10 |
| Endosulfan | 0.1 | 10 |
| Flusilazole | 0.05 | 10 |
| Methyl-parathion | 0.1 | 10 |
| Propiconazole | 1 | 10 |
| Prothiofos | 0.1 | 10 |
| Thiacloprid | 0.5 | 10 |
| Trifloxystrobin | 0.1 | 10 |

## 4.5 Monitoring Results

Monitoring started on the 1st of October 2009 up until the end of February 2010. This coincides with the peak pesticide application period in the catchment. Sampling commenced again for a period of a month (i.e. end of August to end of September) to coincide with the end of the rainy season and the start of pesticide application.

In general the frequency of detection of pesticides for all sites was relatively low, and only seven of the sixteen pesticides analysed for were detected. These were azinphos-methyl, carbaryl, carbendazim, chlorpyrifos, dimethomorph, methyl parathion and prothiofos. In general pesticides were seldom detected in the water phase (23 total detections across all sites). Overall the most commonly detected pesticides in this phase were carbendazim, carbaryl, chlorpyrifos and dimethomorph. Pesticides were more frequently detected in the sediment phase (75 detections across all sites), the most commonly detected being, azinphos-methyl, chlorpyrifos, prothifos and methyl parathion. All of the above-mentioned comprise six of the seven most applied pesticides in the catchment (the exception being mancozeb which could not be analysed for), and contamination would therefore seem to be closely linked to the overall quantity of pesticides applied in the catchment. Similarly, of the nine pesticides not detected, seven were applied in comparatively low quantities, particularly propiconazole, cyfluthrin, alpha-cypermethrin, cypermethrin and trifloxystrobin (Table 26).

The generally low frequency of detection for all pesticides in the catchment is not surprising. As pesticide transport is event driven (i.e. as a result of spraying or rainfall in the catchment), resulting pesticide concentrations are often transient and generally occur in peaks for a relatively short time period after the event (Holvoet *et al.,* 2007). Although designing monitoring programmes to take place during expected peak transport periods (i.e. during the

spraying and runoff seasons) is likely to improve the programmes ability to detect pesticide levels, weekly routine sampling may often miss these peaks and result in non-detectable concentrations, particularly in small catchments (Crawford, 2004; Holvoet et al., 2007).

With respect to contamination at the individual sites, there appears to be a difference in the level of contamination. Of the four tributary sites, BB7 and VW were the least contaminated, with five and three different pesticides being detected in the water phase, respectively, each at low frequencies of occurrence (Table 29 and Table 32). While these pesticides were detected more frequently in the sediment phase (Table 34 and Table 37), the frequency of detection was still lower than for other sites. In contrast sites C and LG4 were more heavily contaminated, with five and seven different pesticides detected in the water phase at each site at comparatively high frequencies of detection (Table 30 and Table 31). All seven pesticides were detected at site LR, representative of the entire catchment (Table 33 and Table 38).

**Table 29:** Concentrations of pesticides detected in water (µg/ℓ) samples collected from Site BB7 in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | **<0.5** | nd | nd | nd | nd | **<0.5** | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 11/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 30** Concentrations of pesticides detected in water (µg/ℓ) samples collected from Site C in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | **<0.5** | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 11/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 31:** Concentrations of pesticides detected in water (µg/ℓ) samples collected from Site LG4 in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<0.05** | **<0.1** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | **0.5** | **0.06** | nd | nd | nd | **<0.5** | nd | nd | nd | nd | **<0.1** | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | **<0.5** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 11/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **0.2** | nd | **0.2** |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 32:** Concentrations of pesticides detected in water (µg/ℓ) samples collected from Site VW in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | **0.1** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 11/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 33:** Concentrations of pesticides detected in water (µg/ℓ) samples collected from Site LR in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | **<0.05** | nd | nd | nd | **<0.5** | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | **<0.5** | **<0.05** | nd | nd | nd | **<0.5** | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 11/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | **0.1** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 34:** Concentrations of pesticides detected in sediment (µg/kg) samples collected from Site BB7 in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd | nd | nd |
| 10/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 12/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 35:** Concentrations of pesticides detected in sediment (µg/kg) samples collected from Site C in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | **<10** | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 07/10/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 15/10/2009 | nd | **<10** | nd | nd | **<10** | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 05/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 10/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 12/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 36:** Concentrations of pesticides detected in sediment (µg/kg) samples collected from Site LG4 in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | **10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 07/10/2009 | nd | **10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 15/10/2009 | nd | **<10** | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 05/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | **10** | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 20/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | **<10** | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 12/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<0.10** | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 37:** Concentrations of pesticides detected in sediment (µg/kg) samples collected from Site VW in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | **10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 12/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 38:** Concentrations of pesticides detected in sediment (µg/kg) samples collected from Site LR in the Lourens River catchment during 2009/2010 (nd: pesticide was not detected; < indicates that the pesticide was detected at levels below the limits of quantification).

| Date | aCYP | AZP | CAP | CAR | CBZ | CPF | CYF | CYP | DIM | aEND | bEND | END | FLZ | PAR | PCZ | PTF | TCP | TXB |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/10/2009 | nd | **10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 07/10/2009 | nd | **<10** | nd | nd | **<10** | **10** | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd |
| 15/10/2009 | nd | nd | nd | nd | **<10** | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | **<10** | nd | nd |
| 21/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 30/10/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 05/11/2009 | nd | 10 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 10/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 26/11/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd | nd | nd |
| 24/12/2009 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **20** | nd | nd | nd | nd |
| 06/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 21/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 28/01/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd |
| 04/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | **10** | nd | nd | nd | nd |
| 12/02/2010 | nd | nd | nd | nd | 10 | nd | nd | nd | nd | nd | nd | nd | nd | **<10** | nd | nd | nd | nd |
| 18/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 24/02/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 20/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/08/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 15/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 23/09/2010 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

Partitioning between the sediment and water phase could largely be explained by the physicochemical properties of the pesticides. Pesticides with $K_{OC}$ values higher than 1000 were found almost exclusively in the sediment phase (i.e. azinphos-methyl, chlorpyrifos, flusilazole, methyl parathion and prothiofos), while those below 1000 were found almost exclusively in the water phase (i.e. carbaryl and dimethomorph) (Table 39). Carbendazim was detected in both the sediment and water phase (in relatively equal proportions). Physicochemical properties of pesticides can vary significantly depending on climatic and soil conditions. Most data on physicochemical properties of pesticides is collected in Europe and North America (i.e. northern, temperate climates). There is often a degree of reservation about using data from more temperate climates as the behaviour of pesticides in the terrestrial ecosystems of southern hemisphere countries can be different due to the inherently diverse chemical properties of soils. Combinations of the chemical properties as well as site-specific conditions determine the fate and behaviour of pesticides (Daam and Van den Brink, 2010). These conditions vary greatly among different agroecological zones making the direct extrapolation of data between geographical regions very challenging (Ahmed and Kookana, 2007). A study on the behaviour of three pesticides in South African soils reported similar $K_{OC}$ values to those reported in the international literature, while half-lives were generally longer in South African soils (Meinhardt, 2009). The partitioning of pesticides sampled and comparison to international $K_{OC}$ values suggests that this overseas data provides a relatively good indication of pesticide behaviour in soils of the Western Cape.

**Table 39:** Summary of the distribution of detections of eight pesticides detected in the Lourens River catchment.

| Active Ingredient | Total Detections | % Water | % Sediment | KOC |
|---|---|---|---|---|
| Azinphos-methyl | 20 | 0 | 100 | 1000 |
| Carbaryl | 4 | 100 | 0 | 211 |
| Carbendazim | 17 | 53 | 47 | 225 |
| Chlorpyrifos | 8 | 25 | 75 | 8151 |
| Dimethomorph | 5 | 100 | 0 | 348 |
| Flusilazole | 2 | 0 | 100 | 1664 |
| Methyl-parathion | 15 | 7 | 93 | 5100 |
| Prothiofos | 25 | 0 | 100 | 24158 |

### 4.6 References

AHMED R and KOOKANA RS (2007) *Geographical extrapolation of pesticide environmental fate data: challenges, risks and opportunities.* In: Rational Environmental Management of Agrochemicals. American Chemical Society. **966**: 100-119.

CRAWFORD CG (2004) Sampling strategies for estimating acute and chronic exposures of pesticides in streams. *Journal of the American Water Resources Association.* **40** (2): 485-502.

DAAM M and VAN DEN BRINK (2010) Implications of differences between temperate and tropical freshwater ecosystems for the ecological risk assessment of pesticides. *Ecotoxicology* **19**(1): 24-37.

HOLVOET KMA, SEUNTJENS P, VANROLLEGHEM PA (2007) Monitoring and modelling pesticide fate in surface waters at the catchment scale. *Ecological Modelling.* **209:** 53-64.

FOOTPRINT (2010) The FOOTPRINT Pesticide Properties Database. http://www.eu-footprint.org/ppdb.html. Last Accessed: [January 2010].

MEINHARDT HR (2009) Evaluation of predictive models for pesticide behaviour in South African soils. PhD Thesis. North-West University.

# 5. RISK INDICATOR APPLICATION

The methodology presented in Section 3 was applied to the Lourens River catchment with the objective being to calculate a PUI, PeXI and PeRI for each sub- catchment (BB7, C, LG4 and VW) and for the entire catchment (LR). As detailed pesticide application and geographical data were available, the most detailed level of each index was calculated (i.e. PUI_3, PeXI_3 and PeRI_3). Outputs of the PUI and PeXI were compared with monitoring data (described in Chapter 3) in an attempt to validate the relative effectiveness of each index (i.e. the ability to predict the relative mobility and thus occurrence of pesticides in water samples collected at each sampling site over the course of the field monitoring study). This comparison was done for each site as well as across sites. While the PeRI, relies on inputs from the PUI and PeXI, the index itself cannot be validated in this study as it provides an indication of ecological risk to the aquatic ecosystem. The PeRI can therefore only be validated by means of conducting laboratory or field-based bioassays using aquatic organisms as test species.

## 5.1 PUI_3

A PUI_3 was determined for all sites in the catchment. Derivation of the total amount of active ingredient applied per crop per sub-catchment is explained in Section 3. Azinphos-methyl application in sub-catchment BB7 was the highest of all applied active ingredients across all sub-catchments (169.9 kg). Thus, pesticide use categories for each active ingredient were expressed as a ratio of 169.9. For the catchment site (LR) azinphos-methyl was also the highest applied pesticide and the PUI score was therefore expressed as a ratio of 665.

### *5.1.1 Results*

Based on the PUI score, sub-catchment BB7 and C show the highest scores, with a number of pesticides falling in the High category (Figure 4). Sites LG4 and VW are predicted as being less contaminated with fewer pesticides falling in the High category. Azinphos-methyl, chlorpyrifos, carbendazim and dimethomorph were consistently among the pesticides with high PUI scores per sub-catchment. Likewise beta-cyfluthrin, cypermethrin, flufenoxuron, propiconazole and trifloxystrobin were consistently in the lower Medium or Low category across all sites. This pattern was similar for site LR (catchment scale – Figure 5). Raw data for calculation of the PUI is included in the Appendix. Interpretation of the PUI scores in relation to field monitoring data is described in Section 6 with a comparison to the PeXI scores.

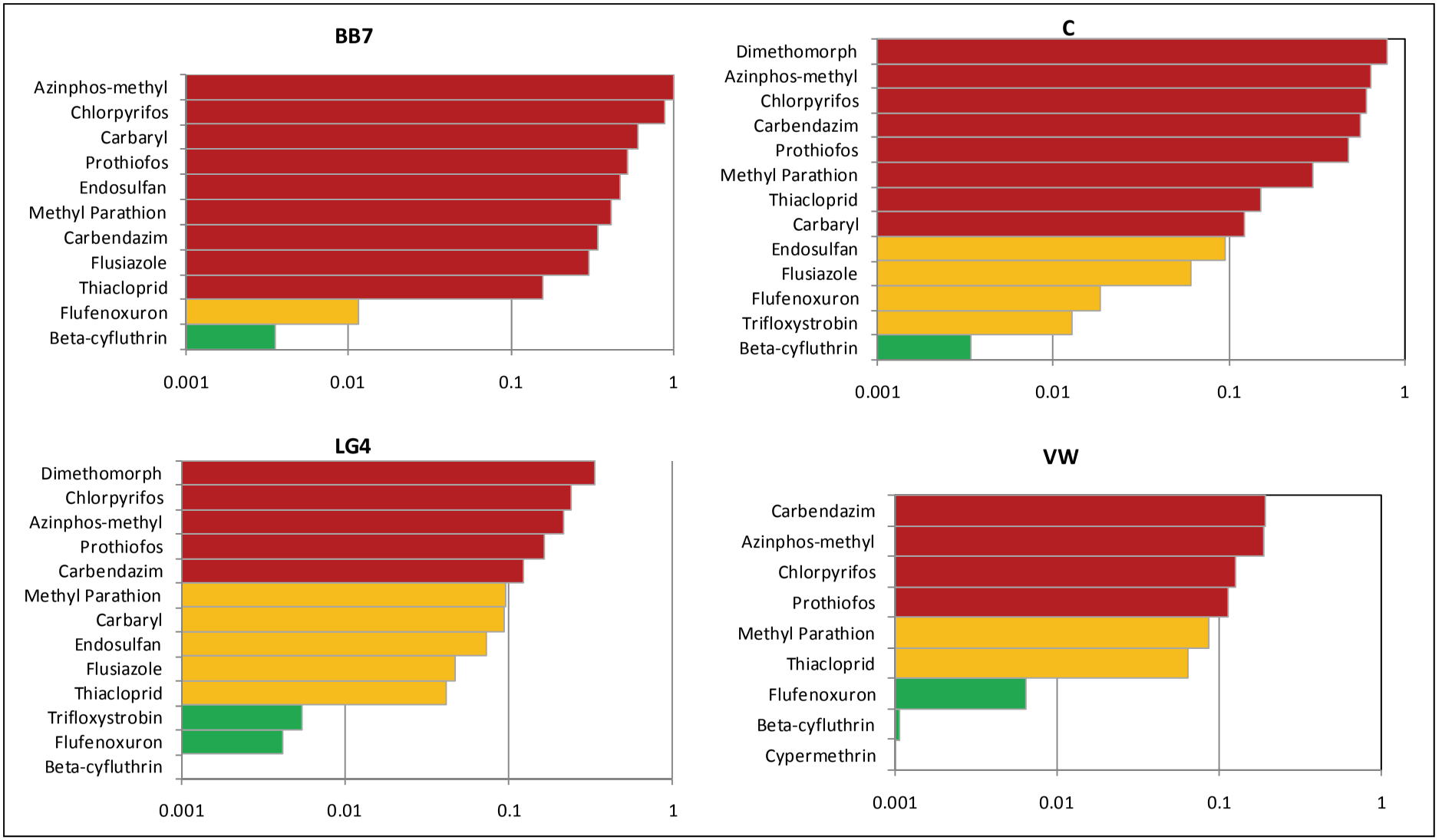



**Figure 4:** Pesticide Use Index (PUI) scores for pesticides applied in four sub-catchments (BB7, C, LG4 and VW) in the Lourens River catchment.

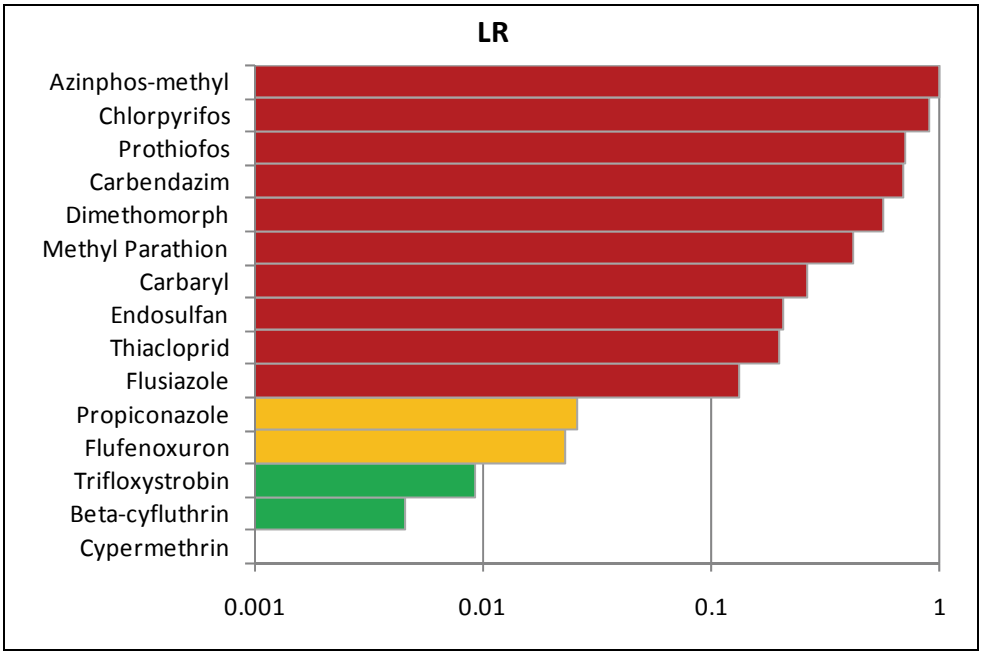



**Figure 5:** Pesticide Use Index (PUI) scores for pesticides applied in the Lourens River catchment.

## 5.2 PeXI_3 (Lourens river)

The PeXI was calculated using the spray drift and runoff models described in Section 3. This section describes how data was collected and analysed and integrated to provide the final PeXI score for each sampling site.

### *5.2.1 Spray Drift*

#### 5.2.1.1 Pesticide Use Data

A PeXI_3 was calculated using the pesticide use data (PEU_3) used to calculate the PUI_3.

#### 5.2.1.2 Geographical Data

Geographical data (i.e. shapefiles) were analysed using ArcGIS 9.3. Orchards were digitised previously (Dabrowski and Schulz, 2003). This orchard shapefile was ground-truthed through a field survey. A number of fields that were previously fruit orchards had changed to grape orchards and were corrected within GIS. The spray drift model (Section 3) requires the distance (buffer zone) of a crop/orchard from an adjacent water body. Various buffer zone distance categories were created for each river stretch in the catchment using GIS (Figure 6). Buffer distances were 5, 7.5, 10, 15, 20, 30 and 40 m (i.e. it was assumed that 40 m is the maximum distance at which contamination would occur). This enabled the identification and selection of orchards falling within each of the buffer distance categories (Figure 6). Only orchards directly adjacent to river reaches fell within any of the afore-mentioned buffer zone widths. Thus only these orchards (together with their associated buffer zone width) and the pesticides applied to them were used as input into the spray drift component of the PeXI.

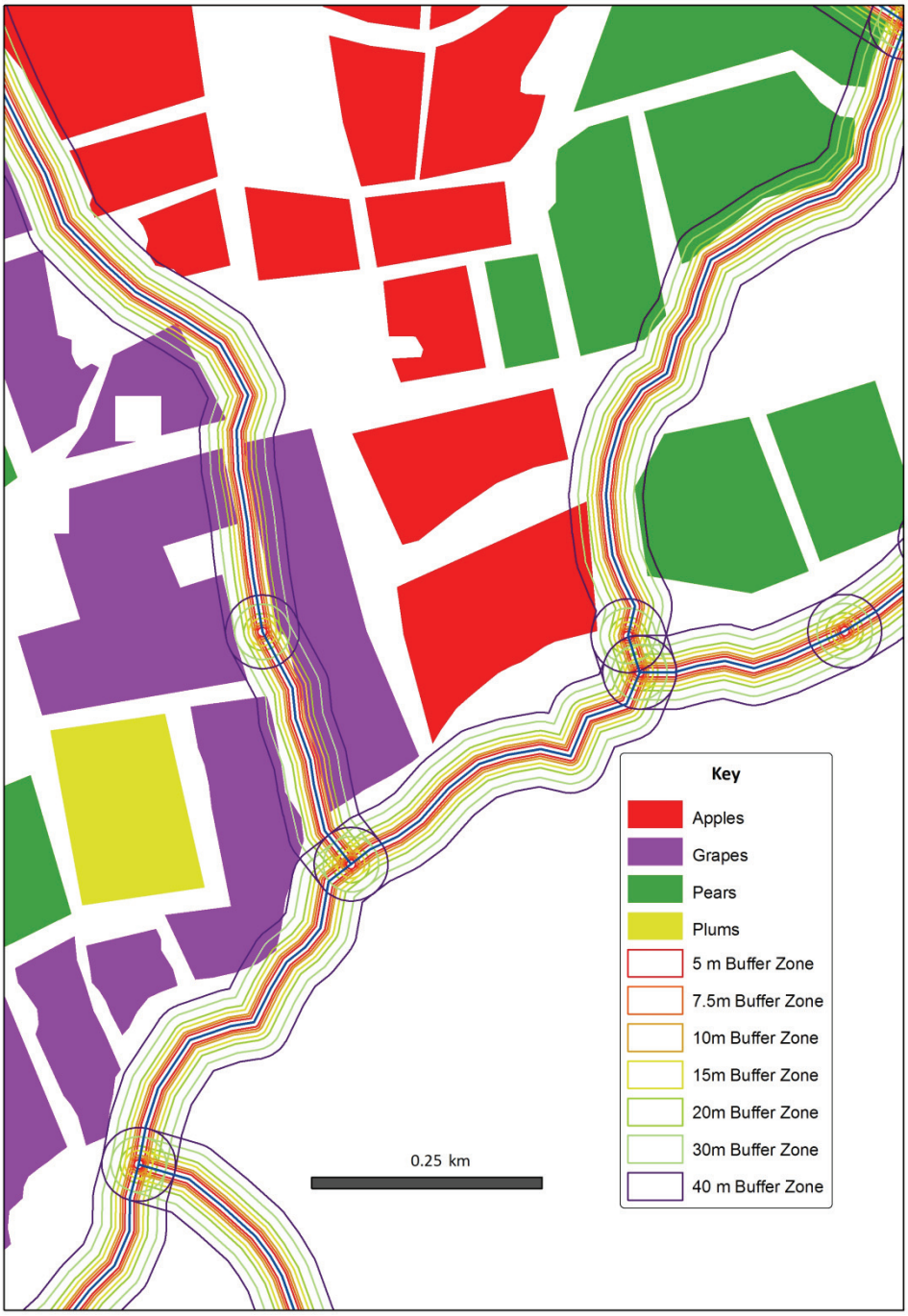



**Figure 6:** Extract from a map illustrating the use of various buffer zone widths to identify the proximity of different crop types to river reaches in the Lourens River catchment.

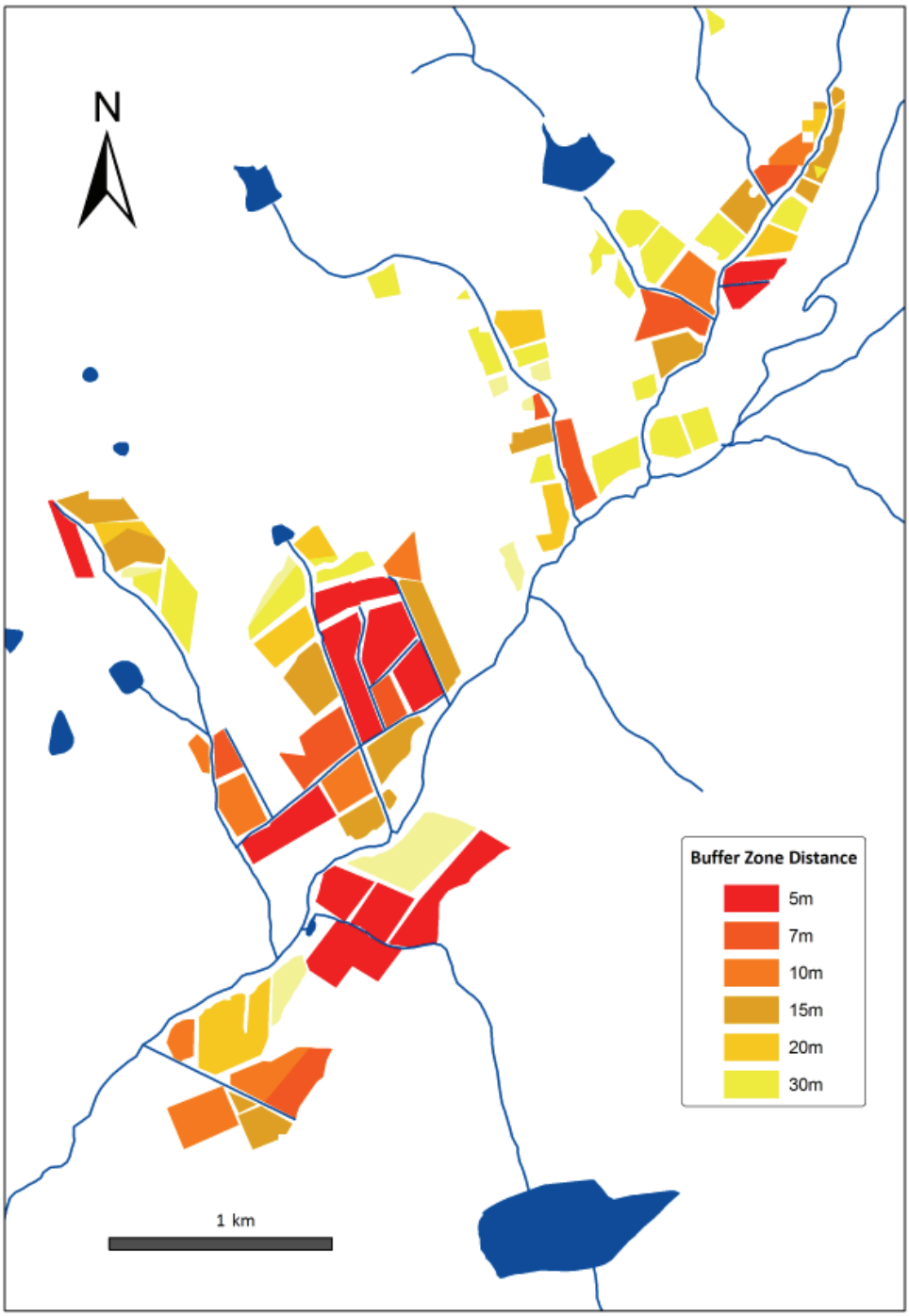



**Figure 7:** Buffer zone widths of orchards included for purposes of calculating the spray drift component of the Pesticide Exposure Index (PeXI) for the Lourens River catchment.

5.2.1.3 Aggregation of Data.

For each field, the total loss of active ingredient per crop type was calculated using the spray drift formula in Section 3. The distance measurement included in the equation was equivalent to the buffer zone width in which the field fell. For each sub-catchment the total loss of each active ingredient was calculated by summing the loss of each pesticide per crop type. For each crop type, the total loss of each active ingredient was multiplied by the Water Index to obtain a final loss (kg) per crop type. The water index (Table 40) was expressed as

a ratio of the total river length adjacent to the crop to the total perimeter of the crop adjacent to the river, and was calculated with the aid of ArcGIS. The total loss of each active ingredient was then calculated by summing the total loss for each crop type (i.e. for those active ingredients applied to more than one crop type).

**Table 40:** The Water Index for each orchard type for each sampling site used as input into the calculation of the spray drift and runoff component of the Pesticide Exposure Index (PeXI).”–“ indicates that the crop type was not present in the catchment.

| Site | Apples | Pears | Grapes | Plums |
|---|---|---|---|---|
| **BB7** | 0.25 | 0.38 | - | - |
| **C** | 0.133 | 0.25 | 0.16 | - |
| **LG4** | 0.27 | 0.2 | 0.3 | - |
| **VW** | - | 0.17 | - | 0.17 |
| **LR** | 0.22 | 0.25 | 0.23 | 0.17 |

### *5.2.2 Runoff Data*

#### 5.2.2.1 Geographical Data

A digital elevation model (DEM) for the catchment area was transformed into slope categories using Spatial Analyst in ArcGIS 9.3 (Figure 8). Only orchards directly adjacent to river reaches were included for analysis in the calculation of the runoff component of the PeXI. For each field, the orchard area was over-layed with the slope profile, so as to generate a shapefile containing a description of crop type and slope (percentage). As some fields would cover more than one slope category, these fields were sub-divided into smaller field segments, each with its own unique slope category.

#### 5.2.2.2 Rainfall Data: Quantity and timing

Calculation of the runoff component of the PeXI required input of the quantity of typical rainfall events and the timing of these events in relation to pesticide application. It is assumed here that runoff will only physically take place during rainfall events in excess of 10 mm. Thus, rainfall data from a weather station in the catchment was assessed over a number of years. The average rainfall for all events above 10 mm was calculated. In this instance the average was 20 mm. The total length of the spraying season is approximately 210 days (i.e. from beginning of August to the end of February). During this time an average of ten rainfall events in excess of 10 mm are expected to occur. The rainfall interval is thus 20 days (i.e. one rainfall event every 20 days). The number of days an application took place after a rainfall event was calculated as the median of the rainfall interval (i.e. 10 days). Considering the rainfall interval of 20 days, a rainfall event could occur at least 0 days after a spraying event or at the most 20 days after the spraying event. Thus the median of this interval was chosen as the median number of days for a rainfall event to occur after application.

The tables developed by Lutz and Maniak (Appendix 2) were used to obtain the Q value corresponding to the average rainfall for events above 10 mm for this catchment (i.e. 20 mm). The Q value used for input into the runoff equation was therefore 4.93. (Loamy bare soil with high soil moisture). The organic carbon content of the soil was assumed to be 0.75%. The plant interception factor was assumed to be 80% (i.e. 80% of the applied substance lands on the crop). A buffer width of 0 m was used as input as throughout the

catchment, deep erosion rills provide a direct pathway between orchards and adjacent water bodies, thus making the effectiveness of any vegetated buffer strip negligible.

**Table 41:** Values used for the input variables for the calculation of the runoff component of the Pesticide Exposure Index (PeXI).

| Input Variable | Value |
|---|---|
| *P* (precipitation amount) | 20 mm |
| *Q* (runoff amount) | 4.93 |
| *% $OC_{soil}$* | 0.75 |
| *PI* (Plant Interception) | 80% |
| *n* (number of days after application) | 10 days |
| *BZW* (buffer zone width) | 0 m |

5.2.2.3 Physicochemical and Use Data

Pesticide physicochemical data was obtained from the EU-Footprint database (FOOTPRINT, 2010 – Table 42). This is a European database and it is important to note that the physicochemical properties of the same pesticides may be different in South African conditions. However this data is not freely available and in many instances the necessary trials have not even been performed in South Africa.

**Table 42:** Physicochemical properties of pesticides applied in the Lourens River catchment during 2009/2010.

| Active Ingredient | CAS No. | Half life (days) | Solubility (mg/l) | KOC |
|---|---|---|---|---|
| Alpha-cypermethrin | 67375308 | 35 | 0.004 | 57889 |
| Azinphos-methyl | 86-50-0 | 10 | 28 | 1000 |
| Beta-cyfluthrin | 68359375 | 13 | 0.0012 | 64300 |
| Captan | 133062 | 0.8 | 5.2 | 97 |
| Carbaryl | 63252 | 16 | 9.1 | 211 |
| Carbendazim | 10605-21-7 | 22 | 8 | 223 |
| Chlorpyrifos | 2921-88-2 | 50 | 1.05 | 8151 |
| Cypermethrin | 52315078 | 60 | 0.009 | 85572 |
| Dimethomorph | 110488705 | 57 | 28.95 | 348 |
| Endosulfan | 115-29-7 | 50 | 0.32 | 11500 |
| Flusilazole | 85509-19-9 | 300 | 41.9 | 1664 |
| Methyl Parathion | 298000 | 12 | 55 | 5100 |
| Propiconazole | 60207901 | 214 | 150 | 1086 |
| Prothiofos | 34643464 | 45 | 0.07 | 24158 |
| Thiacloprid | 111988499 | 15.5 | 184 | 615 |
| Trifloxystrobin | 141517217 | 7 | 0.61 | 2377 |

5.2.2.4 Aggregation of Data

For each field segment (i.e. field with a specific slope category), the total loss of active ingredient per crop type was calculated using the runoff formula in Section 3. For each sub-catchment the total loss of each active ingredient was calculated by summing the loss per crop type. For each crop type, the total loss of each active ingredient was multiplied by the Water Index (Table 40) to obtain a final loss (kg) per crop type. The total loss of each active ingredient was then calculated by summing the total loss across each crop type (i.e. for those active ingredients applied to more than one crop type).

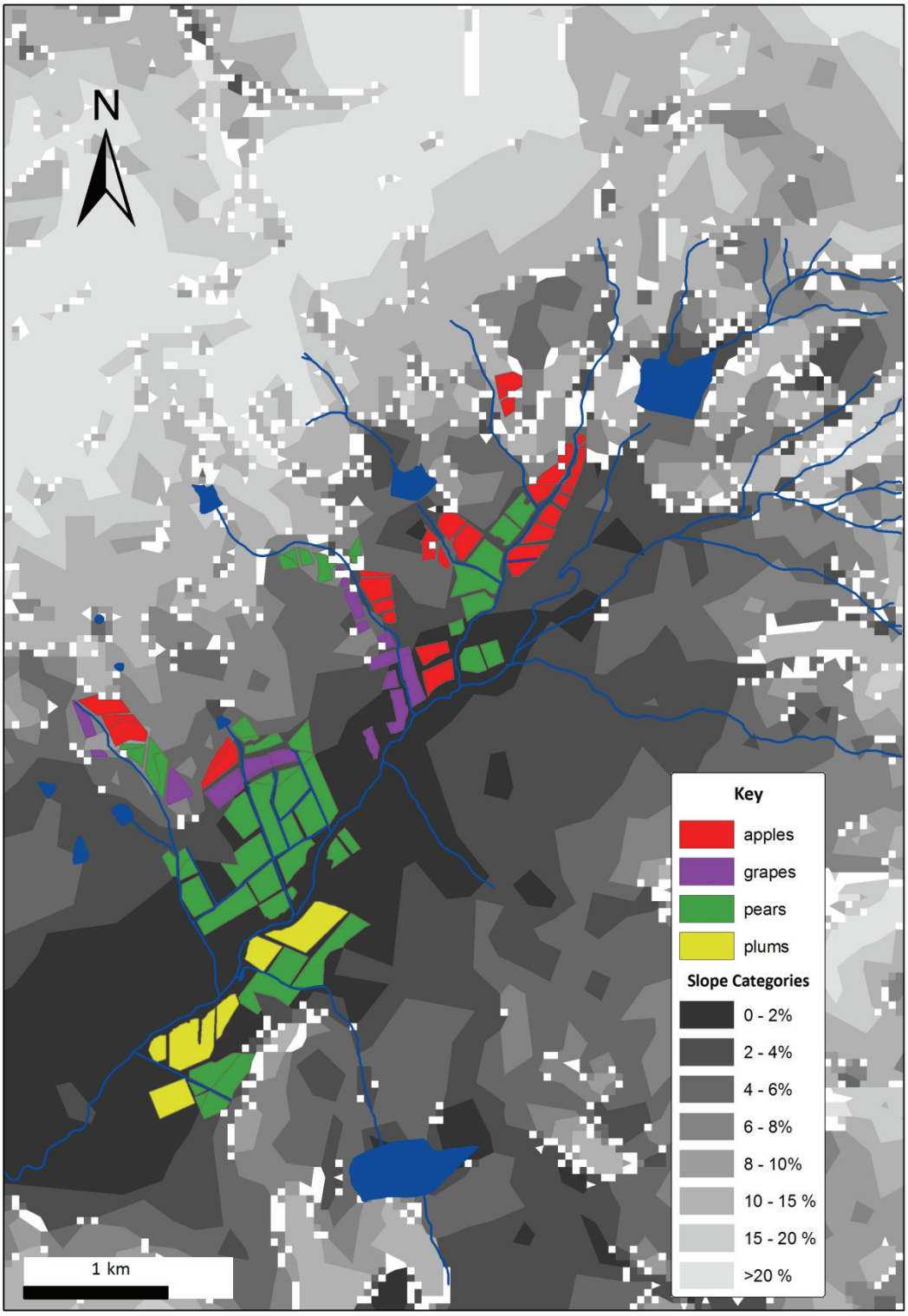



**Figure 8:** Map showing orchards and associated slope categories for calculation of the runoff component of the Pesticide Exposure Index (PeXI) in the Lourens River catchment.

### *5.2.3 Total PeXI Score*

For each sub-catchment the total loss of active ingredient associated with spray drift and runoff was summed to provide a final estimate of pesticide loss (i.e. PEL). The PEC for each pesticide in sub-catchment was calculated based on the equation in Section 3, using discharge data in Table 43 as input. The pesticide with the highest PEC was dimethomorph at site LG4 (176.94 µg/ℓ, Appendix4). Thus all PEC values for all pesticides in each sub-catchment as well as those at LR were divided by 176.94 so as to obtain the final PeXI scores for each pesticide. The pesticides at each sampling site were categorised according to the structure in Table 44.

**Table 43:** Hydrological characteristics of tributaries (BB7, C, LG4 and VW) and the Lourens River (LR).

| Site | Length (m) | Width (m) | Depth (m) | Discharge ($m^3/s$) |
|---|---|---|---|---|
| **BB7** | 3910 | 2 | 0.4 | 1.5 |
| **C** | 3648 | 1.5 | 0.35 | 0.29 |
| **LG4** | 1858 | 1.5 | 0.2 | 0.08 |
| **VW** | 1200 | 1.8 | 0.3 | 0.89 |
| **LR** | 3010 | 5.5 | 0.75 | 4 |

**Table 44:** Pesticide Exposure Index (PeXI) intervals used to determine the mobility category for pesticides applied in a) sub-catchments and b) the entire catchment of the Lourens River.

| Exposure Category | PeXI Score |
|---|---|
| High | > 0.1 |
| Medium | 0.01-0.1 |
| Low | <0.01 |

For each sub-catchment the active ingredient was assigned to a category based on its PeXI score, the results of which are displayed in Figure 9. By calculating both the runoff and spray drift component of the PEL, it is possible to illustrate which transport pathway is the most important with respect to contamination of the water resource Figure 10. This could provide important information with regards to implementing mitigation measures aimed at reducing the input of highly mobile or high risk pesticides. The PeXI scores and relative contribution of runoff and spray drift to the PEL for the LR site are displayed in Figure 9.

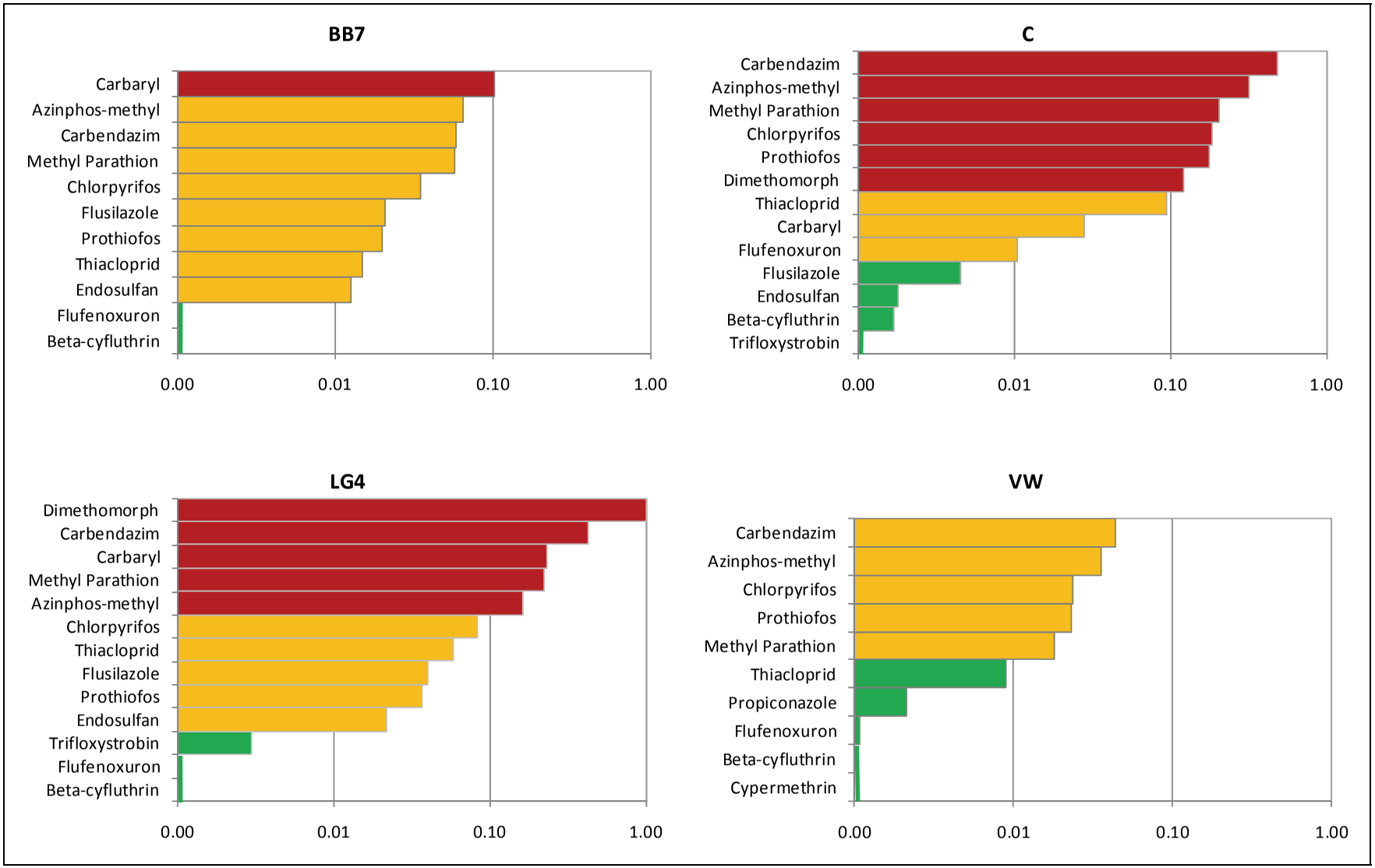



**Figure 9:** Pesticide Exposure Index (PeXI) category for pesticides applied in four sub-catchments (BB7, C, LG4 and VW) of the Lourens River catchment. Red, orange and green bars correspond to High, Medium and Low categories for the PeXI, respectively.

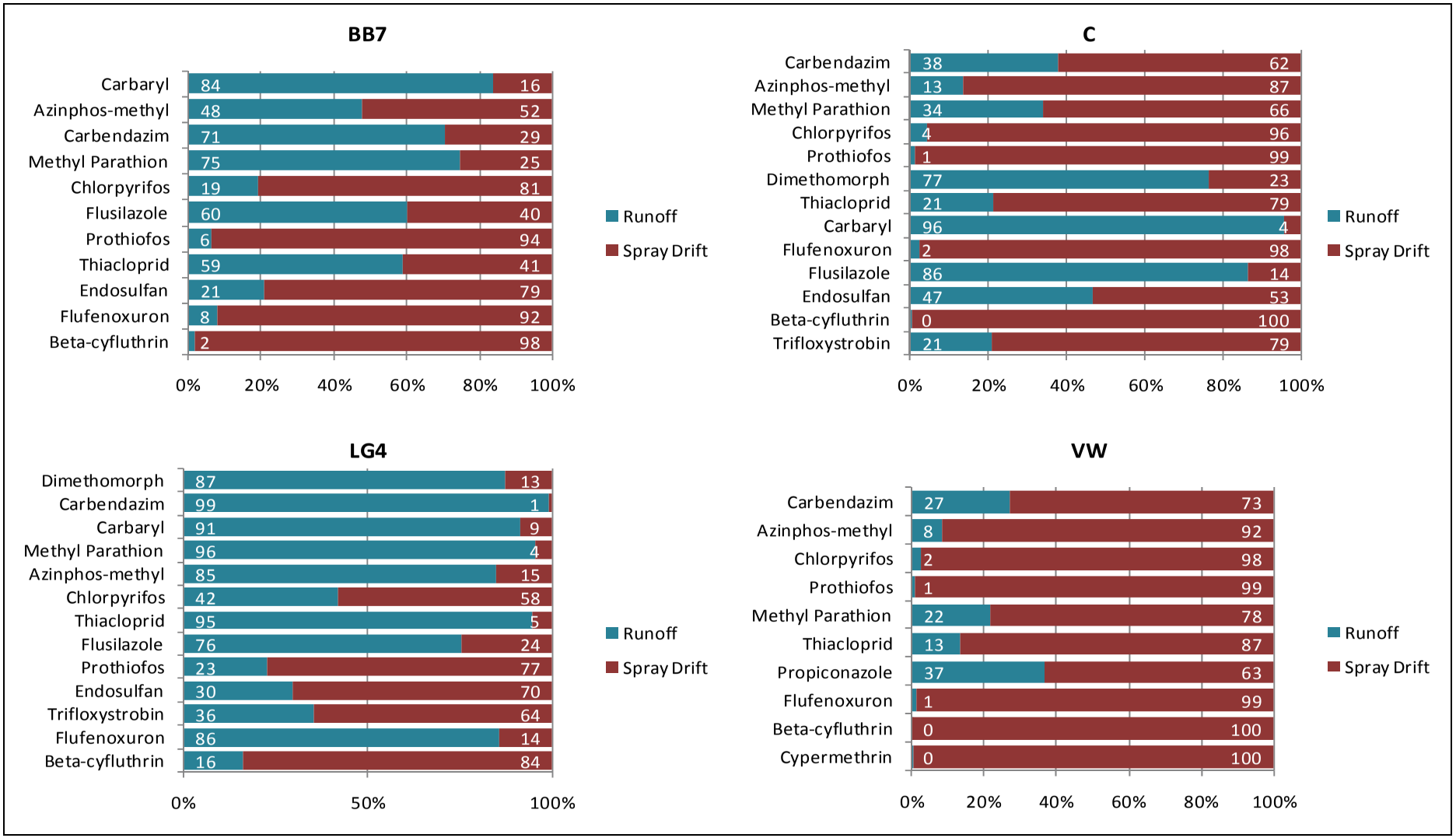



**Figure 10:** Estimated proportion of pesticide loss derived from runoff and spray drift for four sub-catchments (BB7, C, LG4 and VW) of the Lourens River catchment.

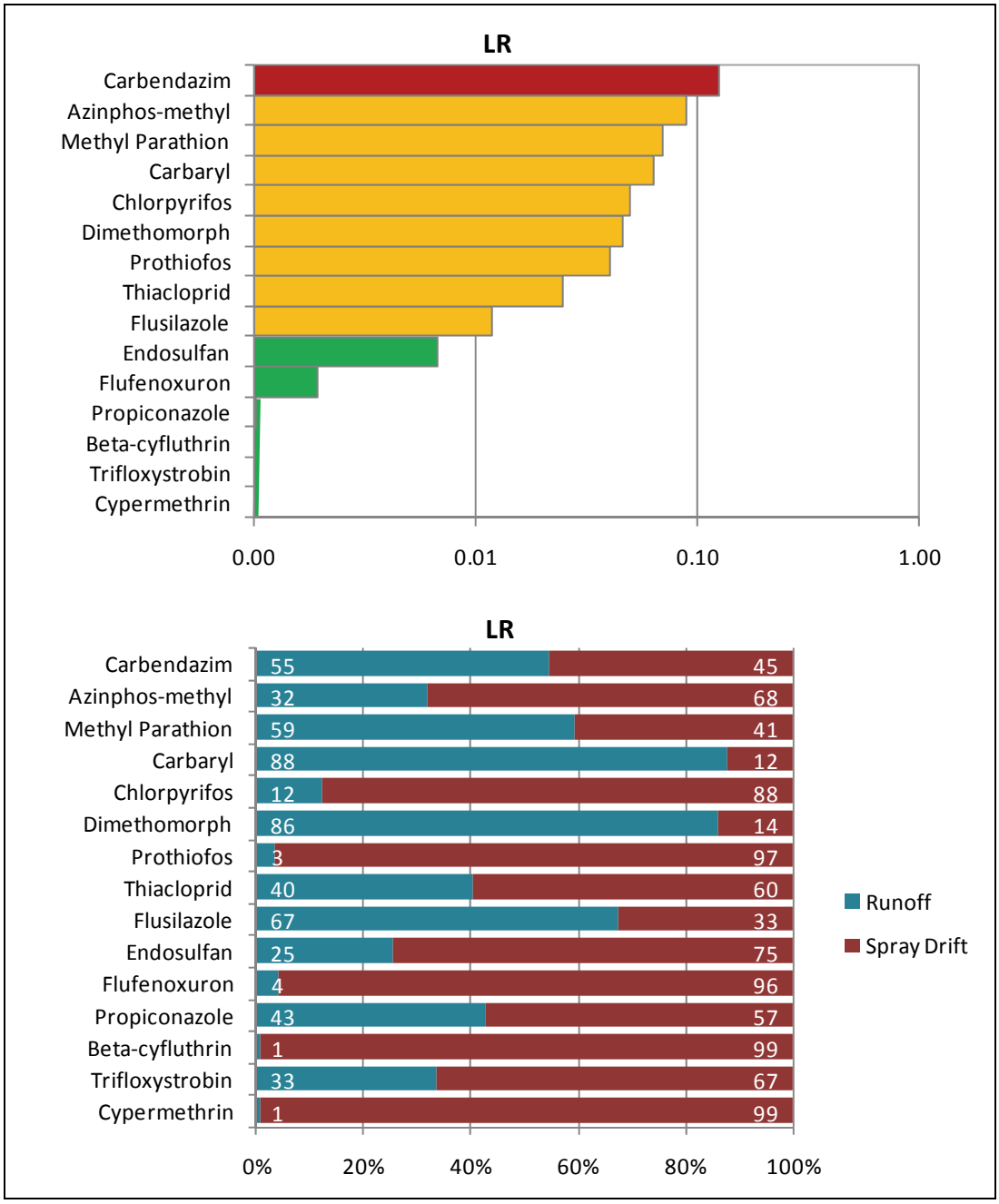



**Figure 11:** Pesticide Exposure Index (PeXI) category for pesticides applied in the Lourens River catchment (left) and the proportion of pesticide loss derived from runoff and spray drift (right).

## 5.3 Toxicity Data

Toxicity data was obtained from the USEPA EcoTox database. SSDs were derived using BurrliOz software (Appendix 3) and the concentration at which 95% of species would be protected was used as the toxicity value for each active ingredient (Table 45). Only LC50 data was used to derive the SSD. For some pesticides, insufficient data was available to construct and SSD. In these instances the PeRI_3 was calculated using LC50 value for *Daphnia magna*. The PeRI_3 was calculated using the method described in Section 3. The PEC for each pesticide in each sub-catchment was divided by the relevant toxicity value to obtain the TER (Toxicity to Exposure Ratio). Chlorpyrifos at site C had the highest TER (190.45) and all TERs for all pesticides in each sub-catchment were divided by this value to

obtain the final PeRI value. These pesticides were assigned a category based on their PeRI score (Table 45) and displayed graphically Figure 12.

**Table 45:** Toxicity values (and the method used to derive the values) used as input into calculation of the Pesticide Risk Index (PeRI).

| Active Ingredient | Pesticide | Toxicity Value (µg/ℓ) | Method |
|---|---|---|---|
| Azinphos-methyl | Insecticide | 0.45 | SSD |
| Beta-cyfluthrin | Insecticide | 0.07 | SSD |
| Carbendazim | Fungicide | 12.18 | SSD |
| Propiconazole | Fungicide | 769.66 | SSD |
| Chlorpyrifos | Insecticide | 0.17 | SSD |
| Carbaryl | Insecticide | 6.14 | SSD |
| Methyl Parathion | Insecticide | 1.31 | SSD |
| Dimethomorph | Fungicide | 620 | LC50 -Daphnia |
| Trifloxystrobin | Fungicide | 27.5 | LC50 -Daphnia |
| Prothiofos | Insecticide | 500 | LC50 -Daphnia |
| Thiacloprid | Insecticide | 30200 | LC50 -Daphnia |
| Cypermethrin | Insecticide | 0.02 | SSD |
| Endosulfan | Insecticide | | SSD |
| Flufenoxuron | Insecticide | 0.043 | LC50 -Daphnia |
| Flusilazole | Fungicide | 1200 | LC50 -Daphnia |

**Table 46:** Pesticide Risk Index (PeRI) intervals used to determine the relative risk category for pesticides applied in the Lourens River catchment.

| Risk Category | PeRI Score |
|---|---|
| High | > 0.1 |
| Medium | 0.01-0.1 |
| Low | <0.01 |

## 5.4 PeRI Score

Whilst there was quite a marked difference in the level of contamination across sites as predicted by the PeXI and validated by field monitoring, from a risk perspective, all sites have pesticides that fall into the High risk category. These pesticides are azinphos-methyl, chlorpyrifos, methyl parathion and flufenoxuron. The high risk of these pesticides is as a result of their relatively high likelihood of transport into surface water (as indicated by their relatively high PeXI scores) and their comparatively high toxicity values (Table 45). Beta-cyfluthrin and cypermethrin both have even higher toxicity (as indicated by their low toxicity concentrations). However both of these pesticides had Low transport potential as reflected by their PeXI scores. Comparing sites, it would appear that site C and LG4 have the highest risk associated with pesticide contamination with four and three pesticides, respectively, falling into the High PeRI category. BB7 and VW also have pesticides falling in the High PeRI category (azinphos-methyl and chlorpyrifos), however the scores were relatively lower than the same pesticides at sites C and LG4. Site VW in particular, would appear to have the lowest risk associated with pesticide contamination with only chlorpyrifos falling in the High category, albeit with a comparatively low PeRI score for this pesticide. This indicates that the toxicity of chlorpyrifos (in particular) and azinphos-methyl is relatively high and differences in transport and hydrological characteristics are not sufficiently different amongst sites to result in large differences in risk amongst sites.

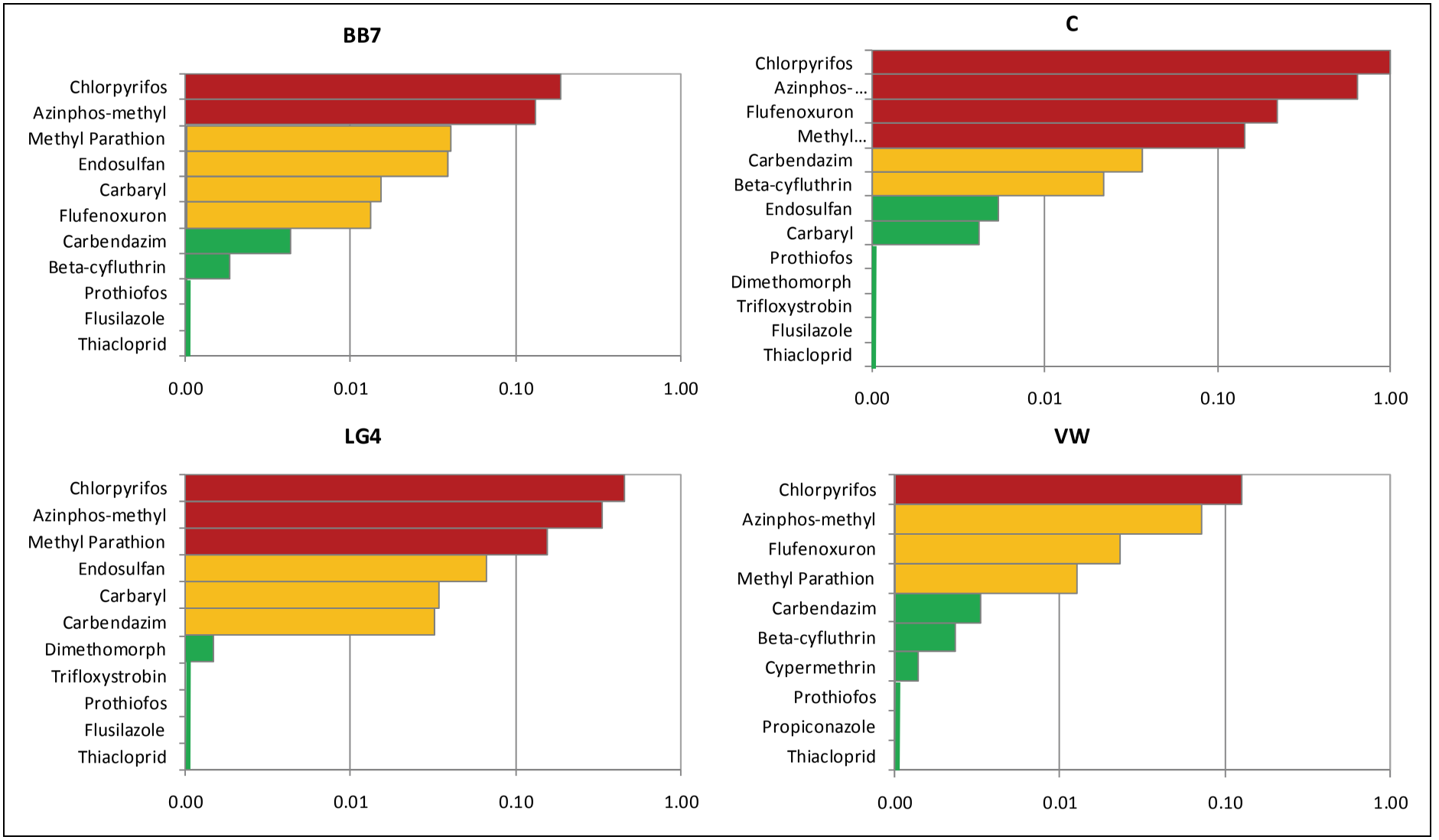



**Figure 12:** Pesticide Risk Index (PeRI) categories for pesticides applied in four sub-catchments (BB7, C, LG4 and VW) of the Lourens River catchment.

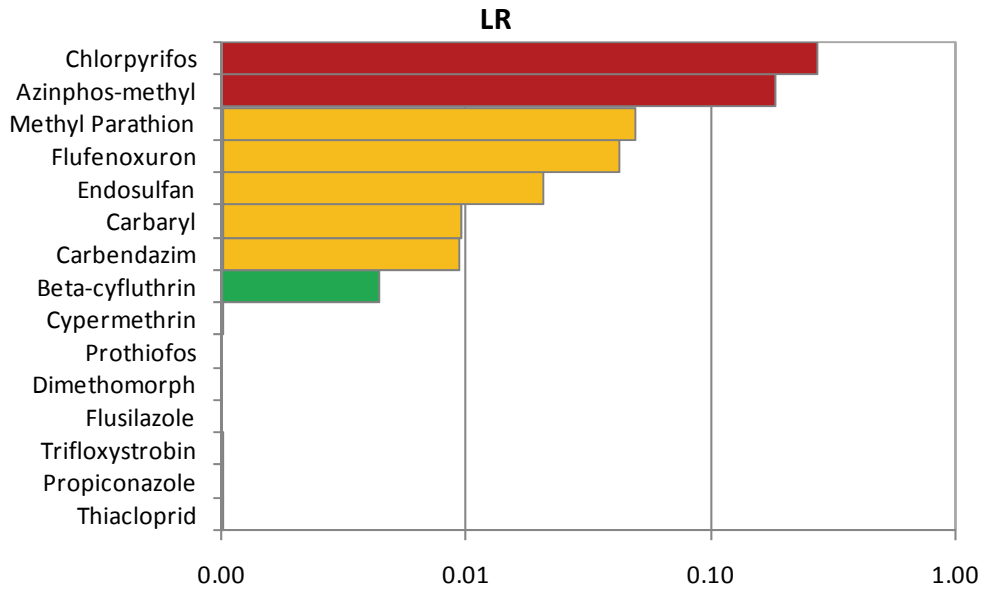



**Figure 12 (cont):** Pesticide Risk Index (PeRI) categories for pesticides applied in the Lourens River catchment.

## 5.5 References

DABROWSKI JM and SCHULZ R (2003) Predicted and measured levels of azinphos-methyl in the Lourens River, South Africa: comparison of runoff and spray drift. *Environ. Toxicol. Chem.* **22**(3): 494-500.

FOOTPRINT (2010) The FOOTPRINT Pesticide Properties Database. http://www.eu-footprint.org/ppdb.html. Last Accessed: [January 2010].

# 6. COMPARISON WITH FIELD DATA

## 6.1 Long-term monitoring data

### *6.1.1 Comparison across sites (hotspot identification)*

Results of the field monitoring exercise have been summarised in Table 47 and Table 48. Comparing the sub-catchment scale sites (BB7, C, LG4 and VW), it is clear that site LG4 and C are more contaminated than sites BB7 and VW. Site LG4 in particular is most contaminated with seven active ingredients detected in the water phase. With regards to sediment, four active ingredients were detected, with azinphos-methyl and methyl-parathion being detected more frequently than at any other site included in the study. This site also showed a comparatively high frequency of detection of prothiofos in the sediment (ten detections). Site C also showed high frequency of detection of azinphos-methyl and prothiofos in the sediment, while carbendazim was detected comparatively regularly in the water phase. In contrast, site BB7 and VW were both comparatively less contaminated, with only two detections in the water phase and fewer detections in the sediment phase than at other sites. This field data is relatively well predicted by the PeXI (Figure 9). The PeXI clearly identifies sites C and LG4 as the highest contaminated sites, with six and five active ingredients, respectively, having a PeXI score falling in the High category. In contrast, only carbaryl at site BB7 was classified as having high exposure potential, whilst all pesticides at VW were classified as having medium or low exposure potential. The fact that a number of pesticides were classified as hiving high potential exposure by the PeXI would imply that contamination at these sites would be relatively higher than at sites BB7 and VW.

### *6.1.2 Site BB7*

This site had only one pesticide that fell into the high category (carbaryl). The PeXI for this particular pesticide was the lowest for all pesticides falling in the same category across all sites and was detected on one occasion in the water phase. Azinphos-methyl, flusilazole, and methy parathion were all detected relatively less frequently than at sites C and LG4 and were all classified as having medium exposure potential. None of the pesticides with PeXI scores in the Low category were detected in routine monitoring. Interestingly, dimethomorph was also detected on one occasion (in the water phase) despite the fact that it is not applied in this sub-catchment. This is most likely as a result of spray drift from a neighbouring sub-catchment or accidental spillage.

### *6.1.3 Site C*

For site C, carbendazim and azinphos-methyl had the highest PeXI scores, and, in comparison to other active ingredients for this site, were detected most frequently in water and sediment, respectively. Carbendazim was also detected on two occasions in sediment. Methyl parathion, chlorpyrifos and prothiofos had comparatively lower PeXI scores, but were also classified as having high exposure potential. Of these active ingredients chlorpyrifos and prothiofos were detected on two and thirteen occasions in the sediment, respectively. Methyl parathion was not detected at this site. Dimethomorph had the lowest PeXI score of those active ingredients in the high category and was detected on one occasion in the water phase. In summary, with the exception of methyl parathion, all of the active ingredients that

were classified as having high exposure potential were detected in water and sediment samples. The two pesticides with the highest PeXI scores were detected most frequently in water and sediment samples. In contrast, none of the active ingredients that fell in the Medium and Low exposure categories were detected in any samples collected during the monitoring exercise.

### *6.1.4 Site LG4*

Dimethomorph applied in the LG4 sub-catchment scored the highest PeXI score for all pesticides included in the index (i.e. 1). However, this pesticide was detected on only one occasion in the water phase at below detection limit concentrations. Carbendazim, carbaryl, methyl parathion and azinphos-methyl were also included in the High category for this sub-catchment. Carbendazim and carbaryl were both detected on two occasions at comparatively high maximum concentrations in the water phase, whilst azinphos-methyl (six detections) and methyl-parathion (seven detections) were detected frequently in the sediment phase (methyl parathion was also detected on one occasion in the water phase at a concentration of <0.1 µg/ℓ). Other active ingredients that were detected in the water phase at this site were chlorpyrifos, prothiofos and trifloxystrobin. These pesticides had comparatively lower PeXI scores, falling in the Medium and Low categories and were detected on only one occasion. Prothiofos was however detected more frequently in the sediment, even more so than azinphos-methyl and methyl-parathion, which scored much higher PeXI scores. This may be as a result of the comparatively high half-life of prothiofos (45 days). Furthermore this stream also had the lowest discharge of all streams monitored, potentially reducing the potential for contaminated sediment to be washed away. Thus the combination of high half-life and low stream discharge could potentially result in this specific pesticide being present in the sediment for a comparatively long period of time, resulting in a high observed frequency of detection. In summary, pesticides that had high PeXI scores were also frequently detected during field monitoring. The exception to this was dimethomorph, which was only detected on one occasion (i.e. similar to those pesticides that fell in the medium PeXI category). Comparatively fewer of the Medium category and none of the Low category pesticides were detected during field monitoring exercises.

### *6.1.5 Site VW*

Similar to site BB7 this site also showed relatively low contamination, with only two detections in the water phase (carbendazim and chlorpyrifos) and a relatively low number of detections in the sediment. All pesticides in this sub-catchment had PeXI scores that fell in the Medium and Low categories – none of the pesticides in the Low category were detected. Of all the pesticides included in the analysis for site VW, carbendazim and chlorpyrifos had the highest and third highest PeXI scores. These pesticides were detected more frequently in the water and sediment phase than any other pesticide applied in this sub-catchment. Azinphos-methyl, with the second highest PeXI score was detected on one occasion in the sediment.

### *6.1.6 Site LR*

Site LR had only one pesticide with a PeXI score falling in the high category (carbendazim). This pesticide, together with methyl parathion was detected most frequently, with three detections in each of the water and sediment phases. Apart from methyl parathion all other pesticides detected at this site were detected less frequently.

**Table 47:** Summary of pesticide concentrations detected in water samples collected in the Lourens River.

| Active Ingredient | BB7 | | | C | | | LG4 | | | VW | | | LR | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max |
| α-CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| AZP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAR | **1** | **<0.5** | **<0.5** | nd | nd | nd | **2** | **<0.5** | **0.5** | nd | nd | nd | **1** | **<0.5** | **<0.5** |
| CBZ | nd | nd | nd | **3** | **<0.05** | **<0.05** | **2** | **<0.05** | **0.06** | **1** | **<0.05** | **<0.05** | **3** | **<0.05** | **<0.05** |
| CPF | nd | nd | nd | nd | nd | nd | **1** | **<0.1** | **<0.1** | **1** | **0.1** | **0.1** | nd | nd | nd |
| CYF | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| DIM | **1** | **<0.5** | **<0.5** | **1** | **<0.5** | **<0.5** | **1** | **<0. 5** | **<0. 5** | nd | nd | nd | **2** | **<0.5** | **<0.5** |
| α-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| β-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| FLZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PAR | nd | nd | nd | nd | nd | nd | **1** | **<0.1** | **<0.1** | nd | nd | nd | nd | nd | nd |
| PCZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PTF | nd | nd | nd | nd | nd | nd | **1** | **0.2** | **0.2** | nd | nd | nd | nd | nd | nd |
| TCP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| TXB | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

**Table 48:** Summary of pesticide concentrations detected in sediment samples collected in the Lourens River.

| Active Ingredient | BB7 | | | C | | | LG4 | | | VW | | | LR | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max | n | Min | Max |
| α-CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| AZP | **4** | **<10** | **<10** | **6** | **<10** | **<10** | **6** | **<10** | **10** | **1** | **<10** | **<10** | **3** | **5** | **10** |
| CAP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CAR | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CBZ | nd | nd | nd | **2** | **5** | **5** | **1** | **<10** | **<10** | **2** | **<10** | **10** | **3** | **<10** | **10** |
| CPF | nd | nd | nd | **2** | **5** | **5** | nd | nd | nd | **3** | **<10** | **<10** | **1** | **10** | **10** |
| CYF | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| CYP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| DIM | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| α-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| β-END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| END | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| FLZ | **1** | **<10** | **<10** | nd | nd | nd | nd | nd | nd | **1** | **<10** | **<10** | nd | nd | nd |
| PAR | **1** | **20** | **20** | nd | nd | nd | **7** | **<10** | **20** | nd | nd | nd | **6** | **<10** | **20** |
| PCZ | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| PTF | **2** | **<10** | **10** | **13** | **<10** | **10** | **10** | **<10** | **20** | **1** | **20** | **10** | **2** | **<10** | **<10** |
| TCP | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| TXB | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |

α-CYP: alpha-cypermethrin
AZP: azinphos-methyl
CAP: captan
CAR: carbaryl
CBZ: carbendazim
CPF: chlorpyrifos
CYF: cyfluthrin
CYP: cypermethrin
DIM: dimethomorph
α-END: alpha-endosulfan
β-END: beta-endosulfan
END: total endosulfan
FLZ: flusilazole
PAR: parathion methyl
PCZ: propiconazole
PTF: prothiofos
TCP: thiacloprid
TXB: trifloxystrobin

### 6.2 Event data (runoff event; 15 November 2009)

An additional method of testing the accuracy of the PeXI is to assess the relative contribution of runoff and spray drift in terms of their relative contribution to the PEL for each of the sub-catchments (Figure 10). Monitoring was performed on a routine basis (i.e. weekly sampling during peak application and rainfall periods). Thus, sampling did not necessarily coincide with actual application or rainfall events. Considering the transient nature of pesticide contamination in surface waters, routine monitoring therefore provides a long-term overview of pesticide contamination in the Lourens River as opposed to characterisation of the relative contribution of runoff and spray drift to pesticide contamination.

However, the monitoring that took place on the 15$^{th}$ of November 2009, coincided with a heavy rainfall event. Total rainfall on this day measured 18 mm and samples were collected towards the latter stage of the rainfall event. The data collected during this monitoring event were compared to the relative contribution of runoff and spray drift to the total PEL for each sub-catchment and the entire Lourens River catchment (Figure 10). Assessment of a runoff event in particular is a good measure of the reliability of the model used to predict PELs and subsequent PECs, as runoff events result in the mobilisation of a number of pesticides simultaneously and the level of contamination is dependent on a number of physicochemical and geographical properties. In contrast the variables resulting in contamination from a spray drift event are far less complex and much easier to predict.

Assuming that the relative contributions of runoff and spray drift to the PEL from each sub-catchment are accurate, one would expect pesticides associated with high runoff loss to be present in samples collected from the field during the runoff event on the 15$^{th}$ of November. Data collected from sampling sites on this date is presented in Table 49 and was compared to graphs Figure 10 illustrating the relative contribution of runoff and spray drift to the PEL:

- For site BB7, carbaryl and methyl parathion are both highly associated with runoff activity, accounting for an estimated 84 and 75%, respectively, of the total PEL when compared to spray drift. Both of these pesticides were detected in samples collected during the runoff event. No pesticides that were predominantly associated with spray drift were detected in collected samples.

- For site C, of the pesticides with PeXI scores falling in the High category (Figure 9), dimethomorph and carbendazim have the highest association with runoff activity (94 and 38%, respectively). Both of these pesticides were detected in the water phase during the runoff event. Azinphos-methyl and prothifos were also detected and could be present as a result of sediment mobilised by the runoff event.

- For Site LG, runoff plays a major role in the transport of pesticides (Figure 10) with high PeXI (Figure 9) scores. Carbaryl, carbendazim, dimethomorph and methyl parathion all have high relative runoff contributions to total loss (91, 99, 87 and 96%, respectively). All four of these pesticides were detected in the water phase during the runoff event.

- For Site VW, the overall contribution of runoff to total pesticide losses is relatively low, with spray drift clearly being estimated as the most important route of pesticide loss. No pesticides were detected in water or sediment samples during the runoff event.

- For Site LR, carbaryl and dimethomorph (88 and 86%, respectively) and to a lesser extent carbendazim (55%) all showed relatively high proportions of runoff contributing

to total pesticide loss. All three pesticides were detected in the water phase during the runoff event.

**Table 49:** Summary of pesticides detected in water and sediment samples collected from the Lourens River during an 18 mm runoff event on the 15th of November, 2009.

| Site | Water (µg/ℓ) | Sediment (µg/kg) |
|---|---|---|
| **BB7** | Carbaryl (<0.05) | Methyl Parathion (20) |
| **C** | Carbendazim (<0.05)<br>Dimethomorph (0.3) | Azinphos-methyl (<10)<br>Prothiofos (10) |
| **LG4** | Carbaryl (0.5)<br>Carbendazim (0.06)<br>Dimethomorph (<0.05)<br>Methyl parathion (0.05) | Azinphos-methyl (<10)<br>Methyl parathion (<10)<br>Prothiofos (10) |
| **VW** | nd | nd |
| **LR** | Carbaryl (0.3)<br>Carbendazim (<0.05)<br>Dimethomorph (0.3) | nd |

Results from this monitoring event therefore indicate that the PEL used to calculate the PeXI can successfully identify those pesticides most likely to be transported as a result of runoff.

### 6.3 Comparison with PeUI

The PeXI provides a more refined estimate of exposure than the PUI. The PeXI categorises fewer pesticides with high potential for exposure. Given the patterns of contamination observed during the field monitoring, it is clear that the PeXI is better supported by field monitoring data than the PUI, which seems to overestimate the level of contamination. This can be clearly seen in the case of BB7. According to the PUI, BB7 is identified as being the most highly contaminated site across the catchment (i.e. pesticide application is generally higher in this sub-catchment than in other sub-catchments included in the study). However, monitoring data indicates that this site is in fact one of the least contaminated sites, which is further supported by the results of the PeXI. Additionally LG4, together with VW are identified as being relatively less contaminated by the PUI. However, monitoring data, as well as the PeXI, indicate that LG4 is in fact one of the highest contaminated sites. These examples highlight the importance of physicochemical, geographical and hydrological characteristics in assessing pesticide exposure in surface waters. The quantity of pesticides applied, while an important component of the overall exposure assessment is not a sufficient indicator on its own to predict relative exposure amongst sites. This is further supported by the poor correlation between PUI and PeXI scores for all pesticides included in the analysis (Figure 13).

The PUI however performs slightly better when comparing the estimated relative exposure of different pesticides within a site. This is reflected by the improved correlations of PeXI against PUI scores on a site by site basis (Figure 14). Site VW in particular showed a strong positive correlation. This is not surprising considering that spray drift is the dominant route of pesticide entry at this site and is very dependent on the quantity of pesticide applied. The site by site comparisons therefore suggest that the PUI may be a reasonable predictor of the relative exposure of different pesticides within a site. However, the PeXI provides a more refined prediction of pesticides within a site and also more accurately predicts the relative exposure potential across sites.

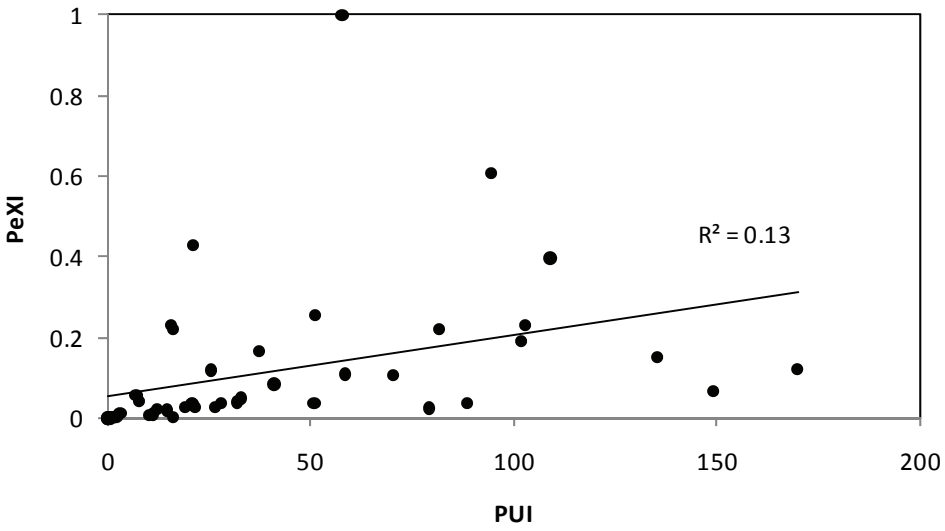



**Figure 13:** A combined scatter plot of PeXI versus PUI scores for all pesticides applied upstream of five sites in the Lourens River catchment.

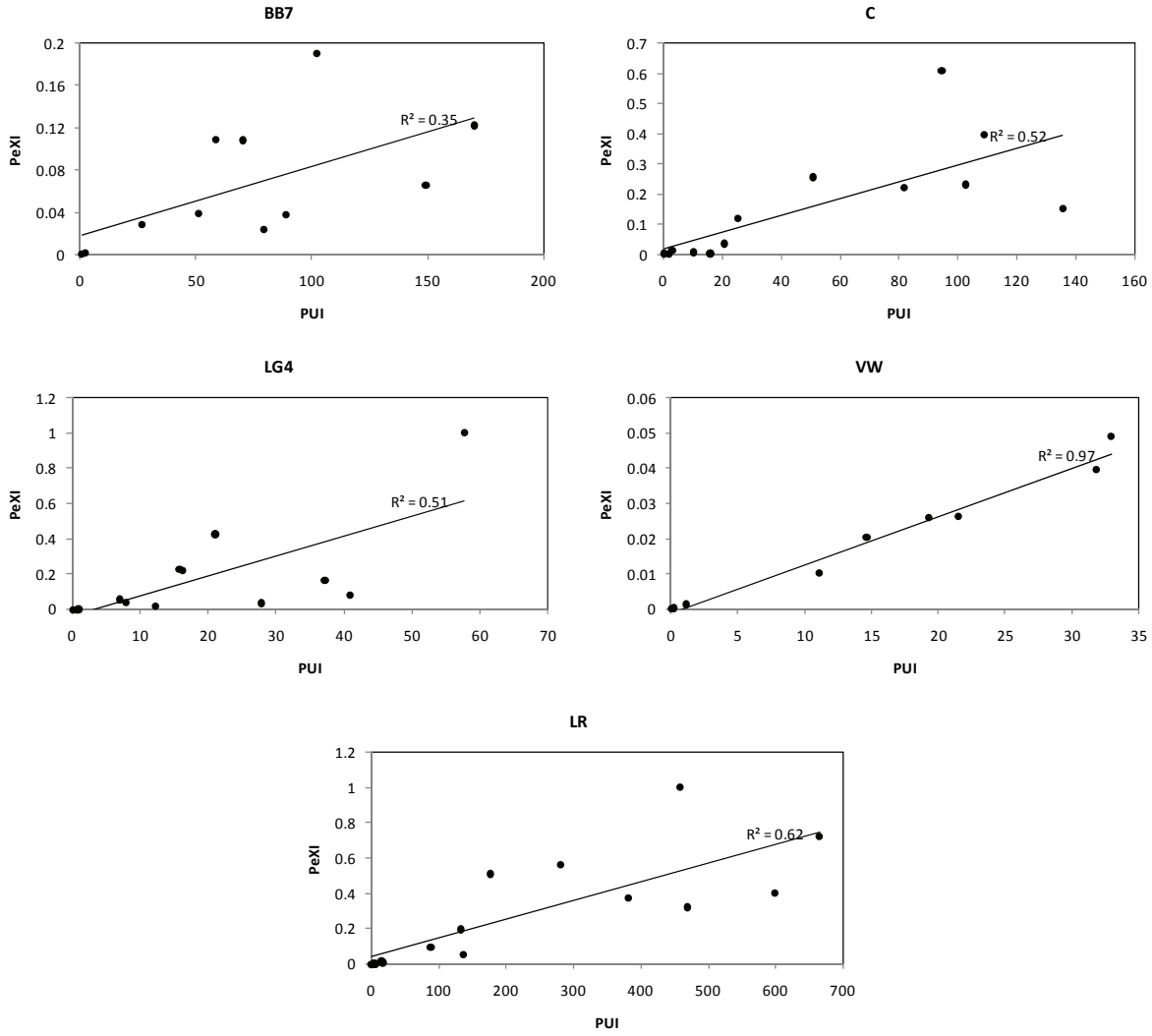



**Figure 14:** A site by site scatter plot of PeXI versus PUI scores for pesticides applied upstream of five sampling sites in the Lourens River catchment.

## 6.4 Sensitivity analysis

A sensitivity analysis was performed to determine the relative importance of input variables in the runoff and spray drift models used to calculate the PeXI. This was performed according to the methodology presented in Dubus *et al.* (2003). The method of analysis is a simple approach and is referred to as one-at-a-time sensitivity analysis. This involves varying input parameters independently, one at a time, all other parameters being constant and observing the influence on model predictions. For this analysis, runoff and spray drift model input parameters were varied in increments within realistic minimum and maximum ranges (Table 50 and Table 51).

The assessment of model sensitivity was based on the ratio of the relative variation in model output to the relative variation in model input. For each variation increment, the relative variation in model input and model output were calculated as follows:

$$Input\ Variation = \frac{I - I_{BC}}{I_{BC}} \times 100$$

$$Output\ Variation = \frac{O - O_{BC}}{O_{BC}} \times 100$$

where $I$ is the value of the input parameter, $I_{BC}$ is the value of the input parameter for the base-case scenario, $O$ is the value of the output variable, and $O_{BC}$ is the value of the output variable for the base-case scenario. The base-case scenario is the set of input variables that are representative of typical or average conditions (i.e. the input variables that provide a general description of the application, physicochemical and geographical characteristics). For both runoff and spray drift, the base case scenario input parameters are displayed at the head of Table 50 and Table 51 respectively. For runoff, the base-case input parameters for physicochemical properties were the median values for those properties for all pesticides applied in the Lourens River catchment. Area, slope and application rate were all defined by the median values for those parameters. Only those input parameters that varied amongst pesticides and sites were included in the sensitivity analysis. For spray drift average distance of crops to streams and median pesticide application characteristics were used for the base-case scenario.

The ratio of variation (ROV) can be defined as follows:

$$ROV = \frac{Output\ Variation}{Input\ Variation}$$

The ratio can be either positive or negative. It takes negative values if a decrease in an input parameter results in an increase in the output value or if an increase in an input parameter results in a decrease in the output value. The sign of the ratio is not critical when the aim is to classify input parameters according to their influence on model output. An ROV of 1 means that a variation in the model input will result at most in the same variation in the model output. An ROV of 10 will result in a maximum variation of the output by 10 times.

**Table 50:** Input variables and their increments used in a sensitivity analysis to determine importance of input variables on the output of the runoff model used in the PeXI calculation.

| Input Variables | | | | | | | Output | ROV Calculation | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Area** | **Slope** | **App. rate** | **n** | **Half-life** | **KOC** | **L%** | **Loss (kg)** | **Input Variation** | **Output Variation** | **ROV** |
| ***Base Case Scenario*** | | | | | | | | | | |
| ***1.5*** | ***3*** | ***0.53*** | ***1*** | ***22*** | ***1664*** | ***0.01423*** | ***0.011*** | ***-66.9*** | ***-66.9*** | ***1.0*** |
| ***Area*** | | | | | | | | | | |
| 0.5 | | | | | | 0.014 | 0.004 | -66.9 | -66.9 | 1.0 |
| 1.0 | | | | | | 0.014 | 0.008 | -33.8 | -33.8 | 1.0 |
| 1.5 | | | | | | 0.014 | 0.011 | -0.7 | -0.7 | 1.0 |
| 2.0 | | | | | | 0.014 | 0.015 | 32.5 | 32.5 | 1.0 |
| 2.5 | | | | | | 0.014 | 0.019 | 65.6 | 65.6 | 1.0 |
| 3.0 | | | | | | 0.014 | 0.023 | 98.7 | 98.7 | 1.0 |
| 3.5 | | | | | | 0.014 | 0.026 | 131.8 | 131.8 | 1.0 |
| 4.0 | | | | | | 0.014 | 0.030 | 164.9 | 164.9 | 1.0 |
| 4.5 | | | | | | 0.014 | 0.034 | 198.0 | 198.0 | 1.0 |
| 5.0 | | | | | | 0.014 | 0.038 | 231.1 | 231.1 | 1.0 |
| ***Slope*** | | | | | | | | | | |
| | 1 | | | | | 0.004 | 0.003 | -66.7 | -70.3 | 1.1 |
| | 2 | | | | | 0.009 | 0.007 | -33.3 | -37.0 | 1.1 |
| | 3 | | | | | 0.014 | 0.011 | 0.0 | 0.0 | 0 |
| | 4 | | | | | 0.020 | 0.016 | 33.3 | 40.7 | 1.2 |
| | 5 | | | | | 0.026 | 0.021 | 66.7 | 85.1 | 1.3 |
| | 6 | | | | | 0.033 | 0.027 | 100.0 | 133.1 | 1.3 |
| | 7 | | | | | 0.041 | 0.032 | 133.3 | 184.8 | 1.4 |
| | 8 | | | | | 0.048 | 0.039 | 166.7 | 240.2 | 1.4 |
| | 9 | | | | | 0.057 | 0.045 | 200.0 | 299.3 | 1.5 |
| | 10 | | | | | 0.066 | 0.053 | 233.3 | 362.0 | 1.6 |
| | 12.5 | | | | | 0.090 | 0.072 | 316.7 | 535.0 | 1.7 |
| ***Application Rate*** | | | | | | | | | | |
| | | 0.05 | | | | 0.014 | 0.001 | 0.1 | 0.1 | 1.0 |
| | | 0.1 | | | | 0.014 | 0.002 | 0.2 | 0.2 | 1.0 |
| | | 0.5 | | | | 0.014 | 0.011 | 0.8 | 0.8 | 1.0 |
| | | 1 | | | | 0.014 | 0.021 | 1.5 | 1.5 | 1.0 |
| | | 5 | | | | 0.014 | 0.107 | 7.6 | 7.6 | 1.0 |
| ***Number of Applications*** | | | | | | | | | | |
| | | | 1 | | | 0.014 | 0.011 | 0.8 | 0.8 | 0 |
| | | | 2 | | | 0.014 | 0.023 | 1.6 | 0.8 | 1.0 |
| | | | 3 | | | 0.014 | 0.034 | 2.4 | 0.8 | 1.0 |
| | | | 4 | | | 0.014 | 0.046 | 3.2 | 0.8 | 1.0 |
| | | | 5 | | | 0.014 | 0.057 | 4.0 | 0.8 | 1.0 |
| ***Half-life*** | | | | | | | | | | |
| | | | | 1 | | 0.000 | 0.000 | -95.5 | -99.9 | 1.0 |
| | | | | 2 | | 0.001 | 0.000 | -90.9 | -95.7 | 1.1 |
| | | | | 5 | | 0.005 | 0.004 | -77.3 | -65.7 | 0.9 |
| | | | | 10 | | 0.010 | 0.008 | -54.5 | -31.5 | 0.6 |
| | | | | 15 | | 0.012 | 0.010 | -31.8 | -13.7 | 0.4 |
| | | | | 20 | | 0.014 | 0.011 | -9.1 | -3.1 | 0.3 |
| | | | | 25 | | 0.015 | 0.012 | 13.6 | 3.9 | 0.3 |
| | | | | 50 | | 0.017 | 0.014 | 127.3 | 19.3 | 0.2 |
| | | | | 100 | | 0.018 | 0.015 | 354.5 | 27.9 | 0.1 |
| | | | | 200 | | 0.019 | 0.015 | 809.1 | 32.4 | 0.0 |

**Table 50 (Continued):** Input variables and their increments used in a sensitivity analysis to determine importance of input variables on the output of the runoff model used in the PeXI calculation.

| Input Variables | | | | | | | Output | ROV Calculation | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Area | Slope | App. rate | n | Half-life | KOC | L% | Loss (kg) | Input Variation | Output Variation | ROV |
| ***KOC*** | | | | | | | | | | |
| | | | | | 10 | 0.178 | 0.143 | -99.4 | 1154.0 | -11.6 |
| | | | | | 20 | 0.167 | 0.133 | -98.8 | 1072.2 | -10.9 |
| | | | | | 50 | 0.140 | 0.112 | -97.0 | 880.4 | -9.1 |
| | | | | | 100 | 0.110 | 0.088 | -94.0 | 670.3 | -7.1 |
| | | | | | 500 | 0.040 | 0.032 | -70.0 | 183.8 | -2.6 |
| | | | | | 1000 | 0.023 | 0.018 | -39.9 | 58.6 | -1.5 |
| | | | | | 5000 | 0.005 | 0.004 | 200.5 | -65.0 | -0.3 |
| | | | | | 10000 | 0.003 | 0.002 | 501.0 | -82.3 | -0.2 |
| | | | | | 50000 | 0.001 | 0.000 | 2904.8 | -96.4 | 0.0 |

**Table 51:** Input variables and their increments used in a sensitivity analysis to determine importance of input variables on the output of the spray drift model used in the PeXI calculation.

| Input Variable | | | | | Output | ROV Calculation | | |
|---|---|---|---|---|---|---|---|---|
| Area | Distance | App. Rate | Frequency | L% | Loss (kg) | Input Variation | Output Variation | ROV |
| ***Base Case Scenario*** | | | | | | | | |
| 1.50 | 10.0 | 0.53 | 1 | 4.652 | 0.037 | | | |
| ***Area*** | | | | | | | | |
| 0.5 | 10 | 0.53 | 1 | 4.652 | 0.012 | -66.7 | -66.7 | 1.0 |
| 1 | 10 | 0.53 | 1 | 4.652 | 0.025 | -33.3 | -33.3 | 1.0 |
| 1.5 | 10 | 0.53 | 1 | 4.652 | 0.037 | 0.0 | 0.0 | |
| 2 | 10 | 0.53 | 1 | 4.652 | 0.049 | 33.3 | 33.3 | 1.0 |
| 2.5 | 10 | 0.53 | 1 | 4.652 | 0.062 | 66.7 | 66.7 | 1.0 |
| 3 | 10 | 0.53 | 1 | 4.652 | 0.074 | 100.0 | 100.0 | 1.0 |
| 3.5 | 10 | 0.53 | 1 | 4.652 | 0.086 | 133.3 | 133.3 | 1.0 |
| ***Distance*** | | | | | | | | |
| 1.5 | 5 | 0.53 | 1 | 12.389 | 0.098 | -50.0 | 166.3 | -3.3 |
| 1.5 | 10 | 0.53 | 1 | 4.652 | 0.037 | 0.0 | 0.0 | 0 |
| 1.5 | 15 | 0.53 | 1 | 2.279 | 0.018 | 50.0 | -51.0 | -1.0 |
| 1.5 | 20 | 0.53 | 1 | 1.330 | 0.011 | 100.0 | -71.4 | -0.7 |
| 1.5 | 25 | 0.53 | 1 | 0.866 | 0.007 | 150.0 | -81.4 | -0.5 |
| 1.5 | 30 | 0.53 | 1 | 0.607 | 0.005 | 200.0 | -86.9 | -0.4 |
| 1.5 | 35 | 0.53 | 1 | 0.449 | 0.004 | 250.0 | -90.4 | -0.4 |
| 1.5 | 40 | 0.53 | 1 | 0.345 | 0.003 | 300.0 | -92.6 | -0.3 |
| ***Application Rate*** | | | | | | | | |
| 1.5 | 10 | 0.005 | 1 | 4.652 | 0.000 | -99.1 | -99.1 | 1.0 |
| 1.5 | 10 | 0.025 | 1 | 4.652 | 0.002 | -95.3 | -95.3 | 1.0 |
| 1.5 | 10 | 0.125 | 1 | 4.652 | 0.009 | -76.4 | -76.4 | 1.0 |
| 1.5 | 10 | 0.625 | 1 | 4.652 | 0.044 | 17.9 | 17.9 | 1.0 |
| 1.5 | 10 | 3.125 | 1 | 4.652 | 0.218 | 489.6 | 489.6 | 1.0 |
| ***Frequency*** | | | | | | | | |
| 1.5 | 10 | 0.53 | 1 | 4.652 | 0.037 | 0 | 0 | 0 |
| 1.5 | 10 | 0.53 | 2 | 4.652 | 0.074 | 100 | 100 | 1.0 |
| 1.5 | 10 | 0.53 | 3 | 4.652 | 0.111 | 200 | 200 | 1.0 |
| 1.5 | 10 | 0.53 | 4 | 4.652 | 0.148 | 300 | 300 | 1.0 |
| 1.5 | 10 | 0.53 | 5 | 4.652 | 0.185 | 400 | 400 | 1.0 |
| 1.5 | 10 | 0.53 | 6 | 4.652 | 0.222 | 500 | 500 | 1.0 |

The plotting of the output variation versus the input variation provides a graphical means to assess the sensitivity of the model to input parameters Figure 15 and Figure 16.

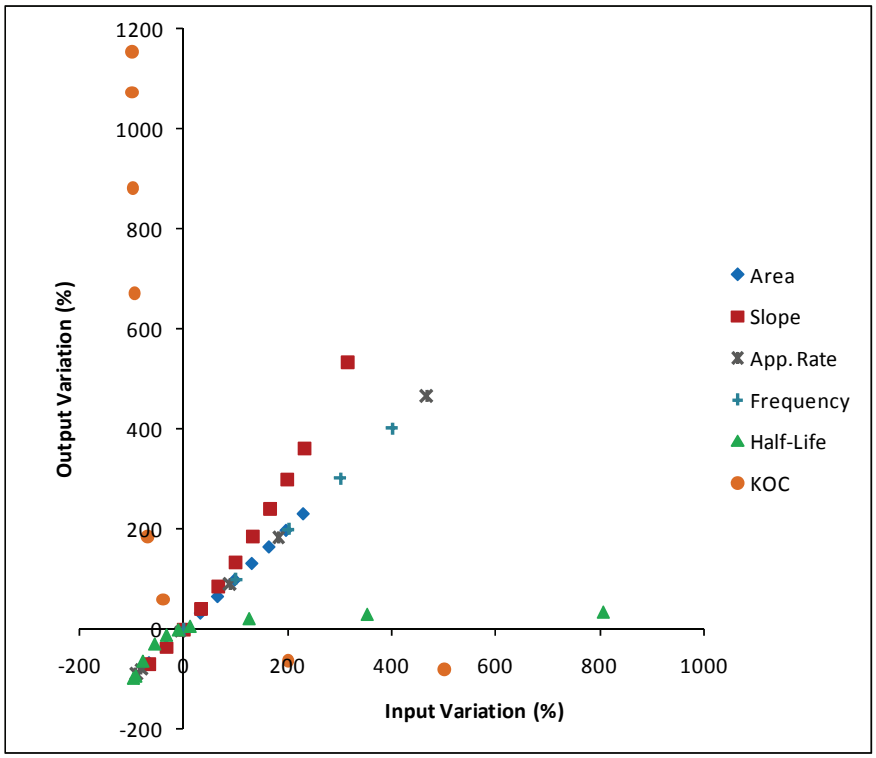



**Figure 15:** Variation in the runoff model predictions used to calculate the PeXI in response to modification of input parameters.

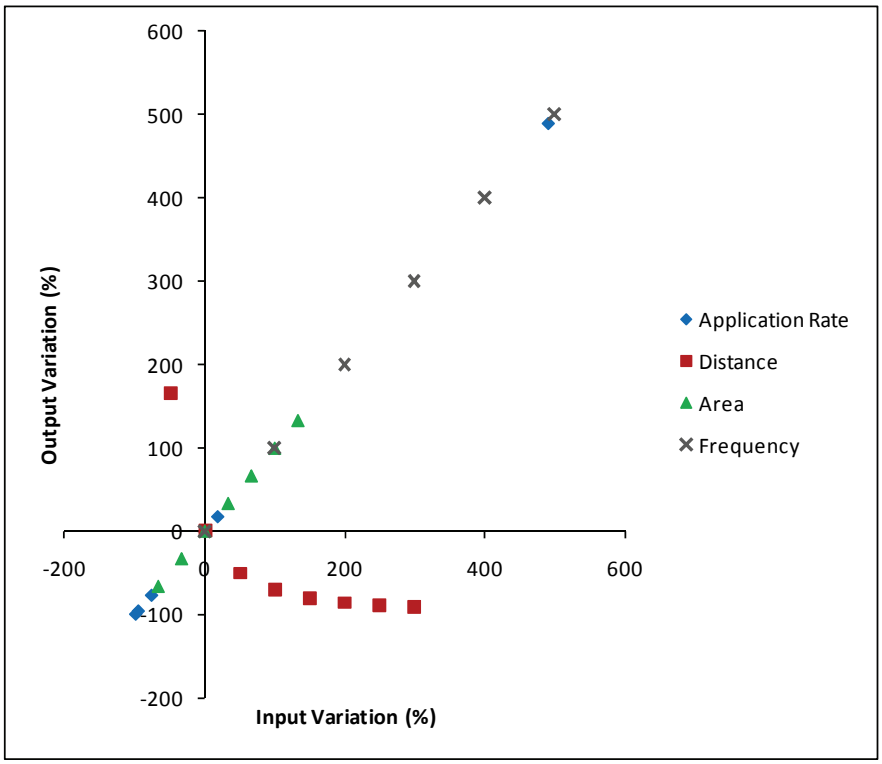



**Figure 16:** Variation in the spray drift model predictions used to calculate the PeXI in response to modification of input parameters.

The closer the curve to the Y axis (the larger the slope of the line linking the origin and a particular point), the more sensitive the model to this parameter. In the same way, the closer the curve to the X axis (the smaller the slope of the line linking the origin and a particular point), the less sensitive the model to this parameter. Curves corresponding to positive influences (an increase in model output resulting from an increase in model input or a decrease in model output resulting from a decrease in model input) are located in the top right and bottom left quadrants while those corresponding to negative influences (an increase in model output resulting from a decrease in model input or a decrease in model output resulting from an increase in model input) are situated in the top left and bottom right quadrants.

Thus, for runoff (Figure 15) the model is most sensitive to the input of $K_{OC}$ and it can be seen that lower input variation (i.e. low $K_{OC}$ values) results in large changes in output variation. For half-life it can be seen that the runoff output is sensitive to shorter half-lives, resulting in decreased model output (i.e. lower transport in runoff). As half-life increases it results in an increase in the model output (i.e. higher pesticide transport in runoff), however the model becomes less sensitive to this parameter at higher half-lives. For slope, variation just about or below the base-case scenario (i.e. the origin) results in almost linear response with respect to model output. However as slope increases further, the model becomes more sensitive to this particular input parameter. Slope is another input variable that results in increasing output with increasing input (i.e. increased slope%). Application rate, frequency of application and the area of the treated crop all display a linear relationship in terms of the effect of input variation on the model output. Within the ranges defined in this study, application rate and frequency of application have a greater influence.

For spray drift (Figure 16) the model is most sensitive to a decrease in distance between the point of application and the water body. As this buffer zone width increases, the model becomes less sensitive and also results in a decrease in the model output. As for runoff, application rate, frequency of application and the area of the treated crop all display a linear relationship in terms of the effect of input variation on model output

## 6.5 References

DUBUS IG, BROWN CD and BEULKE S (2003) Sensitivity analysis of four pesticide leaching models. *Pest Manage. Sci.* **59:** 962-982.

# 7. CONCLUSION

The pesticide risk indicator developed in this project is based on realistic transport runoff and spray drift processes. The assessments of these processes are based on sound scientific principles and are used in a manner that the results are not entirely qualitative but semi-quantitative. The input data required for the indices is readily available or can be easily calculated. The risk indicator takes pesticide use, pesticide properties, pesticide toxicity and geographical characteristics into account.

Data on physicochemical properties of pesticides fate and behaviour in South Africa is not locally available. Thus international databases were consulted in order to obtain the relevant information for input into the runoff model in particular. Studies have shown that physicochemical properties of pesticides can vary geographically, depending on local climatic and soil conditions (Daam and Van den Brink, 2010). Considering this limitation however, the fate and behaviour of pesticides in the Lourens River catchment was still reasonably well predicted by physicochemical data available in international databases. Partitioning of pesticides between the water and sediment phase was well predicted by calculated $K_{OC}$ scores. Furthermore, the PeXI was relatively well validated by field-based monitoring. In particular, the ability of the PEL to distinguish between the relative contribution of runoff and spray drift at a site further confirmed the applicability of these international values to local conditions. Runoff in particular is highly dependent on the physicochemical properties of pesticides (particularly $K_{OC}$ as demonstrated by the sensitivity analysis). The fact that pesticides susceptible to runoff were identified by the PeXI and then detected during an actual runoff event indicates the physicochemical values for individual pesticides used in this study provide a good relative indication of their behaviour in the South African environment. The pesticides identified as being highly mobile in runoff all have low $K_{OC}$ values, indicating that under South African conditions, the values were able to sufficiently differentiate between the mobility of the different pesticides applied in the catchment. $K_{OC}$ values are widely used as measures of the relative mobility of pesticides in soils and fugacity modelling, which attempt to predict the partitioning of pesticides between water, soil at air phases. Many studies have made use of $K_{OC}$ values to compare the relative mobility of pesticides as a decision making aid. Wauchope *et al.* (2002) found that while there is often variation in the $K_{OC}$ value of a specific pesticide, the values are adequate for discriminating between the relative mobility of a number of different pesticides

The outputs of the PeXI and PeRI do not represent the absolute exposure and risk but a relative exposure and risk rating among pesticides or land uses in a catchment. It does not take any pesticide interactions or degradation beyond the point of its entry in waterways, (i.e. it provides the “edge of field” scenario). The PeXI and PeRI can be highly beneficial in customising monitoring programmes or to identify pesticides that required relatively greater attention in terms of their potential behaviour in environment. With respect to the Lourens River, the indicator was successful in the following:

- PeXI scores were able to differentiate between highly contaminated and less contaminated sites.
- PeXI scores were fairly reliable in predicting the relative exposure potential of specific pesticides across and within sites.
- Expressing the PEL as percentage of contribution by runoff and spray drift enabled the identification of the most important exposure route for pesticides at all sites.

The outputs provided by the indicator could therefore clearly lead to improved utilisation of limited resources for monitoring and management. The output of the indicator, as described

in the sections above, show that the PeXI score for the different pesticides applied in the Lourens River catchment are generally consistent with monitoring results.

The indicator can therefore be a useful screening and decision-making tool. The indicator is not a simulation model and is therefore not designed to predict accurate environmental concentrations of pesticide likely to reach surface water, but merely assesses an indicative risk factor with individual pesticides at different sites within a catchment. It is therefore appropriate that results from the indicator are used for first-tier assessment and screening purposes.

An additional advantage of the indicator is that it can help identify appropriate mitigation measures aimed at minimising the transport of pesticides associated with specific transport routes (i.e. runoff or spray drift). For example at site VW, where spray drift is the most important route of entry of pesticides increasing buffer zone width (de Snoo and de Wit, 1998) or the establishment of vegetative barriers in between the crops and adjacent water body would effectively minimise transport of pesticides into this particular tributary. In contrast, at site LG4, where runoff is clearly the predominant route of transport, establishment of vegetative filter strips (Syversen and Bechmann, 2004) or effective drainage of runoff water into a constructed wetland prior to entry into the tributary (Schulz *et al.*, 2003) could potentially reduce pesticide concentrations in this particular tributary. The indices developed in this project provide an overall aggregated assessment of pesticide exposure and risk over an entire season. Considering the PeXI is not linked to precise application characteristics (i.e. it is a more general estimation over the entire season) the field monitoring was well predicted by the PeXI.

## 7.1 Recommendations

### *7.1.1 Accessibility to pesticide use data*

One of the most important parameters required for this indicator was pesticide use data. Often this information is not freely available. While estimates of application rates can be made through those recommended by the Department of Agriculture (e.g. DoA, 2007) it is not possible to identify what active ingredient is actually used on a crop. This is because for any given pest on a specific crop, up to twenty or more different active ingredients can be registered for use on the crop. Thus it is impossible to identify which pesticides are used based on the type of crop and pest (even if this was available).

Given the risk that pesticides pose to the environment and human health it is essential that crop specific pesticide use data are more freely available. These data are essential for prioritising human and environmental risks to agrochemical use and for input into modelling exercises aimed at improving the management of land use practices and their impact on water resources. At the same time, disclosure of pesticide use data may be potentially sensitive and may need to be protected to safeguard the commercial interests of the manufacturers. A collaborative project between researchers and relevant stakeholders (i.e. DAFF and AVCASA) aimed at establishing a national database on crop specific pesticide use is therefore strongly recommended. This database could then be used as a source of pesticide use data for regulatory and policy decision making and environmental modelling and monitoring.

### *7.1.2 Development of a simplified online risk indicator*

Much of the data used in this indicator (i.e. physicochemical properties and toxicity values) is freely available via online resources. Clearly these data can be very beneficial in terms of assessing the risk of pesticides in the aquatic environment. Given the vulnerability of South Africa's resources, both from a water quantity and quality perspective, every effort should be focussed on harnessing available information, analysing it and communicating it in an effective manner, so as to improve decision making and reduce the impact of land use practices on water resources.

The indicator developed in this project had a strong geographical component allowing for the identification of hotspots within a small catchment. However, farmers may often have only one or two fields bordering a surface water resource. In this instance the geographical component becomes less important as the focus is not so much to identify hotspots, but rather to identify potentially problematic pesticides. In this respect the models used in this indicator can still provide a useful indication of the relative exposure and risk potential of a variety of pesticides used. In most cases, a number of different active ingredients are registered for use on a single crop for a single pest problem. Collating databases on physicochemical properties and toxicity data that can be integrated into simple exposure models can therefore inform farmers of which of a variety of pesticides pose the least environmental risk to the aquatic ecosystem. Similarly, such a screening system could also be utilised by catchment managers to identify priority pesticides within a catchment. Thus, it is highly recommended that freely available data and information on pesticide properties and toxicity be collated and analysed to develop an online decision support system tool that allows farmers and or others to evaluate the relative mobility and risk of pesticides based on simple user input parameters (i.e. crop type, pesticide application rate, soil characteristics etc).

### *7.1.3 Validation of the PeRI*

The PeRI estimates relative risk and cannot be validated by exposure data alone. Further potential research could focus on comparing the aquatic health of water resources against outputs of the PeRI. Those resources with higher PeRI scores would be expected to be more adversely impacted than those with lower scores. Care would need to be taken to ensure that no other anthropogenic or biotic stressors are impacting on aquatic ecosystem health. This is generally always a limitation when attempting to verify pesticide risks to the aquatic environment in a field situation.

### *7.1.4 Development of a PeXI for groundwater*

The indicator developed here focussed specifically on surface waters and the risk to the aquatic ecosystem. The impact of pesticides on groundwater is far more relevant from a human and animal health perspective, as these are the most frequent users of the resource. While there is interaction between ground and surface waters, contamination of surface waters is largely attributed to spray drift and runoff as opposed to secondary contamination via groundwater recharge. The ecological impact of groundwater recharge on the aquatic ecosystem is therefore likely to be low. However considering the extent of livestock agriculture and poor access to water for many rural communities, the potential for groundwater contamination by different pesticides should be assessed. A similar methodology, using equally simple empirical tools and relevant human and animal health toxicity endpoints could be developed to assess the relative leaching potential and associated risks of pesticides to groundwater resources. This methodology would need to be developed and validated in an appropriate catchment.

## 7.2 References

DAAM MA and VAN DEN BRINK PJ (2010) Implications of differences between temperate and tropical freshwater ecosystems for the ecological risk of pesticides. *Ecotoxicology.* **19**: 24-37.

DOA (DEPARTMENT OF AGRICULTURE) (2007) A Guide for the Control of Plant Pests. Directorate: Food Safety and Quality Assurance. Department of Agriculture, Pretoria, South Africa

SCHULZ R, HAHN C, BENNETT ER, DABROWSKI JM, THIERE G and PEALL SKC (2003) Fate and effects of azinphos-methyl in a flow through wetland in South Africa. *Environ. Sci. Technol.* **37**(10): 2139-2144.

SYVERSEN N and BECHMANN M (2004) Vegetative buffer zones as pesticide filters for simulated surface runoff. *Ecol. Eng.* **22**: 175-184

WAUCHOPE RD, YEH S, LINDERS JBHJ, KLOSKOWSKI R, TANAKA K, RUBIN B, KATAYAMA A, KORDEL W, GERSTL Z, LANE M and UNSWORTH JB (2002) Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Manage. Sci.* **58**: 419-445

# 8. APPENDICES

## Appendix 1 – Pesticide Application Data for the Lourens River

Pesticide application programme for apples grown in the Lourens River catchment.

| Application Period | Pesticide (Active Ingredient) | [1]Water (ℓ/ha) | [2]Dilution (mℓ or kg/100 ℓ) | [3]g(a.i.) per ℓ or kg | [4]Rate (kg/ha) | [5]Total (kg) |
|---|---|---|---|---|---|---|
| 1 | Chlorpyrifos | 2100 | 100 | 480 | 1.01 | 86.7 |
| 2 | Prothiofos | 2100 | 50 | 960 | 1.01 | 86.7 |
| 3 | Mancozeb | 1800 | 150 | 750 | 2.03 | 174.2 |
| 4 | Mancozeb | 1800 | 150 | 750 | 2.03 | 174.2 |
| 5 | Mancozeb | 1800 | 150 | 750 | 2.03 | 174.2 |
| | Beta-cyfluthrin | 1800 | 5 | 50 | 0.00 | 0.4 |
| 6 | Mancozeb | 1800 | 150 | 750 | 2.03 | 174.2 |
| 7 | Carbaryl | 2400 | 90 | 850 | 1.84 | 157.9 |
| 8 | Mancozeb | 2400 | 75 | 750 | 1.35 | 116.1 |
| | Flusilazole | 2400 | 24 | 400 | 0.23 | 19.8 |
| 9 | Flufenoxuron | 2400 | 25 | 100 | 0.06 | 5.2 |
| 10 | Mancozeb | 2400 | 75 | 750 | 1.35 | 116.1 |
| | Methyl parathion | 2400 | 70 | 240 | 0.40 | 34.7 |
| | Flusilazole | 2400 | 24 | 400 | 0.23 | 19.8 |
| 11 | Mancozeb | 2400 | 75 | 750 | 1.35 | 116.1 |
| | Methyl parathion | 2400 | 70 | 240 | 0.40 | 34.7 |
| | Flusilazole | 2400 | 24 | 400 | 0.23 | 19.8 |
| 12 | Mancozeb | 3000 | 75 | 750 | 1.69 | 145.1 |
| | Thiacloprid | 3000 | 15 | 480 | 0.22 | 18.6 |
| | Flusilazole | 3000 | 24 | 400 | 0.29 | 24.8 |
| 13 | Chlorpyrifos | 3000 | 75 | 480 | 1.08 | 92.9 |
| 14 | Azinphos-methyl | 3000 | 50 | 350 | 0.53 | 45.2 |
| 15 | Azinphos-methyl | 3000 | 50 | 350 | 0.53 | 45.2 |
| 16 | Endosulfan | 3000 | 100 | 475 | 1.43 | 122.6 |
| 17 | Azinphos-methyl | 3000 | 50 | 350 | 0.53 | 45.2 |
| 18 | Azinphos-methyl | 3000 | 50 | 350 | 0.53 | 45.2 |

[1]Spray Volume (pesticide concentrate + water) applied per hectare
[2]Quantity of pesticide concentrate added to application mixture
[3]Quantity of active ingredient (g) per ℓ or kg of pesticide
[4]Quantity of active ingredient applied per hectare
[5]Total quantity of pesticide (kg) applied per crop type

Pesticide application programme for grapes grown in the Lourens River catchment.

| Application Period | Pesticide (Active Ingredient) | [1]Water (ℓ/ha) | [2]Dilution (mℓ or kg/100 ℓ) | [3]g(a.i.) per ℓ or kg | [4]Rate (kg/ha) | [5]Total (kg) |
|---|---|---|---|---|---|---|
| 1 | Folpet | 500 | 200 | | 0 | 0 |
| 2 | Mancozeb | 500 | 200 | 800 | 0.8 | 81.6 |
| 3 | Mancozeb | 500 | 200 | 750 | 0.75 | 76.5 |
| | Trifloxystrobin | 500 | 15 | 500 | 0.0375 | 3.825 |
| 4 | Mancozeb | 750 | 200 | 750 | 1.125 | 114.75 |
| | Trifloxystrobin | 750 | 15 | 500 | 0.05625 | 5.7375 |
| 5 | Mancozeb | 750 | 200 | 750 | 1.125 | 114.75 |
| | Trifloxystrobin | 750 | 15 | 500 | 0.05625 | 5.7375 |
| 6 | Dimethomorph | 750 | 200 | 500 | 0.75 | 76.5 |
| 7 | Dimethomorph | 1000 | 250 | 500 | 1.25 | 127.5 |
| 8 | Dimethomorph | 1000 | 200 | 500 | 1 | 102 |
| 9 | Mancozeb | 1000 | 200 | 750 | 1.5 | 153 |
| 10 | Mancozeb | 1000 | 200 | 750 | 1.5 | 153 |
| 11 | Chlorpyrifos | 1000 | 150 | 480 | 0.72 | 73.44 |
| | Alpha-cypermethrin | 1000 | 20 | | 0 | 0 |
| 12 | Prothiofos | 1000 | 50 | 960 | 0.48 | 48.96 |

[1]Spray Volume (pesticide concentrate + water) applied per hectare
[2]Quantity of pesticide concentrate added to application mixture
[3]Quantity of active ingredient (g) per ℓ or kg of pesticide
[4]Quantity of active ingredient applied per hectare
[5]Total quantity of pesticide (kg) applied per crop type

Pesticide application programme for pears grown in the Lourens River catchment.

| Application Period | Pesticide (Active Ingredient) | [1]Water (ℓ/ha) | [2]Dilution (mℓ or kg/100 ℓ) | [3]g(a.i.) per ℓ or kg | [4]Rate (kg/ha) | [5]Total (kg) |
|---|---|---|---|---|---|---|
| 1 | Chlorpyrifos | 2100 | 100 | 480 | 1.008 | 196.6 |
| 2 | Prothiofos | 2100 | 50 | 960 | 1.008 | 196.6 |
| 3 | Mancozeb | 1800 | 150 | 750 | 2.025 | 394.9 |
| 4 | Mancozeb | 1800 | 150 | 750 | 2.025 | 394.9 |
| 5 | Mancozeb | 1800 | 150 | 750 | 2.025 | 394.9 |
| | Beta-cyfluthrin | 1800 | 5 | 50 | 0.0045 | 0.9 |
| 6 | Beta-cyfluthrin | 1800 | 5 | 50 | 0.0045 | 0.9 |
| 7 | Flufenoxuron | 2400 | 25 | 100 | 0.06 | 11.7 |
| | Benomyl | 2400 | 50 | 500 | 0.6 | 117.0 |
| 8 | Methyl parathion | 2400 | 70 | 240 | 0.4032 | 78.6 |
| | Benomyl | 2400 | 50 | 500 | 0.6 | 117.0 |
| 9 | Methyl parathion | 2400 | 70 | 240 | 0.4032 | 78.6 |
| | Benomyl | 2400 | 50 | 500 | 0.6 | 117.0 |
| 10 | Mancozeb | 3000 | 150 | 750 | 3.375 | 658.1 |
| | Thiacloprid | 3000 | 15 | 480 | 0.216 | 42.1 |
| 11 | Thiacloprid | 3000 | 15 | 480 | 0.216 | 42.1 |
| 12 | Azinphos-methyl | 3000 | 90 | 200 | 0.54 | 105.3 |
| 13 | Azinphos-methyl | 3000 | 90 | 200 | 0.54 | 105.3 |
| 14 | Cyhexatin | 3000 | 50 | 600 | 0.9 | 175.5 |
| 15 | Azinphos-methyl | 3000 | 90 | 200 | 0.54 | 105.3 |

[1]Spray Volume (pesticide concentrate + water) applied per hectare
[2]Quantity of pesticide concentrate added to application mixture
[3]Quantity of active ingredient (g) per ℓ or kg of pesticide
[4]Quantity of active ingredient applied per hectare
[5]Total quantity of pesticide (kg) applied per crop type

Pesticide application programme for pears grown in the Lourens River catchment.

| Application Period | Pesticide (Active Ingredient) | [1]Water (ℓ/ha) | [2]Dilution (mℓ or kg/100 ℓ) | [3]g(a.i.) per ℓ or kg | [4]Rate (kg/ha) | [5]Total (kg) |
|---|---|---|---|---|---|---|
| 1 | Prothiofos | 1680 | 50 | 960 | 1.008 | 196.6 |
| 2 | Chlorpyrifos | 1680 | 100 | 480 | 1.008 | 196.6 |
| 3 | Propiconazole | 1440 | 20 | 250 | 2.025 | 394.9 |
| 4 | Propiconazole | 1440 | 20 | 250 | 2.025 | 394.9 |
| 5 | Propiconazole | 1440 | 20 | 250 | 2.025 | 394.9 |
| 6 | Azinphos-methyl | 2400 | 70 | 350 | 0.0045 | 0.9 |
| 7 | Cypermethrin | 2400 | 5 | 200 | 0.0045 | 0.9 |
| 8 | Cypermethrin | 2400 | 5 | 200 | 0 | 0.0 |

[1]Spray Volume (pesticide concentrate + water) applied per hectare
[2]Quantity of pesticide concentrate added to application mixture
[3]Quantity of active ingredient (g) per ℓ or kg of pesticide
[4]Quantity of active ingredient applied per hectare
[5]Total quantity of pesticide (kg) applied per crop type

## Appendix 2 – Q Values for Runoff Model

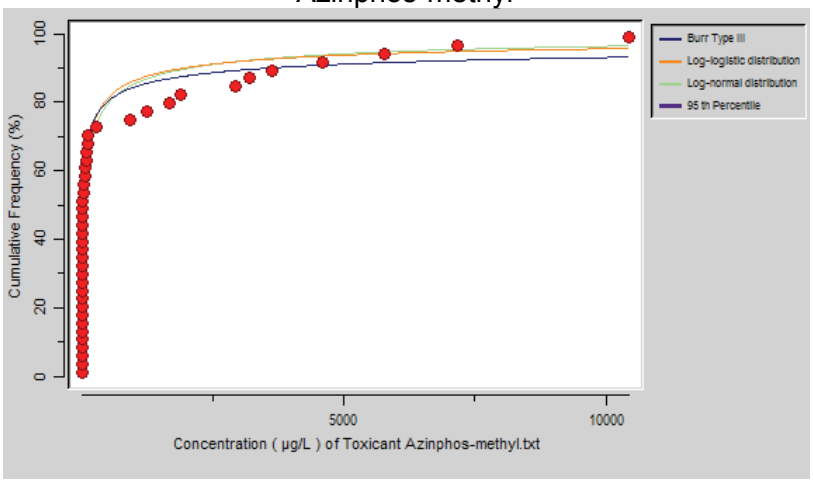
Runoff volumes (Q) corresponding to rainfall amounts (P) for different soil types according to the model of Lutz and Maniak (1984)

| Rainfall (mm) | Runoff Volume (mm) | | | | | |
|---|---|---|---|---|---|---|
| | Scenario 1 | | Scenario 2 | | Scenario 3 | |
| | Sandy Soil | Loamy Soil | Sandy Soil | Loamy Soil | Sandy Soil | Loamy Soil |
| 6 | 0.1 | 0.45 | 0.04 | 0.19 | 0.02 | 0.13 |
| 8 | 0.28 | 0.82 | 0.12 | 0.35 | 0.07 | 0.24 |
| 10 | 0.54 | 1.29 | 0.23 | 0.56 | 0.13 | 0.38 |
| 12 | 0.88 | 1.86 | 0.38 | 0.81 | 0.21 | 0.55 |
| 14 | 1.29 | 2.51 | 0.56 | 1.11 | 0.32 | 0.76 |
| 16 | 1.78 | 3.24 | 0.78 | 1.45 | 0.44 | 0.99 |
| 18 | 2.32 | 4.05 | 1.03 | 1.83 | 0.59 | 1.26 |
| 20 | 2.92 | 4.93 | 1.31 | 2.25 | 0.75 | 1.55 |
| 22 | 3.58 | 5.88 | 1.63 | 2.72 | 0.94 | 1.88 |
| 24 | 4.29 | 6.88 | 1.98 | 3.22 | 1.14 | 2.23 |
| 26 | 5.04 | 7.95 | 2.35 | 3.76 | 1.36 | 2.61 |
| 28 | 5.84 | 9.06 | 2.76 | 4.34 | 1.59 | 3.02 |
| 30 | 6.69 | 10.23 | 3.19 | 4.95 | 1.85 | 3.45 |
| 32 | 7.57 | 11.45 | 3.65 | 5.59 | 2.12 | 3.91 |
| 34 | 8.48 | 12.7 | 4.13 | 6.27 | 2.4 | 4.39 |
| 36 | 9.44 | 14 | 4.65 | 6.99 | 2.71 | 4.9 |
| 38 | 10.42 | 15.34 | 5.18 | 7.73 | 3.03 | 5.44 |
| 40 | 11.43 | 16.71 | 5.75 | 8.51 | 3.36 | 6 |
| 42 | 12.47 | 18.11 | 6.33 | 9.31 | 3.71 | 6.58 |
| 44 | 13.53 | 19.54 | 6.94 | 10.14 | 4.08 | 7.18 |
| 46 | 14.62 | 21.01 | 7.57 | 11.01 | 4.46 | 7.81 |
| 48 | 15.73 | 22.5 | 8.22 | 11.9 | 4.85 | 8.46 |
| 50 | 16.87 | 24.01 | 8.9 | 12.81 | 5.26 | 9.13 |
| 55 | 19.78 | 27.89 | 10.67 | 15.22 | 6.34 | 10.89 |
| 60 | 22.79 | 31.9 | 12.57 | 17.78 | 7.5 | 12.79 |
| 65 | 25.89 | 36.01 | 14.57 | 20.48 | 8.74 | 14.8 |
| 70 | 29.06 | 40.2 | 16.68 | 23.31 | 10.06 | 16.92 |
| 75 | 32.29 | 44.47 | 18.89 | 26.26 | 11.44 | 19.15 |
| 80 | 35.57 | 48.8 | 21.19 | 29.33 | 12.89 | 21.48 |
| 85 | 38.9 | 53.18 | 23.58 | 32.51 | 14.4 | 23.91 |
| 90 | 42.26 | 57.6 | 26.04 | 35.79 | 15.97 | 26.44 |
| 95 | 45.65 | 62.06 | 28.58 | 39.16 | 17.6 | 29.04 |
| 100 | 49.07 | 66.55 | 31.18 | 42.61 | 19.29 | 31.74 |

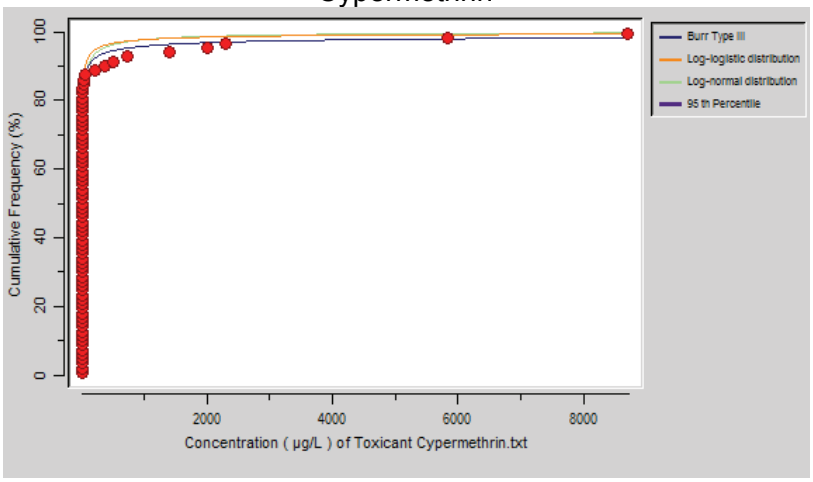
Scenario 1: Bare soil with high soil moisture
Scenario 2: Bare soil with low soil moisture
Scenario 3: Covered soil with low soil moisture

## Appendix 3 – Species Sensitivity Distributions

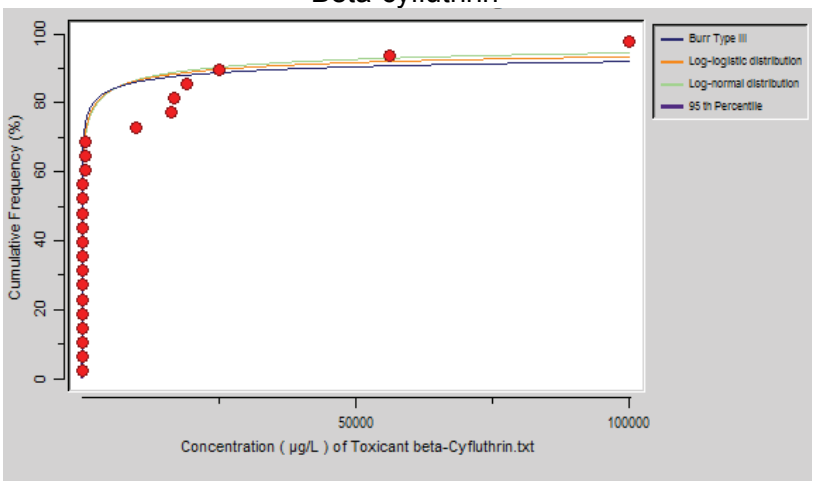
Azinphos-methyl



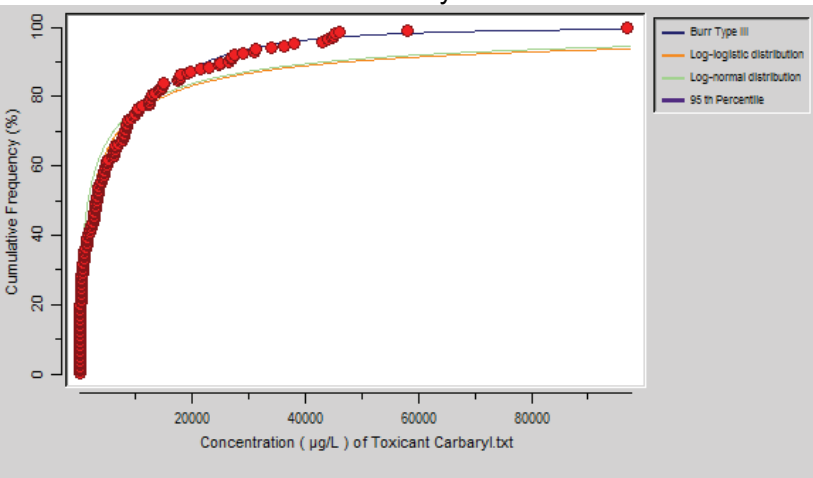

Cypermethrin



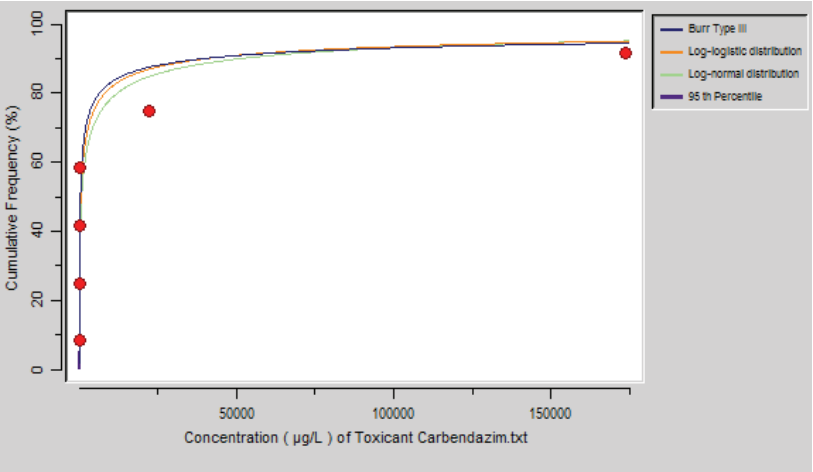

Beta-cyfluthrin



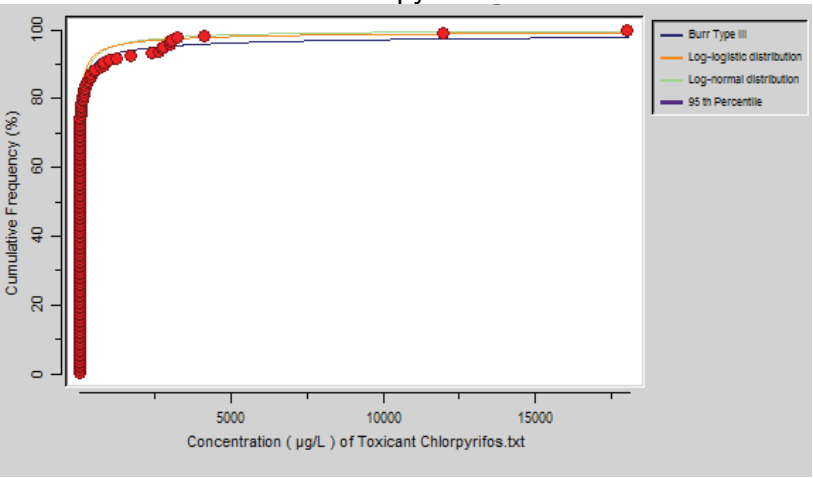
Carbaryl



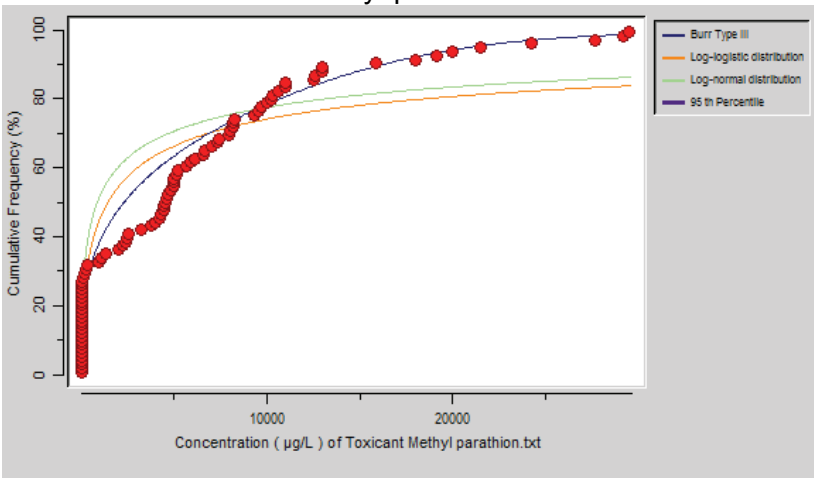

Carbendazim



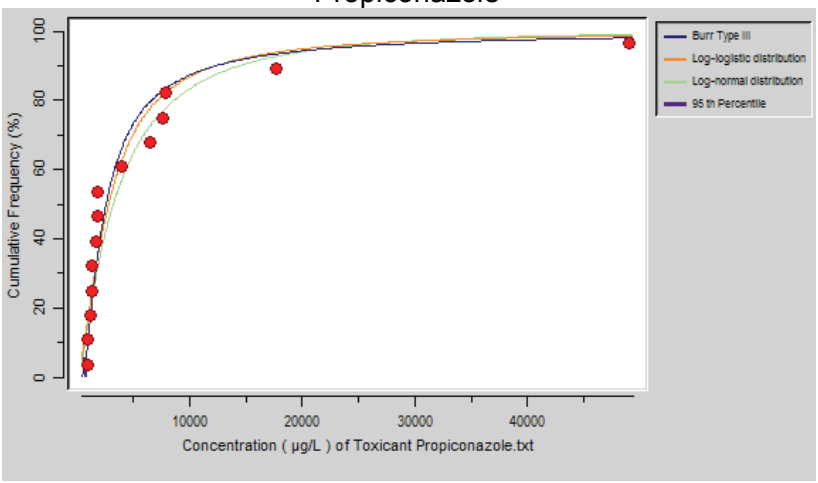

Chlorpyrifos



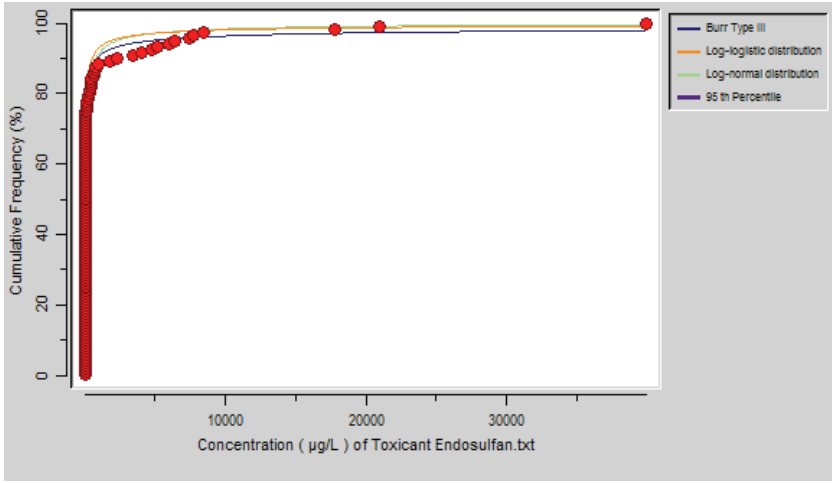
Methyl-parathion




Propiconazole




Endosulfan



## Appendix 4 – Calculated PEL, PEC, TER, PeXI and PeRI Values

| Site | Active Ingredient | Loss (kg) | | Index Values | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Runoff | Spray drift | PEL | PEC | TER | PeXI | PeRI |
| **BB7** | Beta-cyfluthrin | 0.00005 | 0.003 | 0.003 | 0.02 | 0.352 | 0.0001 | 0.002 |
| | Azinphos-methyl | 0.700 | 0.772 | 1.472 | 11.36 | 25.246 | 0.0649 | 0.133 |
| | Carbaryl | 1.929 | 0.368 | 2.297 | 17.73 | 2.887 | 0.1013 | 0.015 |
| | Carbendazim | 0.925 | 0.387 | 1.312 | 10.12 | 0.831 | 0.0578 | 0.004 |
| | Chlorpyrifos | 0.149 | 0.637 | 0.787 | 6.07 | 35.711 | 0.0347 | 0.188 |
| | Endosulfan | 0.060 | 0.225 | 0.285 | 2.20 | 7.332 | 0.0126 | 0.038 |
| | Flufenoxuron | 0.001 | 0.013 | 0.014 | 0.11 | 2.514 | 0.0006 | 0.013 |
| | Flusilazole | 0.278 | 0.184 | 0.463 | 3.57 | 0.003 | 0.0204 | 0.000 |
| | Methyl Parathion | 0.971 | 0.332 | 1.303 | 10.06 | 7.676 | 0.0575 | 0.040 |
| | Prothiofos | 0.029 | 0.419 | 0.448 | 3.46 | 0.007 | 0.0198 | 0.000 |
| | Thiacloprid | 0.199 | 0.139 | 0.338 | 2.60 | 0.0001 | 0.0149 | 0.000 |
| **C** | Azinphos-methyl | 0.188 | 1.203 | 1.391 | 55.51 | 123.365 | 0.3173 | 0.648 |
| | Beta-cyfluthrin | 0.00002 | 0.007 | 0.007 | 0.30 | 4.234 | 0.0017 | 0.022 |
| | Carbaryl | 0.118 | 0.005 | 0.123 | 4.92 | 0.801 | 0.0281 | 0.004 |
| | Carbendazim | 0.803 | 1.330 | 2.134 | 85.15 | 6.991 | 0.4867 | 0.037 |
| | Chlorpyrifos | 0.035 | 0.776 | 0.811 | 32.38 | 190.451 | 0.1850 | 1.000 |
| | Dimethomorph | 0.403 | 0.123 | 0.527 | 21.02 | 0.034 | 0.1201 | 0.000 |
| | Endosulfan | 0.004 | 0.004 | 0.008 | 0.31 | 1.036 | 0.0018 | 0.005 |
| | Flufenoxuron | 0.001 | 0.044 | 0.045 | 1.81 | 42.065 | 0.0103 | 0.221 |
| | Flusilazole | 0.017 | 0.003 | 0.020 | 0.79 | 0.001 | 0.0045 | 0.000 |
| | Methyl Parathion | 0.303 | 0.594 | 0.897 | 35.78 | 27.315 | 0.2045 | 0.143 |
| | Prothiofos | 0.010 | 0.765 | 0.775 | 30.93 | 0.062 | 0.1768 | 0.000 |
| | Thiacloprid | 0.088 | 0.326 | 0.414 | 16.53 | 0.001 | 0.0945 | 0.000 |
| | Trifloxystrobin | 0.0005 | 0.002 | 0.002 | 0.09 | 0.003 | 0.0005 | 0.000 |
| **LG4** | Azinphos-methyl | 0.168 | 0.030 | 0.199 | 28.73 | 63.849 | 0.1642 | 0.335 |
| | Beta-cyfluthrin | 0.00002 | 0.0001 | 0.000 | 0.01 | 0.203 | 0.0001 | 0.001 |
| | Carbaryl | 0.255 | 0.024 | 0.278 | 40.28 | 6.560 | 0.2302 | 0.034 |
| | Carbendazim | 0.514 | 0.003 | 0.517 | 74.78 | 6.139 | 0.4274 | 0.032 |
| | Chlorpyrifos | 0.043 | 0.059 | 0.101 | 14.63 | 86.049 | 0.0836 | 0.452 |
| | Dimethomorph | 1.055 | 0.154 | 1.209 | 174.96 | 0.282 | 1.0000 | 0.001 |
| | Endosulfan | 0.008 | 0.019 | 0.026 | 3.81 | 12.714 | 0.0218 | 0.067 |
| | Flufenoxuron | 0.001 | 0.0001 | 0.001 | 0.11 | 2.460 | 0.0006 | 0.013 |
| | Flusilazole | 0.037 | 0.012 | 0.049 | 7.04 | 0.006 | 0.0402 | 0.000 |
| | Methyl Parathion | 0.256 | 0.012 | 0.268 | 38.73 | 29.566 | 0.2214 | 0.155 |
| | Prothiofos | 0.010 | 0.035 | 0.045 | 6.47 | 0.013 | 0.0370 | 0.000 |
| | Thiacloprid | 0.066 | 0.004 | 0.070 | 10.10 | 0.0003 | 0.0577 | 0.000 |
| | Trifloxystrobin | 0.001 | 0.002 | 0.004 | 0.52 | 0.019 | 0.0030 | 0.000 |
| **VW** | Azinphos-methyl | 0.040 | 0.437 | 0.477 | 6.20 | 13.772 | 0.0354 | 0.072 |
| | Beta-cyfluthrin | 0.000004 | 0.002 | 0.002 | 0.03 | 0.445 | 0.0002 | 0.002 |
| | Carbendazim | 0.161 | 0.430 | 0.591 | 7.69 | 0.631 | 0.0439 | 0.003 |
| | Chlorpyrifos | 0.007 | 0.309 | 0.317 | 4.12 | 24.240 | 0.0236 | 0.127 |
| | Cypermethrin | 0.000002 | 0.0004 | 0.0004 | 0.01 | 0.264 | 0.00003 | 0.001 |
| | Flufenoxuron | 0.0002 | 0.014 | 0.015 | 0.19 | 4.398 | 0.0011 | 0.023 |
| | Methyl Parathion | 0.052 | 0.191 | 0.244 | 3.17 | 2.420 | 0.0181 | 0.013 |
| | Propiconazole | 0.011 | 0.018 | 0.029 | 0.37 | 0.0005 | 0.0021 | 0.000 |
| | Prothiofos | 0.002 | 0.309 | 0.312 | 4.06 | 0.008 | 0.0232 | 0.000 |
| | Thiacloprid | 0.016 | 0.105 | 0.122 | 1.58 | 0.0001 | 0.0090 | 0.000 |
| **LR** | Azinphos-methyl | 1.727 | 3.705 | 5.432 | 15.72 | 34.928 | 0.0898 | 0.183 |
| | Beta-cyfluthrin | 0.0001 | 0.020 | 0.020 | 0.06 | 0.841 | 0.0003 | 0.004 |
| | Carbaryl | 3.364 | 0.471 | 3.835 | 11.10 | 1.807 | 0.0634 | 0.009 |
| | Carbendazim | 4.118 | 3.407 | 7.525 | 21.78 | 1.788 | 0.1245 | 0.009 |
| | Chlorpyrifos | 0.366 | 2.655 | 3.021 | 8.74 | 51.422 | 0.0500 | 0.270 |

| Site | Active Ingredient | Loss (kg) | | Index Values | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Runoff | Spray drift | PEL | PEC | TER | PeXI | PeRI |
| **LR** | Cypermethrin | 0.000004 | 0.001 | 0.001 | 0.002 | 0.113 | 0.00001 | 0.001 |
| | Dimethomorph | 2.430 | 0.389 | 2.819 | 8.16 | 0.013 | 0.0466 | 0.000 |
| | Endosulfan | 0.104 | 0.305 | 0.409 | 1.18 | 3.946 | 0.0068 | 0.021 |
| | Flufenoxuron | 0.005 | 0.114 | 0.119 | 0.34 | 7.980 | 0.0020 | 0.042 |
| | Flusilazole | 0.486 | 0.235 | 0.721 | 2.09 | 0.002 | 0.0119 | 0.000 |
| | Methyl Parathion | 2.511 | 1.719 | 4.230 | 12.24 | 9.344 | 0.0700 | 0.049 |
| | Propiconazole | 0.026 | 0.035 | 0.061 | 0.18 | 0.0002 | 0.0010 | 0.000 |
| | Prothiofos | 0.083 | 2.351 | 2.434 | 7.04 | 0.014 | 0.0402 | 0.000 |
| | Thiacloprid | 0.603 | 0.889 | 1.492 | 4.32 | 0.0001 | 0.0247 | 0.000 |
| | Trifloxystrobin | 0.003 | 0.006 | 0.009 | 0.03 | 0.001 | 0.0001 | 0.000 |