Modelling the Fate of Pesticides: Primary Processes, Non-Point Source Data Collection and Guidelines

Report to the

Water Research Commission

on the project

Development of an Integrated Modelling Approach to Prediction of Agricultural Non-Point Source (NPS) Pollution from Field- to Catchment-Scales for Selected Agricultural NPS Pollutants

by

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This report forms part of a series of five reports, which are

i. GÖRGENS AHM (Editor), LORENTZ SA, VAN DER LAAN M, ANNANDALE JG, JOVANOVIC NZ, MATTHEWS N, GROVÉ B and LE ROUX JJ (2012). *Modelling Agricultural NPS Pollution and Economic-Environmental Trade-offs of Pollution Control Measures. (A Project Overview).* WRC Report No. TT 516/12.

ii. VAN DER LAAN M, ANNANDALE JG, TESFAMARIAM EH, DU PREEZ CC, BENADÉ N, BRISTOW KL and STIRZACKER RJ (2012). *Modelling Nitrogen and Phosphorus Dynamics in Cropping Systems at the Field Scale*. WRC Report No. 1516/1/12.

iii. JOVANOVIC NZ, PETERSEN C, BUGAN RDH and VAN DER WALT E (2012). *Modelling the Fate of Pesticides: Primary Processes, Non-Point Source Data Collection and Guidelines.* WRC Report No. 1516/2/12.

iv. LORENTZ SA, KOLLONGEI J, SNYMAN N, BERRY SR, JACKSON W, NGALEKA K, PRETORIUS JJ, CLARK D, THORNTON-DIBB S and GöRGENS AHM (Editor) (2012). *Modelling Nutrient and Sediment Dynamics at the Catchment Scale.* WRC Report No. 1516/3/12.

v. MATTHEWS N, GROVÉ B and GöRGENS AHM (Editor) (2012). *Modelling Economic-Environmental Trade-Offs of Agricultural Non-Point Source Pollution Control Measures*. WRC Report No. 1516/4/12.

EXECUTIVE SUMMARY

Background and Objectives

Agriculture has been recognised, both locally and internationally, as a significant contributor to non-point source (NPS) pollution of water resources. For this reason, progressively more attention has been given to identify NPS sources and to quantify the extent of the NPS problems, so that appropriate steps could be taken to reverse, halt, or minimise their environmental impacts. Such steps might include bio-physical control measures at field- or farm-scale, or statutory and policy instruments. Bio-physical control measures yield benefits to the water environment, but they usually have a cost associated with them; therefore, it is also important to consider the economics of NPS pollution management.

To address this challenge, the Water Research Commission (WRC) has initiated and funded the long-term Research Project, "*An integrated modelling approach to predict agricultural NPS pollution from field- to catchment scale for selected NPS pollutants*" – the Pesticides component of which is detailed in this Report.

The Research Team was structured into Specialist Task Teams within the discipline areas of Sediments, Pesticides, Nutrients, Economics, and Catchment-Scale Modelling. This document represents one volume out of four Research Reports that accompany the Final Project Overview Report. The overall objective is to present the main outputs produced by the Pesticide Task Team.

Aims of this Report

Aim 1

To prioritize the primary processes for pesticides and to present an overview of pesticide models which are suitable to simulate these priority processes.

Aim 2

Report on the collection of data pertaining to NPS fluxes (sediments, pesticides and nutrients) in a small scale catchment of the Western Cape (one of the two study sites selected in this project) to support integrated modelling at different scales.

Aim 3

Development of an expert system (guidelines) for modelling the fate of pesticides.

Methodology

An extensive knowledge review on modelling NPS processes was conducted in the Scoping Report of this Project. The considerations of pesticide-related processes emanating from that Report led to the identification of priority processes for pesticides at field-scale. An extensive search in international databases was also carried out in order to identify suitable models for simulation of these priority processes.

After the conclusion of the literature and model reviews, it was decided that an expert system (guidelines) for modelling the fate of pesticides at field-scale be developed by the Pesticide Task Team. The identification of priority processes and the knowledge gained from experimental work enriched the compilation of an expert system in the format of a Pesticide Environmental indeX (PestEX) that assesses the mobility of pesticides and their potential for reaching a water resource.

The Pesticides Team established an experimental field research site on the Goedertrou Farm in a 20 ha catchment, located along the mid-reaches of the Berg River, in the vicinity of the town of Riebeeck-Wes in the Western Cape Province of South Africa. The main purpose of this experimental work was to assemble data for verification of integrated modelling of NPS pollutants (nutrients, sediments and pesticides) at point- and field-scale. In the Goedertrou catchment the following data were collected from 2005 to 2009:

- Baseline data (Geological maps, a 20 m Digital Elevation Model and soil form maps).
- Weather data collected with an automatic weather station (temperature, radiation, wind speed and direction, relative humidity, rainfall).
- Yield of wheat in 2005 and 2008, as well as re-growth on fallow land in 2006 and 2007 (the common crop rotation in the area is one season of dryland winter wheat followed by 2 years of fallow land).
- Volumetric soil water contents with Echo sensors connected to a data logger (Decagon Devices Inc.).
- Overland flow volumes and quality measured at Wischmeier runoff plots.
- Pesticide concentrations in water: methomyl and tebuconazole applied in 2005; MCPA (2-methyl-4-chlorophenoxyacetic acid) applied in 2008.
- Nutrient (N and P) concentrations in soil, water and plants during 2005 and 2006.
- Measurements of sediments mobilized from the runoff plots (total sediment concentrations and sediment size distribution with a Saturn Digisizer LASER particle size analyzer, Micromeritics Instrument Corporation).
- Water level in a stock-watering dam collecting overland flow and throughflow from the Goedertrou small scale catchment with an Eijkelkamp Diver (Van Essen Instruments, supplied by Eijkelkamp Agrisearch Equipment).

Results and Discussion

The main results and discussion are based on the three aims of this Report.

Aim 1

- The following priority processes for modelling pesticide NPS pollution were identified: overland flow and pesticide transport; vertical water and pesticide fluxes (including drainage and leaching); preferential flow (macropore or by-pass flow and funneling); throughflow (subsurface lateral water and pesticide fluxes); plant uptake of water and pesticides; processes linked to specific pesticide properties (volatilization, sorption and degradation). Several models were identified which are able to simulate these pesticide priority processes. These are FIRST, GENEEC, HYDRUS-2D, PELMO, PESTAN, PRZM, SWAP, SWAT and VS2DT.

Aim 2

The main findings from experimental work at Goedertrou can be summarized as follows:

- Air temperature varied between 1.8°C and 42.8°C, average relative humidity for the recorded period was 63.9%, average wind speed was 3.0 m/s, and rainfall was approximately 330 mm/a with a highest recorded intensity of 27.8 mm/h.

- Wheat grain yield was between 2 Ton/ha (in 2005) and 3 Ton/ha (in 2008). Total biomass production from fallow land was between 2 and 2.7 Ton/ha (in 2006).

- Volumetric soil water content varied depending mainly on seasonal rainfall and the presence of vegetation. The South-oriented, clayey soil at site 2 retained more water than the North-oriented, lighter-textured soil at site 1. Soil water contents exhibited high spatial variability depending on soil properties and sensors' position. Both types of sensors (EC-20 and Echo-TE, Decagon Devices Inc.) were highly responsive to rainfall events (within an hour).

- Overland flow was measured at Wischmeier runoff plots. It varied between 4 and 19% of annual rainfall, depending on vegetation, soil type, slope and slope orientation.

- Different land uses produced different volumes of runoff and consequently different amounts of mobilized sediment. Uncultivated (bare) soil and less densely planted soil produced more runoff. Different soil properties, slopes and antecedent moisture conditions also produced different volumes of runoff. In general, more overland flow occurred from uncultivated land, and from land oriented Southerly, with steep slopes and clayey soil.

- The maximum flux of pesticides measured in runoff water was 1.38 g/ha for tebuconazole (rainfall/runoff event 2 days after application in 2005). No rainfall occurred after application of methomyl in 2005. Both methomyl and tebuconazole, applied towards the end of the 2005 wheat season (end of rainy winter), degraded rapidly *in situ* and did not largely impact surface waters in the absence of rainfall. Half-lives in dam water were 23.6 d for tebuconazole and 4.4 d for methomyl.

- No detectable traces of MCPA (detection limit 0.2 µg/ℓ) in dam water were observed after application of this herbicide in the first week of July 2008 and subsequent rains that occurred during the 2008 winter season.

- Based on overland flow volumes and NO_3 concentrations measured at Wischmeier runoff plots, it was calculated that between 0.24 and 3.65 kg/ha/a of NO_3 were mobilized via overland flow during 2005. NO_3 and PO_4 concentrations in runoff water collected at the runoff plots varied widely depending mainly on the timing of fertilizer application and rainfall/runoff distribution.

- The temporal patterns of nutrient concentrations in both soils and waters followed mainly fertilizer applications. Very low concentrations of NO_2 were generally measured. A time lag was observed between the application of fertilizer and increase in concentrations of NO_3 in runoff water, as nutrients were washed out by erratic events. The concentrations of NO_3 and PO_4 in the stock-watering dam were in the range of those measured in runoff water.

- Concentrations of sediments in runoff water were between 0 and 22.0 g/ℓ (2.6 g/ℓ on average), depending on rainfall distribution and intensity, slope and vegetation. Total seasonal sediment mobilization ranged between 0.02 and 0.85 Ton/ha/a (0.26 Ton/ha/a on average).

- High concentrations of sediments in runoff water were generally measured when small runoff events occurred (low rainfall amounts and/or intensity). With high rainfall and runoff volumes, sediment concentrations were generally low due to dilution effects. In terms of total sediment load, however, more eroded material was mobilized from the runoff plots during heavy rainfall and runoff events. The bulk of mobilized particles had diameters in the range between 5 and 15 μm (silt range), depending on the soil texture (source of mobilized sediments) and slope (gravity force for transport), and regardless of rainfall and overland flow volumes. The expected sediment particle size distribution in the catchment can be used in conjunction with sorption data to estimate transport of sorbed contaminants, e.g. nutrients and pesticides. In addition, sediment size distribution can be used in conjunction with chemical properties of mineral particles to trace the origin and history of sediment transport in catchments.

- Water levels in the stock-watering dam at Goedertrou varied seasonally and responded within hours of rainfall events.

Aim 3

- An Excel-based Pesticide Environmental indeX (PestEX) was developed that accounts for the main factors affecting the mobility of pesticides and their potential for reaching a water resource. A multi-level approach was used to combine these factors based on their level of occurrence, namely local scale (pesticide drift; position of application in relation to streams and groundwater; general slope of the area; presence of impervious layers in soils and dominant flow direction; tillage practices; soil hydraulic properties; the impact of irrigation practices/rainfall distribution through overland flow and deep percolation; the presence of anti-erosion contours), catchment scale (pesticide properties like sorption, volatilization and decay; the presence of wetlands/buffer strips) and overarching level (pesticide application; sensitivity of the receiving environment). Each of these factors is assigned a rating (using fuzzy logic for numerical variables) and weighting to produce a pesticide mobility score. The normalized score allows for the comparison and minimization of environmental and pollution abatement costs.

- The PestEX calculator was demonstrated using data from the experimental site at Goedertrou, where methomyl and tebuconazole were applied to dryland wheat during the 2005 cropping season, and their mobility to a surface water body (farm dam) and groundwater was scored. It is envisaged that potential users of this tool could be the scientific community, farmers, pesticide consultants and the regulatory authority. Many applications are possible, e.g. comparative analyses of environmental and pollution abatement costs of different chemicals for regulatory or marketing purposes, sensitivity analyses to assess the effects of different mitigation/management measures (e.g. size of wetlands to be constructed), the minimization of costs by changing mitigation/management practices etc.

Conclusions

i. The identification of priority processes for modelling of pesticides fluxes is now sound.

ii. Successful collection of a comprehensive data set of NPS pollutant fluxes (nutrients, pesticides and sediments) at point- and field-scale in the Goedertrou catchment of the Western Cape, in addition to atmospheric, soil and vadose zone, surface- and groundwater data.

iii. Successful establishment of an expert system in the format of a Pesticide Environmental indeX (PestEX) that can be used to assess the mobility of pesticides and their potential for accumulating in a water resource, based on knowledge gained from the priority processes study and experimental work.

iv. The predictive capabilities of existing models/methods and those developed during the course of this project can be used to transfer knowledge to water managers. In particular, scenarios of land use and management can be simulated to recommend the most environmentally and economically acceptable practices.

Lessons Learnt

Research Design

i. The required baseline data for catchment monitoring of NPS pollutants should include geology and hydrogeology, soils, climate, hydrological data (volumes and quality), as well as history of land use, fertilization, pesticide application and land management. It is imperative that monitoring should include all components of the system, namely atmospheric, soil, surface water and groundwater.

ii. Due to the large number of chemicals applied to protect crops, where each of these chemical species has specific properties (volatilization, sorption and degradation), it is recommended that a target spectrum of pesticides be detected at key locations in catchments in order to identify priority species to be monitored.

Approaches to Scaling

iii. The team consisted of researchers and collaborators with complementary expertise in different fields and modellers at different spatial scales. Since the start of the project, modelling and remote sensing capabilities have improved to the point that integration of detailed information at field-scale into large catchment-scale has now become a realistic goal. Intensive monitoring at field-scale of water and nutrient fluxes can therefore serve the purpose of informing processes at catchment-scale. In order to achieve this, it is imperative that databases of detailed information be compiled in order to facilitate the set-up and parameterization of distributed hydrological models operating according to the principle of hydrological response units (e.g. ACRU2000 and SWAT). The database population and handling will be crucial.

Interfacing Natural Resource Management Needs and Scientific Realities

iv. The predictive capabilities of existing models/methods and those developed during the course of this project can be used to transfer knowledge to water managers and to work with water managers. In particular, scenarios of land use and management can be simulated to recommend the most environmentally and economically acceptable practices. It is, however, essential that these scenarios be developed through a participatory approach with stakeholders (scientists and modellers, farmers, Government officials and others) in order to facilitate knowledge transfer.

Recommendations for Future Research

i. A lack of sound data sets for modelling pesticides at different scales and high cost of pesticide measurements were expected shortcomings when this Project started. Therefore, there is a need to strengthen the monitoring network of pesticides nation-wide. It is recommended that a target spectrum of pesticides be detected at key locations in catchments in order to identify priority species to be monitored. Research on endocrine disruptors and ecotoxicology also needs to be strengthened.

ii. The effects of specific pesticides, their residuals and daughter products on soil fertility and food production are often not known. Therefore, it would be beneficial to initiate a soil quality research programme in order to define and quantify soil quality indicators and thresholds for different environmental conditions, as well as to describe and quantify the interactions of soil physical, pedogenetical, chemical and biological processes, as these are likely to directly or indirectly affect water resources.

iii. Alternative methods of pest control, for example, such as integrated pest management need to be investigated.

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1D	One-dimensional model
2D	Two-dimensional model
3D	Three-dimensional model
ACRU	Agricultural Catchments Research Unit hydrological model
C_1	Concentration at time t_1
C_2	Concentration at time t_2
CEMC	Canadian Environmental Modelling Centre
DDT	Dichlorodiphenyltrichloroethane
EIQ	Environmental Impact Quotient (EIQ)
EPA	Environmental Protection Agency
EXPRES	Expert system for assessment of the potential for pesticides to contaminate soil and groundwater
FIRST	FQPA, Food Quality Protection Act, Index Reservoir Screening Tool model to estimate human exposure to pesticides for risk assessment purposes
GCMS	Gas Chromatography Mass Spectrometer
GENEEC	GENeric Estimated Exposure Concentration model to estimate human exposure to pesticides for risk assessment purposes
HPLC	High Pressure Liquid Chromatography
HYDRUS-2D	Model for analysis of water flow and solute transport in variably saturated porous media
IGWMC	International Ground Water Modeling Center
Ipest	Agro-ecological indicator to assess the environmental effects of pesticides
K	Degradation rate constant
LIMPACT	Expert system used to indicate whether a stream is contaminated with pesticides or not, based on macroinvertebrate indicators
MCPA	2-methyl-4-chlorophenoxyacetic acid
MCS	Mike Cotton Systems, Cape Town
NPS	Non-Point Source
P1	Runoff plot 1

P2	Runoff plot 2
PAM	polyacrylamide
PELMO	One-dimensional, multi-layer model for pesticide fate in the unsaturated zone
PESTAN	Analytical, one-dimensional model that simulates transport of dissolved organic solutes in the unsaturated zone
PestEX	Pesticide Environmental indeX
PPRI	Plant Protection Research Institute
PRZM3	Pesticide Root Zone Model that links the PRZM and VADOFT models to predict pesticide and nitrogen transport and transformation through the crop root and vadose (unsaturated) zones down to the water table
REM	Register of Ecological Models
S_1D_DUAL	Dual permeability soil water flux and preferential flow model
S1	Runoff plot site 1
S2	Runoff plot site 2
SABS	South African Bureau of Standards
SASS 5	Indicator for pollution tolerance of macroinvertebrate species used South African River Health Programme SASS 5
SSC	Small Scale Catchment
SWAP	Soil Water Atmosphere Plant 2D, transient model for water flow and solute transport in the unsaturated and saturated zones
SWAT	Soil and Water Assessment Tool 2D hydrological model
SWC	Soil water content
SWMS_2D	Model for simulating water and solute movement in two-dimensional variably saturated media
$T_{1/2}$	Half-life
T2	Tank 2 at runoff plots
t_2	Time 2
VS2DT	Variably Saturated 2-D flow and Transport finite-difference model for cross-sectional or cylindrical variably saturated flow in porous media
WRC	Water Research Commission

1 INTRODUCTION

1.1 BACKGROUND AND RATIONALE

Agriculture has been recognised, both locally and internationally, as a significant contributor to non-point source (NPS) pollution of water resources. For this reason, in recent years, progressively more investment has been made in identifying agricultural NPS contributors and quantifying the extent of the NPS problems, so that appropriate steps could be taken to reverse, halt, or minimise their environmental impacts. Such steps might include bio-physical control measures at field- or farm-scale, or statutory and policy instruments. Bio-physical control measures yield benefits to the water environment, but they usually have a cost associated with them; therefore, it is also important to consider the economics of NPS pollution management.

To address this challenge, the Water Research Commission (WRC) initiated the following long-term, multi-scale, multi-disciplinary Research Project: "*An integrated modelling approach to predict agricultural NPS pollution from field- to catchment scale for selected NPS pollutants*" – the Pesticides component of which is detailed in this Report.

As the Project title indicates, the primary aim was to develop an integrated modelling approach to prediction of agricultural NPS pollution from field- to catchment-scale for selected NPS pollutants. A secondary aim was to develop a modelling approach for examination of the economic-environmental trade-offs of agricultural pollution control measures, the effects of which were to be modelled by use of the field- and catchment-scale models. The specific objectives of the Project stated in the original TOR were as follows:

- Establishment of fate-of-NPS-pollutant and other requisite data sets at field-, laboratory-, and quaternary catchment-scale, suitable for model improvement, development and verification.
- Improvement of understanding of on-farm NPS pollution control measures and their modelling requirements.
- Establishment of an improved field-scale model for simulation of agricultural NPS pollution loadings for phosphorus, nitrogen, selected pesticides and sediments, as well as for simulating the beneficial impacts on nearby receiving waters of on-farm NPS pollution control measures.
- Establishment of an improved quaternary catchment-scale model for simulation of agricultural NPS pollution loadings for phosphorus, nitrogen and sediments, as well as for simulating the downstream benefits of on-farm NPS pollution control measures at the catchment-scale.
- Development of guidelines about model usage to examine economic trade-offs and feasibility of agricultural NPS pollution control measures at field- and catchment-scale.

1.2 PROJECT SCOPE AND EXTENT

The duration of the Project was from April 2005 to February 2012 and involved researchers from nine different institutions and organisations: the Universities of Pretoria, the Free State, KwaZulu-Natal and the Western Cape, respectively, as well as the Agricultural Research Council (ARC), CSIR, SA Sugar Research Institute (SASRI), CSIRO (Australia) and Aurecon, who provided project leadership.

The Project was structured into four parallel but overlapping phases to ensure research effort synergies and inter-linked research outputs:

- Phase One: Observation and monitoring of NPS pollution processes at point-, field- and catchment-scales (nutrients, sediments and pesticides).

- Phase Two: Developing field-scale NPS pollution predictive capability via a bio-physical field-scale model (nutrients and sediments), as well as an expert system (pesticides).

- Phase Three: Developing catchment-scale NPS pollution predictive capability via catchment-scale bio-physical models (nutrients and sediments).

- Phase Four: Developing economic-environmental trade-off modelling ability, supported by the above bio-physical models.

This Report documents the research conducted by the Pesticides Task Team during Phases One and Two of the Project.

1.3 TECHNOLOGY TRANSFER

The Project yielded five published final reports: an Overview Report and four detailed technical accounts of the research on the field-scale bio-physical modelling, the field-scale expert system for pesticides, the catchment-scale modelling and the economic-environmental trade-off modelling, respectively.

i. GÖRGENS AHM (Editor), LORENTZ SA, VAN DER LAAN M, ANNANDALE JG, JOVANOVIC NZ, MATTHEWS N, GROVÉ B and LE ROUX JJ (2012). *Modelling Agricultural NPS Pollution and Economic-Environmental Trade-offs of Pollution Control Measures. (A Project Overview).* WRC Report No. TT 516/12.

ii. VAN DER LAAN M, ANNANDALE JG, TESFAMARIAM EH, DU PREEZ CC, BENADÉ N, BRISTOW KL and STIRZACKER RJ (2012). *Modelling Nitrogen and Phosphorus Dynamics in Cropping Systems at the Field-scale*. WRC Report No. 1516/1/12.

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The Project also yielded 14 journal papers and presentations at conferences and symposia and at least three more are in progress. The Overview Report is not a detailed scientific presentation of the research conducted during this Project; rather, it presents a narrative of the Project, its challenges, its achievements and its learnings in the hope that a wider audience would find it accessible and useful.

1.4 CAPACITY BUILDING

Given the research nature of the Project, as well as the involvement of a number of academic and research institutions, a large capacity building component was maintained throughout and the Project supported 13 post-graduate students.

1.5 PROJECT TEAM COMPOSITION

The Project Team was composed of four individual Task Teams, comprising one or more Specialists within each of the domains of agricultural nutrients, sediments, pesticides, field-scale bio-physical modelling, catchment-scale bio-physical modelling, and agricultural economics. As stated earlier, the Specialists were drawn from a range of academic and research institutions. The research consulting firm, Sigma Beta, was appointed to provide leadership, coordination and administration to the Research Team, with Professor André Görgens in the Project Leader role. In 2009 Sigma Beta was absorbed into Aurecon, a global professional consulting firm, who continued with the functions previously performed by Sigma Beta.

1.6 STRUCTURE OF THIS REPORT

The overall objective of this Report is to present the main research outputs produced by the Pesticide Task Team during the course of this Project. This volume is structured into three sections:

i. Prioritization of primary processes for pesticides and pesticide models.

ii. NPS data collection at a field research site in the Western Cape.

iii. Expert systems and development of guidelines for modelling the fate of pesticides.

2 DESCRIPTION OF PRIMARY PROCESSES FOR PESTICIDES AND PESTICIDE MODELS

2.1 INTRODUCTION

This Chapter includes two sections, respectively, primary processes and overview of models.

The first section deals with the description and prioritization of primary NPS processes for production of pesticides. The aim was to identify all the field-scale processes that should be described in a conceptual field-scale model. A second objective was to prioritise those key field-scale processes that should be simulated in a deterministic field-scale model. This chapter also includes interfaces between the different NPS pollutants.

The second section provides an overview of models available to simulate pesticide processes at local and regional scale. It also includes a motivation for selection of the most suitable field-scale models for pesticides in terms of priority processes and their algorithms.

2.2 PRIMARY PROCESSES

An extensive knowledge review on modelling NPS processes was done in a WRC Scoping Study by Rossouw and Görgens (2004). The considerations for pesticide-related processes emanating from this report led to the identification of the following priority processes concerning water and solute fluxes:

- Overland flow and pesticide transport.
- Vertical water and pesticide fluxes, including drainage and leaching.
- Preferential flow (macropore or by-pass flow and funneling).
- Throughflow (subsurface lateral water and pesticide fluxes).
- Plant uptake of water and pesticides.
- Processes linked to specific pesticide properties. These main properties were identified to be:
    - Volatilization
    - Sorption
    - Degradation (decay)

These processes are described below, along with the main mechanisms and factors involved, quantification approaches (measurements and predictions) as well as mitigation measures.

2.2.1 Overland flow and pesticide transport

Along with leaching, pesticide transport via overland flow is the most direct process involved in the contamination of water resources (Wasson, 1998). Pesticide concentrations in runoff are important as they affect the potability of the water (Blanchoud *et al*., 2004); they may cause health problems (McConnell *et al*., 1999) and effects on living organisms in agricultural streams. The effects of pesticides in runoff are documented for benthic macroinvertebrates (Berenzen *et al*., 2005; Thiere and Schulz, 2004), plant life through inhibition of photosynthesis (Frankart *et al*., 2003), vegetation richness of stream border ecotones (Hald, 2002), and also in coastal areas (Oros *et al*., 2003) and estuarine environments (Arnold *et al*., 2004).

Both urban and rural areas have been identified as sources of pesticide pollution via runoff (Blanchoud *et al*., 2004). Golf courses were also identified as a major source of pollution in urban and peri-urban areas (Mankin, 2000). Besides direct application, leakage from storage sites and washing of spraying equipment can also be considerable sources (Neumann *et al*., 2002), as well as atmospheric deposition and roof wash-off of deposited pesticides (Zobrist *et al*., 2000).

Many studies indicate that transport via overland flow is the dominant process causing contamination from pesticides. For example, Gallagher *et al*. (2001) reported that 82% of the copper leaving agricultural fields was found in the runoff with the majority, 74%, sorbed to suspended solids. Ueoka *et al*. (1997) found no groundwater contamination from dithianon and vinclozolin in the soils of the South Australian Riverland, due to low mobility and high degradation rate of these pesticides. Kladivko *et al*. (2001) indicated that pesticide concentrations and mass losses are usually much lower in subsurface drainage than in surface runoff, often by an order of magnitude.

Runoff generally occurs as concentrated flow in rills or gullies (McLaughlin *et al*., 1998). Finer-sized soil particles are selectively transported during inter-rill erosion. These particles generally have a high adsorption capacity leading to pollution enrichment. In runoff water, pesticides are transported as both solutes and adsorbed on suspended particles (Rose and Ghadiri, 1992) and organic matter.

Pesticide transport via overland flow depends mainly on natural conditions (in particular rainfall) (Cryer *et al*., 1998), application rates and physico-chemical properties of pesticides (Nakano *et al*., 2004), type of vegetation (Joslin and Schoenholtz, 1997) as well as management practices (Schreiber *et al*., 1996). Pesticide transport via overland flow is enhanced by the presence of erosion rills and high slopes (Dabrowski *et al*., 2002) and by soil compaction (Soane and Van Ouwerkerk, 1995). Gao *et al*. (1997) reported experimental data where atrazine and bifenox were mainly transported via overland flow from inclined areas, but their transport pattern and metabolism schemes showed some differences according to their physico-chemical properties.

The dynamics of pesticide transport via overland flow generally exhibits a peak at the beginning of the storm event when high concentrations of pesticides occur (“first flush”), followed by reduced concentrations as overland flow continues. Kreuger (1998) confirmed this hypothesis of peak concentrations occurring during runoff events and after pesticide application. Schulz (2001) indicated that short-term exposure, for example through a rain storm, has the potential to result in long-term contamination of surface waters. Hyer *et al*. (2001) studied atrazine transport processes after agricultural application. They indicated that a rapid, short-duration overland-flow pulse contributed most of the atrazine. They also concluded that reduced pesticide application (rather than elimination of overland flow or soil water contributions) was necessary to improve the episodic streamflow composition. From these literature studies, we can conclude that the beginning of the rainy season is the critical period in terms of pesticide transport via overland flow.

Vegetated buffer areas (Bouldin *et al*., 2004a; Syversen and Bechmann, 2004), inter-row vegetative filter strips (Watanabe and Grismer, 2003) and agricultural ditches (Bouldin *et al*., 2004b) can provide mitigation to non-point source pollution from agriculture. Other mitigation measures to pesticide transport via overland flow are conservation tillage (Holland, 2004), in particular by incorporating pesticides in the soil, constructed wetlands (Sherrard *et al*., 2004) and water soluble polymers, like anionic polyacrylamide (PAM), which prevents erosion and enhances infiltration (Entry *et al*., 2002). Changing cropping system can also be seen as a mitigation strategy (Eltun *et al*., 2002). Kladivko *et al*. (2001) reported that the presence of a subsurface drainage system generally increases the volume of infiltration and consequently decreases the volume of surface runoff water and sediment. The presence of subsurface drainage decreases surface runoff losses of sorbed compounds such as pesticides, both because of lower runoff volumes and because of lower concentrations in the runoff resulting from the delayed initiation of runoff. Carluer and De Marsily (2004) warned, however, that artificial networks may act as conduits or short-circuits for the transport of contaminants, either dissolved or sorbed on soil particles, by-passing some of the retardation mechanisms such as sorption in the soil, retention of surface runoff by grass verges, biodegradation in the unsaturated zone, etc.

Overland flow volumes and quality can be measured using runoff plots, where runoff water is funnelled from a surface area and collected at an outlet, where it can be sampled for laboratory analysis of soluble pesticides. In a similar manner, sediments can be collected at the outlet for laboratory chemical analysis of sorbed pesticides.

2.2.2 Vertical water and pesticide fluxes

Along with runoff, leaching is the most direct process involved in the contamination of water resources. Leaching is the flux of pesticide dissolved in the solution through the bottom of the active root zone. It is therefore directly linked to vertical water and solute fluxes.

Pesticide movement in the soil profile occurs by convection, mechanical dispersion due to variations in velocity through pores of different sizes, and diffusion governed by Fick's law and based on differences in concentration gradients over limited distances (Bresler *et al*., 1982). The main process that causes movement of contaminants downwards in the unsaturated zone is infiltration, which is driven by gravity and large suction gradients between the wetting front and the dry media. The wetting front is the zone that water invades advancing into an initially dry medium, with matric potentials typically just below saturation (between 0 and -2 J kg^{-1} or 2 kPa suction). Flushing of solutes downwards generally occurs at the edge of the wetting front. In this way, a centre of mass of solutes is generated and transported downwards during infiltration events.

Vertical fluxes of pesticides can therefore cause contamination of groundwater, particularly in areas with negligible slope, high rainfall and highly permeable soils. The depth of the groundwater table is also very relevant, as indicated by Johnson *et al.* (2001). Vertical fluxes depend on rainfall/irrigation conditions (Schierholz *et al*., 2000). Generally, areas with high water tables are more susceptible to contamination from pesticides as travel time through the vadose zone is reduced. Reichenberger *et al*. (2002) indicated that the irrigation method (e.g. ponding) may enhance leaching, whilst Blackwell (2000) singled out furrowing. Perillo *et al*. (1999) found more preferential flow and pesticide leaching occurring on flood irrigated plots at high application rates, compared to sprinkler irrigation. Tillage may also affect vertical fluxes through changes in the soil matrix, saturated hydraulic conductivity and porosity in subsurface soils (Malone *et al*. 2003).

Although the principles of water and pesticide fluxes in the vadose zone are similar to those typical for porous media (Hantush *et al*., 2000), the rates of pesticide transfer and transformation in sub-soils are often unknown and difficult to establish (Vanclooster *et al*., 2000). In some cases, it is justified to assume that the properties of the sub-soil are similar to the properties of the overlying soil. In other cases, however, different properties between soil and weathered bedrock are measured (Hubbert *et al*., 2001). The vadose zone generally differs from the overlying soil root zone because of a lack of organic matter, different temperatures, microbial activity, water content, texture and structure. It is, however, clear that this part of the system may represent an important defensive barrier to groundwater contamination. Rae *et al*. (1998) demonstrated that sand in primary aquifer sediments has a high sorption capacity for pesticides.

Vertical fluxes, however, exhibit spatial variability. Beulke *et al*. (2004a) reported that variability in a number of soil properties needs to be taken into account. Lennartz (1999) and Netto *et al*. (1999) investigated the variability in transport characteristics of pesticides, concluding that this was affected mainly by preferential flow.

The recommended measurement approach for vertical fluxes of pesticides is sampling of the vadose zone and groundwater, and laboratory analysis.

2.2.3 Preferential flow

Fetter (1993) classified preferential flow as short-circuiting, fingering and funnelling. Short-circuiting occurs due to movement of infiltrating water along preferential paths (e.g. plant roots, soil cracks, etc.). Fingering occurs due to pore-scale variations in permeability, especially at boundaries where finer sediment overlies coarser sediment. Funnelling occurs whenever water is funnelled on sloping impermeable layers, and concentrated at the end of these layers where it percolates vertically. Funnelling is therefore typical for layered soil or sediment profiles.

Renaud *et al*. (2004a) considered five processes to explain different patterns of leached pesticide loads, and placed preferential flow at the top of the list. The processes considered were: (1) relative extent of preferential flow, (2) sorption capacity of the compounds to the different soils, (3) extent of degradation of the compounds in the soil, (4) variation in sorption kinetics between compounds associated with pesticide diffusion into soil aggregates, and (5) combination of intra-aggregate diffusion and the presence of preferential flow pathways.

Larsson *et al*. (1999) found that leaching to tile drains with shallow groundwater increased by about 80% because of preferential finger flow (from 1.2% to 2.2% of the amount of pesticide applied) in a sandy soil. The effect of soil properties and preferential flow on pesticide leaching was observed both in breakthrough curve experiments carried out by Kamra *et al*. (2001) and in field experiments (Novak *et al*., 2001). Haria *et al*. (2003) found contamination of shallow groundwater by pesticides due to high rates of both matrix and preferential flow, whilst where the groundwater was deeper, ‘intermediate’ storage sites remained empty and unsaturated water potential profiles showed that rainfall pulses were attenuated as these sites absorbed the downward water fluxes. Ray *et al*. (2004) reported that the volume fraction of the macropores affects the amount of pesticides leaving the root zone. They developed a dual-permeability model (S_1D_DUAL) and ran it for a test case to show that water flux in the preferential flow domain was three times more than in the matrix for selected storm events. Bergstrom (1995) discussed that water flow in cracks may move some of the pesticide rapidly through the top-soil into the sub-soil. Once the compound reaches the sub-soil, degradation rates are reduced and the pesticide residues are stored for later leaching.

Zehe and Flühler (2001) found deep penetrating earthworm burrows to be a cause of preferential flow and that pesticides are also transported by mobile soil particles in macropores and soil cracks. They indicated that the main pre-condition for the occurrence of preferential flow events is the presence of sufficient deep-penetrating macropores inter-connected to the soil surface. In an experiment carried out on large Alfisol monoliths during long-duration simulated rain events, Lægdsmand *et al*. (1999) observed that the first flush of water mobilized loosely bound colloids that had a high organic content relative to the bulk soil. During the late leaching phase, the rate of colloid mobilization was positively correlated with flow velocity. De Jonge *et al*. (1998) also discussed the colloid-facilitated transport of pesticide in undisturbed soil columns.

Christiansen *et al*. (2004) reported that the spatial variations in macropore flows caused by the variation in topography and depth to groundwater table within a catchment are so large that this has to be accounted for in up-scaling process descriptions and results. Preferential flow can be estimated with the use of common dyes or tracers.

2.2.4 Throughflow

Contamination of surface waters can also occur via interflow (throughflow), in particular in layered soils, where movement of water and pesticides may occur on sloping impermeable layers. Muller *et al*. (2003) reported that single rainfall events leading to runoff and interflow dominated NPS pollution in a catchment in Germany. Pan *et al*. (2004) also indicated that sediment layering could cause considerable lateral flow. On the other hand, Nimmo *et al*. (2002) showed that low-permeability sediment layers in the unsaturated zone divert some flow horizontally, but do not prevent rapid transport to the aquifer, and that transport rates under these conditions may exceed 14 m d^{-1}. Knowledge about sedimentary structures in the unsaturated zone is therefore important for monitoring contaminant transport and for remediation purposes (Sovik *et al*., 2002). Pesticide transported through interflow can be intercepted by the root zone of vegetative filter strips (Watanabe and Grismer, 2003).

In order to estimate the fluxes of water and pesticides via throughflow, detailed information on soils and geology of a catchment needs to be collected.

2.2.5 Plant uptake

From the commercial point of view, the three main properties of pesticides are persistence, efficacy and selectivity. Persistence (degradation) has major implications to surface and groundwaters and it will be discussed later in detail. Efficacy and selectivity are directly related to plant uptake. Plant uptake needs to be quantified not only to improve crop production and efficacy of pesticides, but also to gain insight into the fate and transport of pesticides (Leib and Jarrett, 2003). Hantush *et al*. (2000) described the mechanisms of crop uptake of pesticides used in models.

Severinsen and Jager (1998) modelled the influence of terrestrial vegetation on the fate of xenobiotics in the environment on a regional scale. The fate processes included were uptake from soil with transpiration stream, diffusive exchange with air, stomatal uptake from air of micropollutant sorbed to fine particles, metabolism, plant death and harvest. Other examples were found in the literature on the modality of plant uptake. Chamel and Vitton (1996) found a linear correlation between concentrations of atrazine and simazine, and their uptake through isolated tomato and pepper fruit cuticles. Sun *et al*. (2004) investigated the capability of different plant species to accumulate aldicarb. Accumulation in different plant organs was also studied. For example, Martin *et al*. (2000) indicated that arsenic from arsenical pesticides is confined mainly to heartwood near the pith and active xylem tissue in the most recent annual growth rings of fruit trees.

Many factors are involved in plant uptake of pesticides. Finlayson and MacCarthy (1973) listed the plant species, growth stage, intended use, soil characteristics such as pH, temperature, clay fraction, moisture content and particularly organic matter content. Kaufman (1983) indicated more factors, for example the type of pesticide, the pesticide formulation, the method of application and the mode of action. Garcinuño *et al*. (2003) investigated the uptake of different herbicides and insecticides by *Lupinus angustifolius* seeds. They indicated the following factors affecting pesticide uptake: properties of the chemical (structure, stability, octanol-water partitioning coefficient and diffusion rate), type of water, flow rate and concentration, contact time, pH, temperature, organic matter content and composition, and seed characteristics (permeability of the seed coat, seed biomass, seed saturation and speed of retention). Tao *et al*. (2004) found that the uptake of DDT by wheat increased considerably in the presence of water soluble organic carbon, while it was negatively correlated to the content of water insoluble organic carbon. Behrendt *et al*. (1995) modelled the pesticide root uptake in the transpiration stream of cereals. The pesticide root uptake was closely interlinked to sorption and degradation.

The effect of uptake of pesticides by non-target organisms is particularly interesting from the point of view of environmental protection and remediation. Klöppel and Kördel (1997) found that fenpropimorph and chlorothalonil applied to cereals resulted in high concentrations in non-target plants. Schweiger *et al*. (2001) and Qiu *et al*. (2004) indicated that side effects of pesticides on non-target organisms should be considered, like for example the reduced uptake of nutrients. Another sink of pesticides are soil-dwelling organisms (Gyldenkærne and Jørgensen, 2000). The use of pesticides was related to the decline of wildlife on agricultural land by Sotherton (1998). The removal of plants or animals that have taken up pesticides may represent an important component of the pesticide field balance. The ultimate fate of those residues depends on how plants or animals are handled.

Laboratory protocols and procedures for measurement of pesticides can be found on the following Environmental Protection Agency (EPA) web site: (http://www.epa.gov/microbes/methmans.html, accessed on 28 January 2010).

2.2.6 Volatilization

Volatilization is the process whereby solutes move from the medium in which they are dissolved, into the atmosphere. In the context of this project, this process is more related to pesticide atmospheric transport than to transport via water. Volatilization may occur from soil and plant surfaces (Rüdel, 1997), from water surfaces (Bidleman and McConnell, 1995) as well as from the soil matrix. Volatilization from the soil can occur from the very thin surface film after spraying and before rainfall and/or irrigation, as well as from the soil matrix via vapour fluxes (Boesten, 1999). Volatilization from the plant surface is most likely a function of saturated vapour pressure (Woodrow *et al*., 1997; Smit *et al.*, 1998).

Volatilization of pesticides can cause off-target movement and contamination of the environment both in urban and rural areas (Yeo *et al*. 2004), causing undesired effects to humans and the environment (Van der Werf, 1996), as well as wildlife (Freemark and Boutin, 1995). This process is particularly hazardous to non-target crops grown in areas which are downwind from the site of application (Dejong *et al*. 1995; Klöppel and Kördel, 1997). Ramaprasad *et al*. (2004) measured volatilization of organophosphorus insecticide from wetted leaf surfaces. Castro *et al*. (2002) measured a volatilization rate of nearly 1% of the initial amount of endosulfan per hour for the first 24 h at room temperature from tomato leaves under laboratory conditions.

Voutsas *et al*. (2005) tested the volatilization of organic compounds from soil surfaces using several models. Scheyer *et al*. (2004) measured increased volatilization of organochlorine pesticides from the soil surface due to high temperatures compared to periods when temperatures were lower. Haenel and Siebers (1995) found volatilization rates to be remarkably influenced by micrometeorological conditions. Volatilization can also occur during melting of aged snow (Herbert *et al*., 2004). In the soil air, volatilization may be influenced by the exchange of immobile/mobile water fluxes (Hantush *et al*., 2002).

Volatilization is, however, difficult to estimate due to the canopy and soil surface roughness, as well as due to other processes that may occur simultaneously, e.g. chemical and photochemical degradation (Scholtz *et al*. 2002). It can be measured by air sampling (Clément *et al*., 2000), using tracers (Bidleman *et al*., 1998) and sensors at laboratory and field-scale (Alvarez *et al*., 1998), or by measuring residue disappearance (Haenel and Siebers, 1995). Rüdel (1997) and Bedos *et al*. (2002) measured volatilization of trifluralin in wind tunnels. Alvarez-Benedi *et al*. (1999) measured volatilization of terbutryn in volatilization chambers. Scholtz *et al*. (2002) measured the fluxes of trifluralin and triallate using the relaxed eddy-accumulation technique.

2.2.7 Sorption

Adsorption is the attraction of pesticide molecules to soil solid particles. This process influences the pesticide fluxes by retarding or enhancing pesticide migration. Pesticide sorption occurs mostly on organic matter rather than soil mineral particles. Sorption can also be associated with runoff and transport of sediments and colloids.

Pesticide sorption onto soil particles is one of the most important processes determining the fate of pesticides and it depends on several factors (Hesterberg, 1998). The following factors influencing sorption were reported in the literature:

- Pesticide properties (Tuxen *et al*., 2000);

- Solution properties, e.g. the presence of ortho-phosphates, ionic strength and dominant cations (De Jonge and De Jonge, 1999);

- Soil-chemical contact time (aging) (Park *et al*., 2004);

- Soil properties like soil organic carbon and humic substances (Spark and Swift, 2002; Cooke *et al*., 2004), soil particle sizes determining the surface area and sorption sites (Li *et al*., 2000), type and nature of clay (Torrents and Jayasundera, 1997; El-Nahhal *et al*., 2001; Inacio *et al*., 2001), soil pH (Sheng *et al*., 2005; De Jonge and De Jonge, 1999) and soil temperature (Beulke *et al*., 2004b);

- Soil management practices like tillage (Düring *et al*., 2002).

Weber *et al*. (2004) provided a database of sorption coefficients for numerous pesticides and depending on soil properties. Gerstl (2000) suggested normalizing soil sorption data to soil organic matter content, arguably the most important sorption-related soil property, in order to estimate sorption where actual data is lacking.

Besides the above-mentioned factors, other processes may complicate the estimation of pesticide sorption. For example, Martins and Mermoud (1998) studied the antagonistic or synergistic effects in herbicide mixtures. They demonstrated that the more soluble herbicides strongly decreased the sorption of the more hydrophobic ones on the soil organic fraction. In addition, they showed that ionic strength affects sorption levels dramatically. The competitive sorption was also responsible for the observed increase of herbicide biodegradation presumably by keeping molecules bioavailable for microbial attack. Sorption is also a time-dependent process where partitioning of pesticide to soil particles was found to be governed by diffusion (Renaud *et al*., 2004b). Differences in sorption-desorption properties and the phenomenon of sorption hysteresis were studied by González-Dávila (1995).

A number of measures can be applied to artificially modify sorption of pesticides. Sorption properties can be modified through organic amendments used to enrich soils of low organic matter contents, e.g. olive oil mill wastewater (Cox *et al*., 1997), liquid sewage sludge (Cells *et al*., 1998), organic fertilizer (Li *et al*., 2005), city refuse compost and surfactants (Sánchez-Camazano *et al*., 1997). Carrizosa *et al*. (2000) indicated that organoclays can be used as pesticide carriers in slow release formulations to immobilize pesticide in a contaminated soil and to protect soil and water. Worrall *et al*. (2001), however, showed that no amount of organic amendment would protect against pollution from highly water-soluble compounds.

Measurements of sorption can be done using EPA standardized laboratory techniques (http://www.epa.gov/microbes/methmans.html, accessed on 28 January 2010). Kördel *et al*. (1995) immobilized humic acids and clay minerals on silicagel phases and used them as stationary phases in High Pressure Liquid Chromatography (HPLC) columns. Sorption coefficients can also be inferred using soil column experiments and breakthrough curves (Xu *et al*., 1999).

Sorption can be described with linear and non-linear isotherms (Giles, 1972). Giles *et al*. (1960) classified sorption isotherms into four main classes and discussed the shapes of the curves describing the partitioning of chemicals into soluble and solid phase.

2.2.8 Degradation (decay)

The factors controlling the degradation rate of pesticides are not always well understood (Boesten, 1999), as degradation (persistence) is a very complex process. The ideal pesticide and environmental conditions will induce enough activity for the pesticide to have the desired effect on pests, but enough short persistence to limit leaching and contamination of water resources. Degradation is generally expressed through half-life. Half-life is the amount of time (in days) it takes for one half the original mass of the chemical to be deactivated. Half-life is sometimes defined as the time required for half the amount of the chemical to be completely degraded and released as carbon dioxide and water (Hornsby, 1999). Degradation may occur through microbial activity depending mainly on pH, temperature and moisture (biodegradation), through photochemical reactions due to absorption of electromagnetic energy by a pollutant (photodecomposition), or chemically by reacting with oxygen (oxidation) or water (hydrolysis).

Degradation or decay depends on a number of factors and processes (Guerin, 2001). Johnson *et al*. (2004) suggested that the nature of the indigenous microbial community influences pesticide degradation in groundwater, as well as groundwater chemistry. Vink and Van der Zee (1997) indicated the importance of nutrient availability on microbial life and degradation of pesticides, in particular in field ditches and channels. Indirectly, plants can also promote degradation in the rhizosphere by enhancing microbial life (Sun *et al*., 2004). Di Primo *et al*. (2003) suggested that degradation is affected by the history of pesticide application on a field and the consequent changes in microbial life, which confirms the need for rational use of pesticides to maintain their efficacy. Worrall *et al*. (2001) indicated the strong dependence of carbofuran on pH. Soil temperature was also reported as one of the main factors affecting pesticide degradation (Paraiba *et al*., 2003). Mixtures of pesticides were also found to affect the biodegradability of individual pesticides due to competitive sorption, by keeping molecules bioavailable for microbial attack (Martins and Mermoud, 1998). The modality of application also plays a role. For example, encapsulated chemicals in alginate beads were more persistent than those applied with seed treatment (Pussemier *et al*., 1996). Patterson *et al*. (2002) showed degradation of atrazine to increase in a contaminated aquifer by delivery of oxygen using an in situ polymer mat system.

The reaction pathways and mechanisms of photodegradation of pesticides were discussed by Burrows *et al*. (2002). Photodecomposition occurs at the plant and soil surface exposed to sunlight, before the first rainfall/irrigation event for many pesticides (Walker, 1974), and there is evidence that it can contribute considerably to the pesticide balance (Bavcon, 2003). However, due to the difficulties in micro-measurements at the soil surface, similarly to volatilization, this process was not studied enough. Both photodecompositon and volatilization can be reduced or eliminated by shallow incorporation of the pesticide applied into the soil (Bromilow *et al*., 1999).

Patterson *et al*. (2000) estimated pesticide half-lives using a combination of coring and suction cup data in sandy vadose zones. Andreu and Picó (2004) discussed sampling and sample-preparation technologies for soil analysis. They evaluated a number of methods like liquid extraction (pressurized liquid extraction or microwave-assisted extraction) and solid-phase based methods (headspace solid-phase micro-extraction, solid-phase micro-extraction or matrix-solid-phase dispersion). Methods for analysis of pesticides are generally by gas chromatography or liquid chromatography coupled to different detectors, especially mass spectrometers. Andreu and Picó (2004) also discussed alternative and/or complementary methods, using capillary electrophoresis, biosensors and bioassays. Standard procedures for analyses of many pesticides are available on the EPA web site: (http://www.epa.gov/microbes/methmans.html, accessed on 28 January 2010).

2.3 OVERVIEW OF MODELS

This section reports an overview of models (catchment- and field-scale) and supplies a motivation for the selection of most suitable field-scale models for pesticides. It was envisaged that modeled flux scenarios on a local scale would serve to inform modeling fluxes on a regional scale.

2.3.1 Model screening

An extensive literature search was carried out in order to identify suitable models for simulation of priority pesticide processes. The literature search was based on several databases available on the web:

- Register of Ecological Models (REM) (http://ecobas.org/www-server/index.html, accessed on 28 January 2010)
- U.S. Environmental Protection Agency
- (http://www.epa.gov/crem/relatedlinks.html#pest, accessed on 28 January 2010)
- International Ground Water Modeling Center (IGWMC), Golden, Colorado, USA (typhoon.mines.edu/software/igwmcsoft, accessed on 2 March 2005)
- Scientific software group, Sandy, Utah, USA

  (www.scisoftware.com/environmental_software, accessed on 28 January 2010)
- Canadian Environmental Modelling Centre (CEMC) of Trent University, Canada (www.trentu.ca/cemc/models, accessed on 28 January 2010)
- Alterra, Wageningen (http://www.alterra.wur.nl/NL/Producten/Modellen, accessed on 28 January 2010)

The models were screened for several criteria, especially their ability to simulate priority processes for pesticides. A database was compiled including:

1. **Name** (acronym) of model.
2. **Reference**.
3. **Source** (web site).

4. **Availability/Cost** of the model. The models available at no cost were downloaded from the web site.

5. **Dimensions**. The models were screened for their ability to simulate multi-dimensional systems. Two-dimensional (2D) and three-dimensional (3D) models were preferred compared to one-dimensional (1D) models.

6. **Layering**. Multi-layer models that account for different layers were preferred compared to models that treat the unsaturated zone as one layer with homogeneous properties. This is particularly important when subsurface horizontal water and solute fluxes need to be quantified.

7. **Geohydrological processes (runoff, water flow, drainage/recharge, preferential flow)**. The models were screened for their ability to simulate processes that were identified to be relevant to the estimation of water fluxes. Water flow-related processes (runoff, unsaturated zone flux in the vertical dimension and throughflow in the horizontal dimension) are relevant to the water balance and they represent the driving forces for solute transfer by convection. Drainage and recharge are relevant to leaching and contamination of groundwater. Concerning preferential flow, both models capable of simulating flow through cracks in soils and flow through rock fractures were considered.

8. **Type of chemicals**. This indicates the type of solutes that models can simulate. In the screening process, dedicated pesticide models were mainly searched for. Generic chemical models that account for both inorganic and organic chemicals were also considered, as they could be adapted to simulate pesticide fate and behaviour.

9. **Geochemical processes (solute fluxes)**. The geochemical processes were extremely relevant to the objectives of this project in order to conduct mechanistic modeling of the pesticide balance at local and regional scale. For this purpose, the models were screened for their ability to simulate pesticide fluxes in the vertical dimension, solute movement via runoff and throughflow in the horizontal dimension, as well as leaching of solutes. The ability to simulate processes linked to the three main properties of pesticides (volatilization, sorption and degradation) was also accounted for in the screening, as these processes are very relevant to the fate and behaviour of pesticides. In addition, models that can simulate uptake of pesticide by plants were also screened.

10. **Main applications**. The main purpose of a specific model was indicated. Several models were found to be adaptable/applicable to a wide range of problems.

The details on model screening, including a brief theoretical description, main applications, as well as main input requirements and main output data of models, can be found in Deliverable 3 (2004/05) of this project. Models that were freely available from the Web were downloaded and simulation trials were run.

2.3.2 Identification of suitable models

Several models were found to be suitable for the purpose of this research, in terms of availability and ability to simulate 2D, layered systems as well as relevant geohydrological and geochemical processes for pesticides. Very few models were found to simulate uptake of pesticides by plants, mainly due to the complexity and high costs of measurement of this process. Amongst the models that were screened and downloaded from the Web, the following satisfied most of the criteria: FIRST, GENEEC, HYDRUS-2D (including the code originating from SWMS_2D), PELMO, PESTAN, PRZM, SWAP, SWAT and VS2DT.

FIRST (FQPA, Food Quality Protection Act, Index Reservoir Screening Tool) and GENEEC (GENeric Estimated Exposure Concentration) are models used to estimate human exposure to pesticides for risk assessment purposes (Parker *et al*., 1995). They are single event models, as they assume that one single large rainfall/runoff event occurs and removes a large quantity of pesticides from the field (runoff-prone watershed) to a small drinking water reservoir of defined size, simultaneously. The modeling (standard) scenario currently accounts for region-specific rainfall, soil, and hydrologic/runoff factors. GENEEC differs from FIRST in that longer-term, multiple-day average concentration values are calculated based on the peak day value and subsequent values accounting for degradation processes.

HYDRUS-2D is one of the better-known models for analysis of water flow and solute transport in variably saturated porous media (Simunek *et al*., 1999). It includes a mesh generator for unstructured finite element grids (MESHGEN-2D) and a user interface particularly suited to hydrologic representations. Its cost is about 1,200 USD. The code from which HYDRUS-2D was developed (SWMS_2D) is available free of charge.

PELMO is a 1D, multi-layer model for pesticide fate in the unsaturated zone (Klein *et al*., 2000). It includes estimates of potential evapotranspiration, soil temperature, runoff and erosion, pesticide degradation and sorption. The water flow model uses a cascading principle. Preferential flow is not accounted for.

PESTAN is an analytical, 1D model that simulates transport of dissolved organic solutes in the unsaturated zone (http://www.epa.gov/crem/relatedlinks.html#pest, accessed on 28 January 2010). It accounts for constant recharge rate, constant velocity of solutes through the soil based on hydraulic conductivity under unsaturated conditions, advection, dispersion, reactions with the solid phase and decay. The model assumes leachate concentration equals solubility of the contaminant and the slug of contaminant enters the soil at a velocity equal to the ratio of the recharge rate to the pore water content.

PRZM3 links the PRZM and VADOFT models to predict pesticide and nitrogen transport and transformation through the crop root and vadose (unsaturated) zones down to the water table (www.scisoftware.com/environmental_software, accessed on 28 January 2010). PRZM is used to represent the root zone, whilst VADOFT, with a more rigorous representation of unsaturated flow making use of Richards' equation, is used to simulate the thicker vadose zone.

SWAP (Soil-Water-Atmosphere-Plant) is a 2D, transient model for water flow and solute transport in the unsaturated and saturated zones (Kroes and Van Dam, 2003). The unsaturated zone model is based on Richards' equation for water flow and the convection-dispersion equation for solute transport. It includes interactions between soil, plant and atmosphere, as well as interactions between surface water, soil water and groundwater (runoff, run-on, inundation, drainage and infiltration, preferential flow, throughflow for up to five different levels, groundwater recharge and capillary rise). Concerning solutes, SWAP includes processes like non-linear adsorption, plant root uptake, leaching and drainage to drains and ditches. In this way, solute transport from the soil surface to the surface waters can be simulated.

SWAT (Soil and Water Assessment Tool) is a 2D model that predicts the effects of climate and vegetative changes, reservoir management, groundwater withdrawals and water transfer on hydrology, pesticide and nutrient cycling, erosion and sediment transport in large, complex, rural river basins

(Arnold *et al*., 1995). The hydrology is based on the water balance. SWAT also provides for runoff, by-pass (preferential) flow, lateral water flux, sediment yield and size, interactions between surface and groundwater, whilst the SWAT-GIS linkage incorporates advanced visualization tools capable of statistical analysis of output data.

VS2DT (Variably Saturated 2-D flow and Transport) is a 2D, finite-difference model for cross-sectional or cylindrical variably saturated flow in porous media (Healy, 1990). The model accounts for non-linear storage, conductance, sink terms, non-uniform soil and boundary conditions. Processes included are infiltration, evaporation, plant root uptake, seepage, first-order decay, Freundlich adsorption isotherms and ion exchange.

2.4 CONCLUSIONS

A number of primary NPS processes for production of pesticides were identified and prioritized. These processes need to be quantified for modeling purposes.

Pesticide transport via overland flow can be measured in runoff plots by sampling runoff water for laboratory analysis. It should be modelled in conjunction with sediment transport, as a portion of the transported pesticides is adsorbed onto solid particles of minerals and/or organic matter.

Vertical water and pesticide fluxes can be estimated by sampling soil for laboratory chemical analysis. Pesticide leaching through the vadose zone, preferential flow and throughflow should also be estimated as they may affect the pesticide balance.

Concerning pesticide properties, volatilization is more related to pesticide atmospheric transport than to transport via water. Sorption of specific chemicals can be measured in the laboratory for specific soils. Pesticide degradation can also be measured in the laboratory; however, half-lives to be used in models depend largely on environmental conditions.

Several models were screened for their ability to simulate priority processes for pesticides. HYDRUS-2D, SWAP and SWAT were used at different stages of this project and for different purposes.

3 COLLECTION OF NPS DATA IN A SMALL SCALE CATCHMENT (WESTERN CAPE)

3.1 INTRODUCTION

Two experimental pilot study sites were established in this project, namely in the Wartburg catchment (KwaZulu-Natal) and in the Goedertrou small scale catchment (Western Cape). These two catchments are characterized by different environmental, climatic and geomorphological conditions, and consequently by different land use and management practices. This Chapter reports on collection of continuous datasets of NPS fluxes (sediments, pesticides and nutrients) in the Goedertrou catchment in the Western Cape. The Chapter includes:

1) Motivation for site selection (Deliverable 4, 2004/05)

2) Location of small scale catchment

3) Experimental procedure

4) Results (report on data collection, in particular nutrients, sediments and pesticides)

5) Main conclusions

Data, in the Goedertrou catchment, were collected at point (local) and field-scale. The point (local) scale was represented by runoff plots established in the field at the beginning of the experiment. The field-scale was represented by a stock-watering dam intercepting overland flow and throughflow from the entire catchment. The main purpose was to generate data to support integrated modelling at different scales. The complete report on data collection in the Goedertrou catchment is available in Deliverable 12 (2008/09) of this project.

3.2 SITE SELECTION

The experimental site in the Western Cape is located on the Goedertrou farm outside Riebeeck-Wes, in the Berg River catchment. The site was interpreted to be suitable for this Project for the following reasons:

- The site is logistically accessible from Cape Town, about 1.5 to 2 hours drive.

- Historical data existed and new data sets were assembled. The Berg River catchment had been used in previous and current research funded by the WRC:

    - Dryland Salinity Impacts on Western Cape Rivers – A Pilot Study (Report No. 1342/1/04).

    - Water Quality Information System for the Berg River Catchment (Report No. 2005/10/01).

    - Land Use Impacts on Salinity in the Berg River Catchment (Report No. K5/1503).

- The Berg River catchment was monitored (water quality, quantity and climate data) by the Department of Water Affairs and Forestry since the mid-70’s.

- Time-efficient and cost-effective cooperation with an overlapping WRC Project on Land Use Impacts on Salinity in the Berg River Catchment.

- Commitment, support and cooperation of the land owner.
- The catchment is located in an important agricultural area of the country.
- The catchment is representative of small-scale catchments in the Western Cape.
- The catchment is a potential source of pollutants (fertilizers, pesticides and sediments).
- The impacts of pollutants originating from agriculture, different land uses or specific agricultural management practices were expected to be high.
- Hydrological set-up:
    - Steep slopes.
    - Presence of anti-erosion contour banks that attenuate pollutant fluxes.
    - Presence of a stock-watering dam intercepting overland flow and throughflow.
    - Preferential flow through soil cracks due to salinity and biological activity.
- Future research value. The site has the potential to become an experimental station serving:
    - University training through field visits and field schools.
    - Community awareness.
    - Scientific conference field programmes, etc.

3.3 LOCATION OF A SMALL SCALE CATCHMENT IN THE WESTERN CAPE

The site in the Western Cape is located in the Berg River catchment. The monitoring site at Goedertrou is located near Riebeeck-Wes (**FIGURE 1**). The Goedertrou catchment is in a semi-arid area that receives less than the average rainfall for the Berg river catchment due to topographic conditions (approximately 330 mm/a). Rainfall occurs mainly in winter (from May until October).

FIGURE 2 shows the experimental scheme in the Goedertrou catchment on a Google Earth map, where runoff and interflow water is retained in a dam (latitude 33°18’33.16” S; longitude 18°53’40.67” E; altitude = 120 mamsl). The size of the Goedertrou catchment is ~20 ha. Two standard Wischmeier runoff plots (22.3 m x 2 m), the one parallel to the other, were established at each site 1 and 2. The runoff sites were chosen to represent typical hydrological units for modelling purposes. Site 1 was North-oriented, whilst site 2 was South-East-oriented. The soils at the two sites are different: 0.4 m deep sandy clay loam Glenrosa form (Soil Classification Working Group, 1991) – Cambisol (FAO, 1998) – overlying a relatively impervious Proterozoic marine deposit of Malmesbury shales at site 1; deep clay loam Swartland form (Soil Classification Working Group, 1991) – Luvisol (FAO, 1998) – at site 2. The slope of site 1 is 9.1%, whilst the slope at site 2 is 12.4%. Site 1 is located on a saline patch (bulk soil electrical conductivity is about 160 mS m^{-1}). Both sites were representative for areas between two man-made contours.

The common crop rotation in the area is one season of dryland winter wheat followed by two years of fallow land to somewhat regenerate soil fertility and for re-growth of previously cultivated grasses (e.g.

wheat or medic grass) for pasture. The Goedertrou catchment was planted to wheat in 2005 and 2008. During 2006, 2007 and 2009, it was left uncultivated.

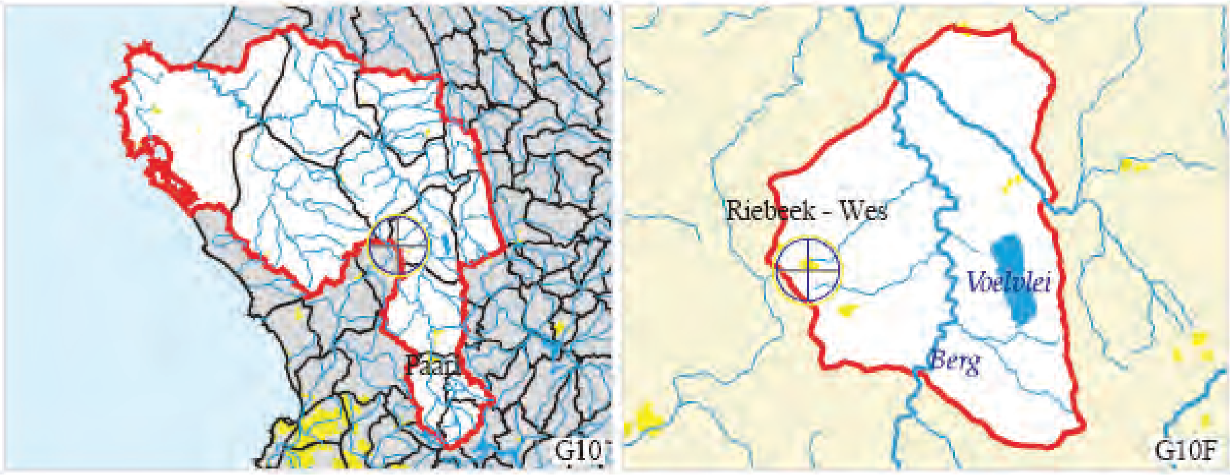


FIGURE 1: Maps with the location of the Goedertrou small scale catchment in the Berg river basin (http://www.dwaf.gov.za/iwqs/wms/data/g10/g10_101945.pdf accessed on 28 January 2010)

3.4 EXPERIMENTAL PROCEDURES

3.4.1 Weather data

An automatic MCS (Mike Cotton Systems, Cape Town) weather station was installed in the catchment (**FIGURE 2**) on 25 April 2005. The following weather variables were measured and stored on an hourly basis: rainfall, solar radiation, temperature, relative humidity, leaf wetness, and wind speed and direction. Weather data collection for this project lasted from April 2005 to December 2009.

3.4.2 Crop growth

Dryland wheat was planted on 8 May 2005 at the Goedertrou catchment with a planting density of 400,000 plants ha^{-1}. The soil was shallow-cultivated to break up the surface crust. Wheat was harvested on 12 November 2005. During 2006 and 2007, the Goedertrou catchment was left uncultivated for cattle and sheep grazing. Winter wheat was planted again on 21 May 2008 at a seeding density of 60 kg ha^{-1}. Common agronomic practices for the area were adopted, including shallow cultivation to break up the soil surface crust. Wheat was harvested during mid-November 2008.

The yield of wheat in 2005 was obtained from the farmer at harvest. In addition, the yield of wheat and planting density were measured on 3 replications of 1 m^2 representative areas in each runoff plot. The biomass of wheat, medic grass and other species' re-growth for the 2006 season was measured on 21 September 2006. Three replicated samples were harvested from areas of 0.5 m^2 in a strip between runoff plots that was left ungrazed. Yield of wheat in 2008 was obtained from the farmer at harvest.

FIGURE 2: Experimental scheme in the Goedertrou small scale catchment on a Google Earth map

3.4.3 Hydrological measurements

Two standard Wischmeier runoff plots were established, the one parallel to the other, at each runoff site (**FIGURE 2**). Each runoff plot covered an area of 44.6 m^2. Soil physical, hydraulic and chemical properties were measured in pits representative of the two runoff sites and these were reported by De Clercq *et al*. (2010). One plot at site 1 was left under bare soil through the occasional application of Glyphosate to allow for the comparison of different land uses at the same site (bare soil vs. wheat and pasture land). The following measurements were carried out at each runoff plot (sites 1 and 2):

- **Overland flow.** A flow splitter was installed in order to divide water and sediment flow into two portions (**FIGURE 3**). The first portion from the flow splitter lead into a tipping bucket fitted with a magnetic switch, in order to record overland flow electronically. The tipping bucket was calibrated so that every tip corresponded to 1 L of water. Water volume data were collected every 10 min and stored with an MCS data logger. The first flow portion was wasted thereafter. The second flow portion from the splitter lead into two sediment traps (**FIGURE 3**).

The flow splitter was calibrated in the field to determine the exact fraction of water diverted onto the tipping bucket and sediment traps. The splitter was levelled during each field visit to ensure the calibration was correct at all times. Water volumes were also measured manually during field visits, by measuring the litres of water collected in the tanks (sediment traps). The sediment tanks were emptied and washed during each field visit after the required measurements were taken.

- **Sediments.** The first sediment trap in the sequence was used to trap coarser sediments (white bucket in **FIGURE 3**). Water and suspended solids then overflowed into the second sediment trap in the sequence, where finer sediments were collected (black bucket in **FIGURE 3**). The sediment traps were used to collect water and sediment samples for laboratory analysis.

- **Runoff water quality.** In 2005, water samples collected during field visits were used to determine the quality of runoff water (N, P and pesticides). In 2008, pesticides were measured. The aim was to determine the quantities of nutrients and pesticides mobilized from wheat land via overland flow.

- **Rainfall.** Rainfall at runoff sites 1 and 2 was recorded every 10 min with tipping bucket rain gauges and data were stored with MCS data loggers. The data loggers were enclosed in a box and powered via battery and solar panel.

- **Soil water content.** From 3 November 2005, volumetric soil water content at site 2 was measured electronically with four Echo sensors connected to an Echo logger (Decagon Devices Inc.). The Echo sensors are 20 cm long capacitance probes. Two sensors were installed vertically close to the top of the runoff plots, and the other two sensors close to the bottom of the runoff plots. Measuring depths were 0-20 cm and 40-60 cm. From 9 December 2005, four Echo sensors were also installed vertically at site 1 and connected to an Echo data logger. Two sensors were installed close to the top and the other two sensors close to the bottom of the runoff plots. Measuring depths were 0-20 and 30-50 cm. The individual sensors were calibrated using the calibration supplied by the manufacturer in DataTrac software (Decagon Devices Inc.), based on measured field capacities (volumetric soil water content at 10 kPa) (De Clercq *et al*., 2010).

From 29 August 2006, ECH2O-TE sensors (Decagon Devices Inc.) were installed for simultaneous measurement of volumetric soil water content, soil temperature and electrical conductivity. The sensors were connected to Echo loggers and they made use of the calibration provided by the manufacturer in DataTrac software. The ECH2O-TE sensors were inserted horizontally at the same positions as the soil moisture Echo sensors described in the previous paragraph. The depths of installation were 10 cm and 40 cm at site 1, and 10 cm and 50 cm at site 2. All electronic measurements of volumetric soil water content were recorded on an hourly basis.

FIGURE 3: Flow splitter, tipping bucket for measurement of overland flow and two plastic tanks for water and sediment sampling

The purpose of the electronic measurement of soil water content was to identify the building up of temporary shallow water tables in winter, and to quantify throughflow using water retention curves and saturated hydraulic conductivities. Subsurface flow was a very important component of the water balance due to the soil and geological characteristics of the area, i.e. shallow soils overlying Malmesbury shale.

Soil water content was measured gravimetrically by sampling during field visits in 2005. The soil samples were taken at the top and bottom of each runoff plot. Sampling was done outside the runoff plots to avoid disturbance, at sites representative of the conditions inside the plots. Sampling depths were at 10 cm and 40 cm (at the top of the weathered Malmesbury shale layer) at runoff site 1. At runoff site 2, sampling was at 10 cm and 50 cm soil depth. The samples were sealed in plastic bags, weighed in the laboratory, placed in the oven at 105°C for a few days, and re-weighed to determine the gravimetric soil water content. The gravimetric soil water content was then converted into volumetric soil water content using bulk densities for the corresponding soils and sampling depths. The purpose of the gravimetric soil water content sampling and measurement was to test the calibration of the Echo-sensors.

- **Soil chemical properties.** During 2005, the soil samples collected to measure water content gravimetrically were also used to measure soil chemical properties, in particular N, P and pesticides.

3.4.4 Measurements of pesticides

Pesticides were applied during the 2005 season on the wheat crop. The pesticides, applied according to recommended rates, were Folicur and Methomex. Folicur (active ingredient tebuconazole) was sprayed in solution at 30 L ha^{-1} with an aircraft on 21 August 2005. The solution was 0.8 L ha^{-1} of active ingredient diluted in 30 L of water. Methomex (active ingredient methomyl) was sprayed in solution at 30 L ha^{-1} with an aircraft on 21 October 2005. The solution was 200 g ha^{-1} of active ingredient diluted in 30 L of water.

In the few weeks following application, soil and water samples were collected in order to determine the fate of the two pesticides and for modelling purposes. The sampling dates are summarized in Table 1. Soil and water samples, collected in sealed bags and amber glass bottles respectively, were immediately stored in a dark cool container in the field, in order to limit the degradation of any pesticide residue within the sample.

The water and soil samples collected for pesticide analyses in 2005 were shipped and analyzed at the Plant Protection Research Institute (PPRI) in Roodeplaat (Agricultural Research Council, ARC). At PPRI, the samples were stored in freezers at -20 ºC. They were then analyzed with a Gas Chromatography Mass Spectrometer (GCMS), after measuring protocols were developed (calibrations, spectral analysis, resolution of interfering peaks, etc.).

No pesticides were applied to fallow land during 2006 and 2007. Pesticides were applied again during the 2008 season on the wheat crop. The herbicide Roundup (glyphosate) was applied at 1 L ha^{-1} on the day before planting. In addition, a mixture of herbicides was applied by tractor spraying in the first week of July 2008. The herbicides were Derby (floerasulam/flumetsulam) at 50 mL ha^{-1}, Brusch-Off (metsulfuron-methyl) at 3 g ha^{-1}, Puma Super (fenoxaprop-P-ethyl) at 430 mL ha^{-1} and MCPA (potassium salt, 2-Methyl-4-chlorophenoxyacetic acid) at 400 mL ha^{-1}.

TABLE 1: Date of sampling and number of environmental samples collected for pesticide analyses

Date	Number of environmental samples
04/07/2005	1 dam water sample 4 soil samples (baseline data)
22/07/2005	2 runoff samples (baseline data)
18/08/2005	1 runoff sample (baseline data)
21/08/2005	***Application of fungicide – Folicur* *(active ingredient tebuconazole)***
23/08/2005	1 dam water sample 1 runoff sample 4 soil samples
30/08/2005	4 soil samples
08/09/2005	1 dam water sample 4 soil sample
14/10/2005	1 dam water sample
21/10/2005	***Application of insecticide – Methomex (active ingredient methomyl)***
28/10/2005	1 dam water sample 2 soil samples
03/11/2005	1 dam water sample 2 soil samples
08/12/2005	1 dam water sample 2 soil samples

In the few weeks following pesticide application, soil and water samples were collected in order to determine the fate of pesticide products. Sampling dates were 29/07/2008, 05/08/2008, 22/08/2008, 03/09/2008 and 15/09/2008. Soil and water samples, collected in sealed bags and amber glass bottles respectively, were stored in a dark cool container in the field immediately after sampling, in order to limit the degradation of any pesticide residue within the sample. Five samples of dam water were shipped to the South African Bureau of Standards (SABS) for analysis of MCPA. It was found that the SABS was the only laboratory that has methods and protocols for measurement of MCPA. No methods and protocols were readily available for measurements of the other pesticides by SABS, nor by the PPRI in Roodeplaat (ARC). The SABS measured MCPA with the in-house method No. 038/2008 *Determination of Selective Herbicides in Water*. Recovery determinations were carried out by adding known amounts of MCPA to known volumes of tap water and analyzing these concurrently with the samples.

3.4.5 Measurements of nutrients

During the 2005 wheat season, fertilization consisted of 40 kg ha^{-1} N and 20 kg ha^{-1} P at planting (08/05/2005), and 60 kg ha^{-1} N in the middle of July as top dressing. Soil and water samples were collected in the Goedertrou catchment for N and P analysis during the 2005 wheat season.

The soil samples were taken at the top and bottom of each runoff plot. Sampling was done outside the runoff plots to avoid disturbance, at sites representative of the conditions inside the plots. Sampling depths were at 10 cm and 40 cm at runoff site 1. At runoff site 2, sampling was at 10 cm and 50 cm soil depth. The samples were sealed in plastic bags, dried in the oven at 105°C for a few days, and shipped to the University of Stellenbosch (Department of Soil Science) for N and P analyses.

Water samples were collected during field visits after major rainfall events in 2005. Water was sampled from the sediment tanks at the runoff plots, from the contours just below the runoff plots as well as from the dam. The number of water samples taken depended on whether any water collected in the sediment tanks and contours after rainfall events. The dates of sampling and number of samples collected for analyses of nutrients in 2005 are summarized in **TABLE 2**. The water samples were shipped to the University of Stellenbosch (Department of Soil Science) for N and P analyses. The complete chemical analyses for the soil and water samples can be found in De Clercq *et al*. (2010).

During the 2006 fallow season, no fertilizer was applied. Soil samples were collected on 21/03/2006 and 29/06/2006 for spot checks. Two samples were collected at site 1 (10 and 40 cm soil depth) and at site 2 (10 and 50 cm soil depth). The samples were shipped to the University of Pretoria for N and P analyses.

TABLE 2: Date of sampling and number of water samples collected for nutrient analyses

Date	Number of environmental samples
13/04/2005	2 dam water sample 3 runoff samples (Baseline data)
08/05/2005	***Application of fertilizer at planting***
10/06/2005	4 runoff samples

TABLE 2: Date of sampling and number of water samples collected for nutrient analyses

Date	Number of environmental samples
23/06/2005	6 runoff samples
Middle of July 2005	***Top dressing of N***
11/08/2005	4 runoff samples
30/08/2005	3 runoff samples
08/09/2005	2 runoff samples
18/09/2005	2 runoff sample
14/10/2005	1 dam water sample 2 runoff samples
03/11/2005	1 dam water sample

Plant samples were collected on 21/09/2006 for nutritional analyses of N and P on wheat, medic grass and other species' re-growth (fallow land mixture). Two samples were collected in the vicinity of each runoff measurement site. The plant samples were representative of the area within, and surrounding the runoff plots. The samples were shipped to the University of Pretoria, where they were analyzed at the Institute for Soil, Climate and Water (ARC, Pretoria).

During the 2008 wheat season, 125 kg ha^{-1} PLANF 13Z were applied at planting and 130 kg ha^{-1} as top dressing in the last week of June 2008. No measurements of nutrients were done during 2008.

3.4.6 Measurements of sediments

Water and sediment samples were collected during field visits that were planned after major rainfall events (approximately weekly in winter). The samples were collected from the sediment tanks at the runoff plots, from the contours just below the runoff plots as well as from the dam. The number of water samples collected depended on whether any water collected in the sediment tanks and contours. Sampling from the sediment tanks was done by scratching the bottom of the tanks with a clean spade and collecting water samples in plastic bottles, whilst grab samples were taken from the contours and dam.

Total sediment mass was measured in the laboratory, after evaporating water from sub-samples of known volume. Sediment size and distribution were measured with a LASER particle size analyzer (Micromeritics Instrument Corporation) at the University of Stellenbosch. Data were analyzed with Saturn Digisizer 5200 software.

3.4.7 Additional measurements

Additional measurements in the Goedertrou catchment were carried out at the dam. Water collecting in the stock-watering dam (**FIGURE 2**) originates both from overland flow and throughflow. Water level and salinity were measured hourly with an Eijkelkamp Diver (Van Essen Instruments, supplied by

Eijkelkamp Agrisearch Equipment) during 2008, and these were reported in detail by De Clercq *et al*. (2010). Water levels in the dam at Goedertrou varied seasonally and responded within hours of rainfall events. Water samples were collected during field visits for quality analyses, in particular N, P and pesticides.

Nine boreholes were drilled in the Goedertrou catchment, which were monitored for water level and groundwater quality. Due to the geohydrological set-up, where runoff and throughflow are thought to be the dominant water balance processes, agricultural activities carried out during the course of this project had little effect on groundwater contamination. The results of groundwater monitoring can be found in De Clercq *et al*. (2010).

3.5 RESULTS

3.5.1 Weather data

Weather data were collected from April 2005 to December 2009, specifically average hourly air temperature (**FIGURE 4**), average hourly relative humidity (**FIGURE 5**), total hourly rainfall (**FIGURE 6**) and average hourly wind speed (**FIGURE 7**). During some periods, data were not collected due to malfunction of sensors' electronics or storm damage. The calibration of the temperature sensor was incorrect for a period during 2007.

The highest recorded temperature was 42.8°C on 7 December 2008, whilst the lowest temperature was 1.8°C measured on 19 August 2005. The average air temperature for the recorded period was 18.1°C. Maximum relative humidity of 100% was recorded on several occasions particularly in winter, whilst the lowest relative humidity was 5.5% measured on 24 April 2008. Average relative humidity for the recorded period was 63.9%. Average wind speed was 3.0 m s^{-1}, with a peak of 17.6 m s^{-1} on 23 May 2006. The highest recorded hourly rainfall was 27.8 mm h^{-1} on 24 February 2009.

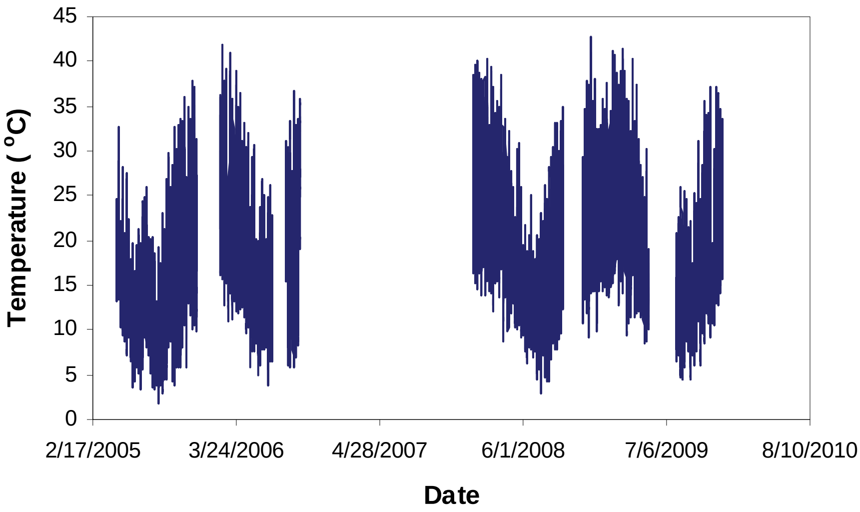


FIGURE 4: Hourly air temperature measured with an automatic weather station in the Goedertrou small scale catchment

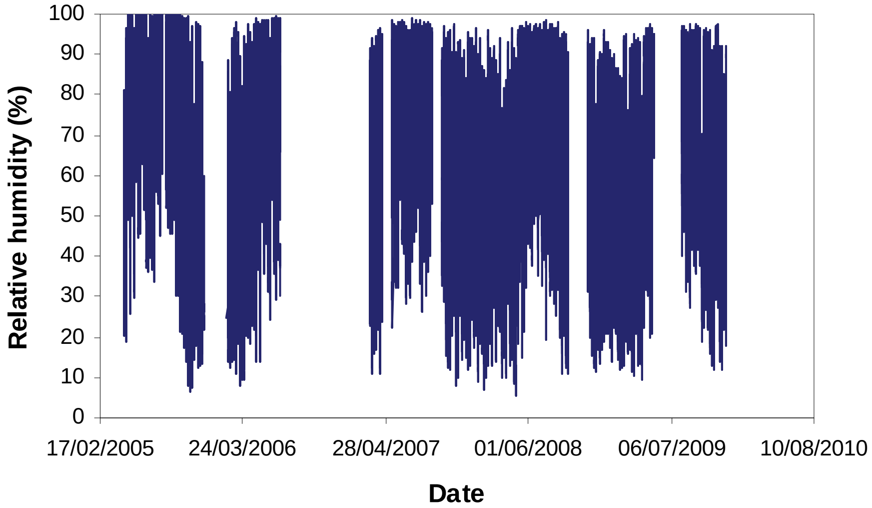


FIGURE 5: Hourly air relative humidity measured with an automatic weather station in the Goedertrou small scale catchment

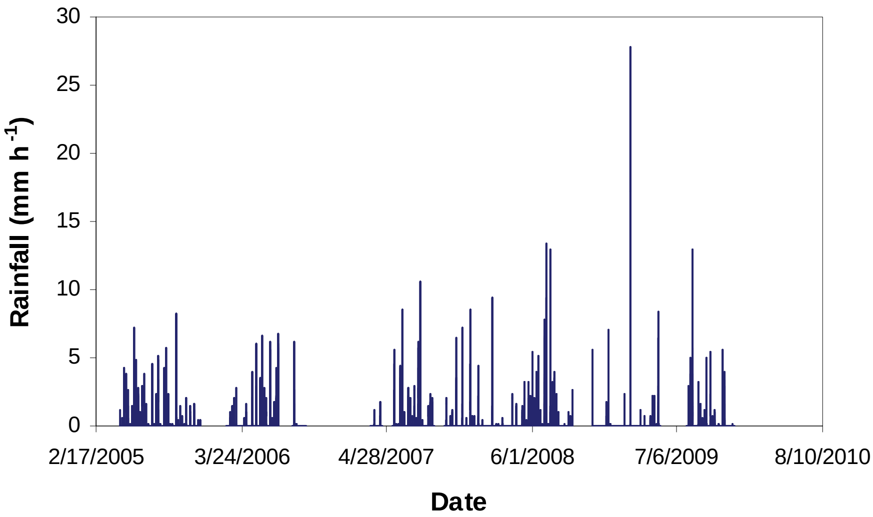


FIGURE 6: Hourly rainfall measured with an automatic weather station in the Goedertrou small scale catchment

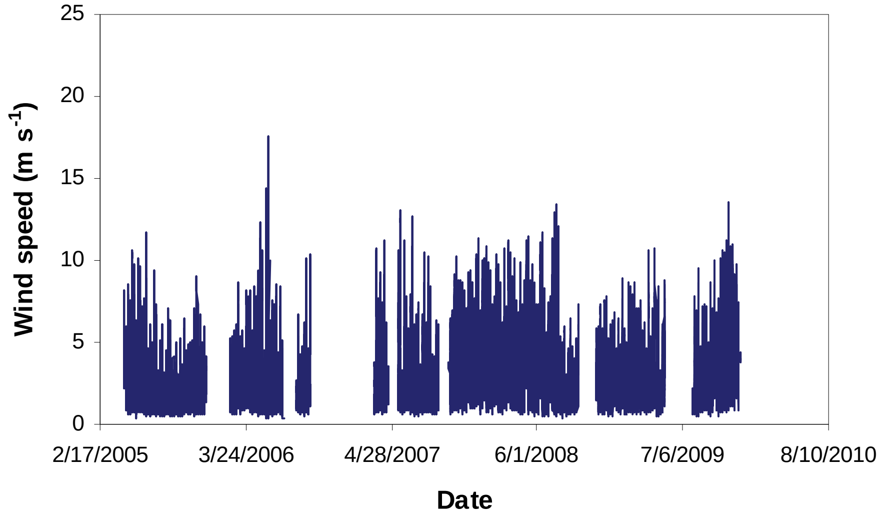


FIGURE 7: Hourly wind speed measured with an automatic weather station in the Goedertrou small scale catchment

3.5.2 Crop growth

Plant densities and yield data are summarized in **TABLE 3**. Runoff plot 1 at site 1 was left uncultivated in 2005 and 2008, and under bare soil in 2006.

TABLE 3: Planting densities and yield data from 2005 to 2008

Season	Growth variable	Site 1		Site 2	
		Runoff plot 1	Runoff plot 2	Runoff plot 1	Runoff plot 2
Wheat (2005 season)	Planting density (plants m^{-2})	-	40±7.2	39±5.0	39±7.9
	Grain yield (t ha^{-1})	-	2.0	2.0	2.0
Fallow land re-growth (2006 season)	Total biomass (t ha^{-1})	-	2.7±0.7	2.0±0.2	
Wheat (2008 season)	Grain yield (t ha^{-1})	-	3.0	3.0	

3.5.3 Volumetric soil water content

Volumetric soil water content data were collected with Echo soil water sensors, recorded and stored with data-loggers on an hourly basis. The data of volumetric soil water content obtained with the 20 cm Echo probes are shown in **FIGURE 8** (site 1) and 9 (site 2), whilst those obtained with the ECH2O-TE sensors are presented in **FIGURE 10** (site 2) for the entire duration of the experiment.

In general, soil water content values varied depending mainly on seasonal rainfall and the presence of vegetation. During some periods, data were not available due to the formation of cracks and loss of contact between sensor and soil matrix. This was particularly evident in the clayey soil at site 2 and for shallow sensors. In cases of loss of signal of shallow sensors, water was added at the surface to improve contact between sensors and soil. Signals of some sensors were lost permanently, in particular ECH2O-TE sensors at site 1. The ECH2O-TE sensors at site 1 were dug out on 6 December 2007, corrosion was observed on their surface, and they were shipped to the manufacturer for replacement. On two occasions, damage to the installation occurred due to storms and cattle trampling.

Lower values of soil water content were generally observed for shallow sensors when compared to the deeper sensors. Higher values of soil water content were generally recorded for Site 2 compared to Site 1. Site 1 is characterized by soil with lower water holding capacity (sandy clay loam) compared to site 2 (clay loam). Volumetric soil water content values measured with 20 cm probes and ECH2O-TE sensors were in the same range for a large part of the measurement period. However, there were also periods when large differences occurred. The two types of sensors were installed at the same positions in proximity of each other. However, the Echo 20 cm sensors were installed vertically whilst the ECH2O-TE sensors horizontally. All sensors, in particular the shallow ones, generally responded to rainfall (**FIGURE 6**).

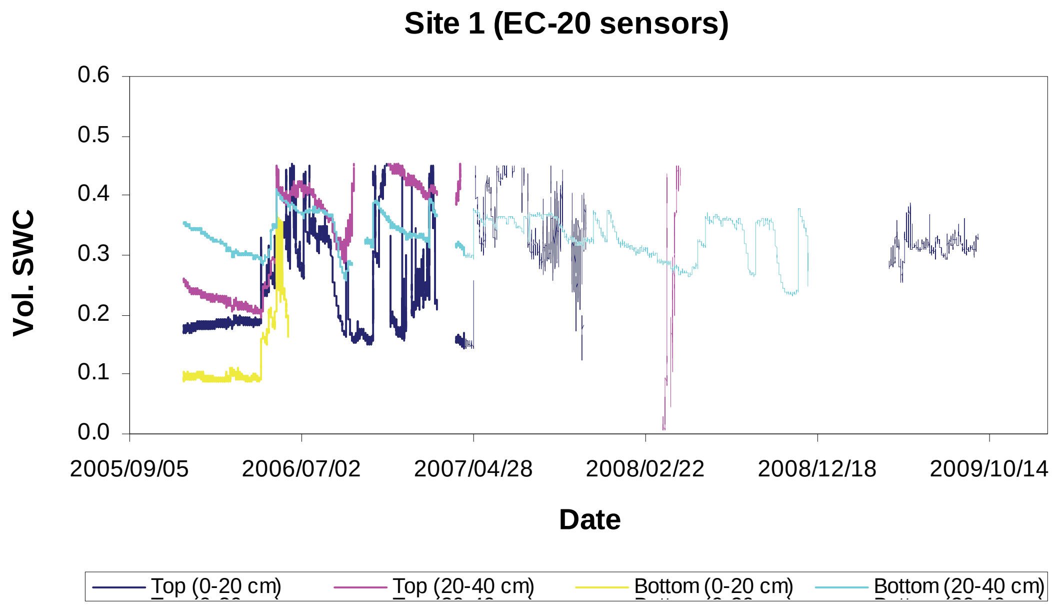


FIGURE 8: **Volumetric soil water content (SWC) measured with 20 cm Echo probes in the Goedertrou small scale catchment at site 1.**

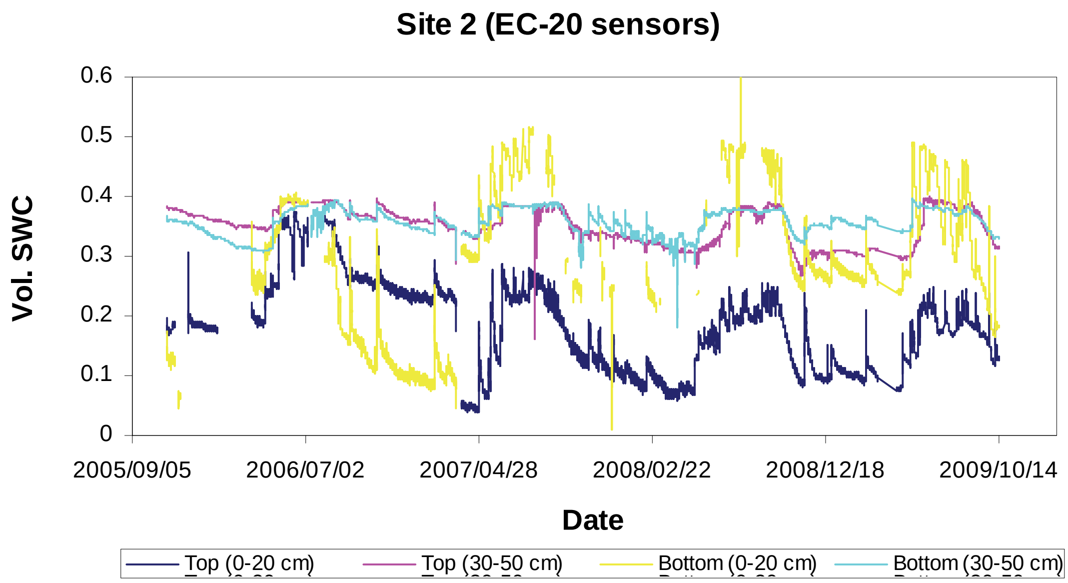


FIGURE 9: **Volumetric soil water content (SWC) measured with 20 cm Echo probes in the Goedertrou small scale catchment at site 2**

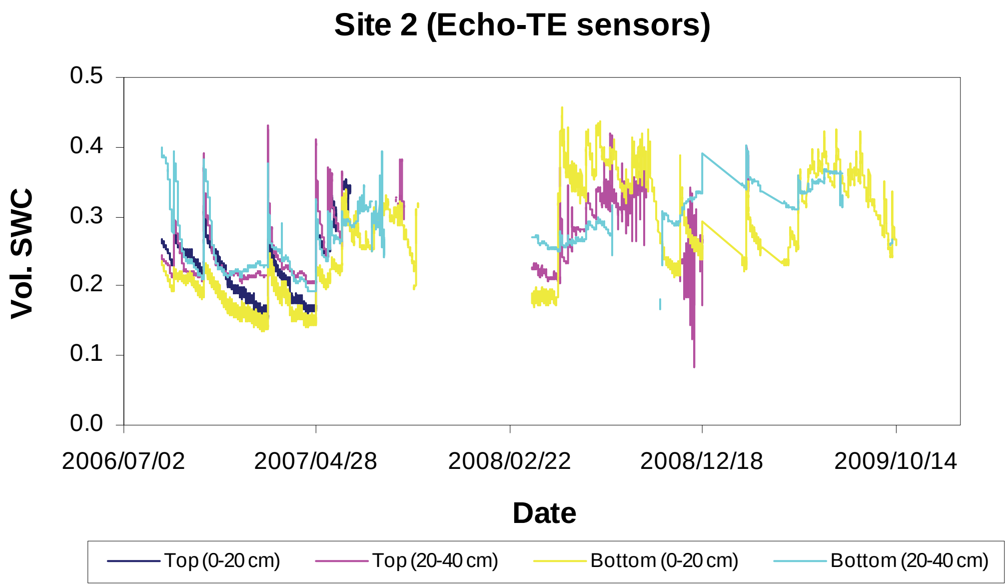


FIGURE 10: Volumetric soil water content (SWC) measured with Echo-TE probes in the Goedertrou small scale catchment at site 2

3.5.4 Overland flow measurements

All volumes of overland flow recorded during the experiment (from 2005 to 2008) are presented in **TABLE 4 to 11** for both sites and both runoff plots at each site. The asterisks in **TABLE 4 to 11** denote that the automatic data were not available and both sediment tanks overflowed. Overland flow was therefore > 2.93 mm (131 L per plot corresponding to the capacity of both tanks). Most of these data were recorded during 2005 (**TABLE 4 and TABLE 5**), when the electronics at the runoff plots was still being installed. For the remaining measurements from 2006 to 2008, electronic data of overland flow volumes were occasionally lost due to malfunction of the runoff tipping buckets caused by storm and cattle damage. Measured total rainfall at the weather station was 264 mm in 2005, 232 mm in 2006, 367 mm in 2007, 456 mm in 2008 and 355 mm in 2009.

In general, more overland flow occurred from uncultivated land (site 1, runoff plot 1 compared to runoff plot 2), and from land oriented towards the South, with steeper slope and more clayey soil (site 2 compared to site 1). At both sites, plot 1 generated consistently more overland flow than plot 2. This was due to uncultivated land at site 1, runoff plot 1, and possibly due to uneven growth of vegetation in the two runoff plots at site 2. Generally, volumes of overland flow generated from the runoff plots depended on antecedent moisture conditions, rainfall intensity and duration.

TABLE 4: Runoff volumes from site 1, runoff plots 1 (uncultivated) and 2 during 2005, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 (uncultivated)		Site 1 Runoff plot 2 Runoff volume	
		L/plot	L/m^2	L/plot	L/m^2
10-Jun-05	42	131*	2.94*	106	2.38
23-Jun-05	34	131*	2.94*	60	1.34
4-Jul-05	12	131*	2.94*	26	0.58
22-Jul-05	29	131*	2.94*	40	0.90
11-Aug-05	31	131*	2.94*	40	0.89
18-Aug-05	-	42	0.95	39	0.88
23-Aug-05	16	109	2.44	26	0.59
30-Aug-05	15	131*	2.94*	131*	2.94*
8-Sep-05	8	5	0.12	9	0.20
3-Nov-05	35	4	0.10	0	0
17-Nov-05	8	4	0.10	2	0.05

* denotes overflow from both tanks and no electronic measurement

TABLE 5: Runoff volumes from site 2 runoff plots 1 and 2 during 2005, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 2 Runoff plot 1 (bare soil)		Site 2 Runoff plot 2 Runoff volume	
		L/plot	L/m^2	L/plot	L/m^2
10-Jun-05	42	13	0.30	34	0.76
23-Jun-05	34	116	2.60	59	1.33
4-Jul-05	12	77	1.73	33	0.74
22-Jul-05	29	131*	2.94*	51	1.13
11-Aug-05	31	131*	2.94*	21	0.48
18-Aug-05	-	17	0.37	23	0.50
23-Aug-05	16	88	1.97	17	0.39
30-Aug-05	15	131*	2.94*	131*	2.94*
8-Sep-05	8	0	0	0	0
3-Nov-05	35	2	0.05	0	0
17-Nov-05	8	2	0.05	0	0

* denotes overflow from both tanks and no electronic measurement

TABLE 6: Runoff volumes from site 1 runoff plots 1 (uncultivated) and 2 during 2006, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 (bare soil)		Site 1 Runoff plot 2 Runoff volume	
		L/plot	L/m^2	L/plot	L/m^2
25-Apr-06	22	22	0.49	-	-
9-May-06	24	100	2.24	10	0.22
23-May-06	46	131*	2.94*	38	0.85
1-Jun-06	12	24	0.54	-	-
29-Jun-06	-	456	10.22	-	-
18-Jul-06	-	23	0.52	1	0.02
25-Jul-06	29	250	5.61	12	0.27

TABLE 6: Runoff volumes from site 1 runoff plots 1 (uncultivated) and 2 during 2006, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 (bare soil)		Site 1 Runoff plot 2 Runoff volume	
		L/plot	L/m^2	L/plot	L/m^2
3-Aug-06	17	14	0.31	-	-
10-Aug-06	14	378	8.48	324	7.26

* denotes overflow from both tanks and no electronic measurement

TABLE 7: Runoff volumes from site 2 runoff plots 1 and 2 during 2006, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 2 Runoff plot 1 (bare soil)		Site 2 Runoff plot 2 Runoff volume	
		L/plot	L/m^2	L/plot	L/m^2
25-Apr-06	15	8	0.18	0	0
9-May-06	24	8	0.18	8	0.18
23-May-06	46	131*	2.94*	131*	2.94*
1-Jun-06	-	-	-	-	-
29-Jun-06	123	752	16.86	244	5.47
18-Jul-06	34	131*	2.94*	112	2.51
25-Jul-06	25	432	9.69	174	3.9
3-Aug-06	25	292	6.55	-	-
10-Aug-06	32	986	22.11	270	6.05

* denotes overflow from both tanks and no electronic measurement

TABLE 8: Runoff volumes from site 1, runoff plots 1 and 2 during 2007, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 (uncultivated)		Site 1 Runoff plot 2 Runoff volume	
		L/plot	mm	L/plot	mm
21-Feb-07	-	131*	2.93*	15.9	0.36
7-Mar-07	-	-	-	-	-
4-May-07	6.2	131*	2.93*	2.1	0.05
17-May-07	-	4.2	0.09	-	-
22-May-07	9	90	2.02	-	-
12-Jun-07	100.2	131*	2.93*	131*	2.93*
27-Jun-07	23.8	131*	2.93*	12.7	0.28
10-Jul-07	7	6.3	0.14	6.3	0.14
17-Jul-07	8.6	4.2	0.09	2.1	0.05
1-Aug-07	76	164	3.68	131*	2.93*
8-Aug-07	-	131*	2.93*	131*	2.93*
15-Aug-07	-	131*	2.93*	378	8.48
28-Aug-07	16.6	4.2	0.09	35.9	0.81
18-Sep-07	4.2	131*	2.93*	42.2	0.95
Total	252	1190	26.62	888	19.91

* denotes overflow from both tanks and no electronic measurement

TABLE 9: Runoff volumes from site 2, runoff plots 1 and 2 during 2007, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 Runoff volume		Site 1 Runoff plot 2 Runoff volume	
		L/plot	mm	L/plot	mm
21-Feb-07	-	131*	2.93*	11.6	0.26
7-Mar-07	-	10.6	0.24	-	-
4-May-07	6.2	117.7	2.64	27.5	0.62
17-May-07	-	4.2	0.09	10.6	0.24
22-May-07	9.0	-	-	131*	2.93*
12-Jun-07	100.2	131*	2.93*	131*	2.93*
27-Jun-07	23.8	-	-	73.5	1.64
10-Jul-07	7.0	-	-	-	-
17-Jul-07	8.6	2.1	0.05	2.1	0.05
1-Aug-07	76.0	131*	2.93*	1330	29.82
8-Aug-07	-	248	5.56	131*	2.93*
15-Aug-07	-	446	10.00	200	4.48
28-Aug-07	16.6	131*	2.93*	6.3	0.14
18-Sep-07	4.2	131*	2.93*	131*	2.93*
Total	252	1484	33.23	2186	48.97

* denotes overflow from both tanks and no electronic measurement

TABLE 10: Runoff volumes from site 1, runoff plots 1 and 2 during 2008, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 Runoff volume		Site 1 Runoff plot 2 Runoff volume	
		L/plot	mm	L/plot	mm
23-Jun-08	102	131*	2.93*	131*	2.93*
14-Jul-08	133	131*	2.93*	131*	2.93*
29-Jul-08	25	131*	2.93*	78.05	1.75
05-Aug-08	10	62.4	1.40	0	0
22-Aug-08	15	0	0	0	0
03-Sep-08	52	544.2	12.20	315.8	7.08
15-Sep-08	33	410.4	9.20	267.6	6.00

* denotes overflow from both tanks and no electronic measurement

TABLE 11: Runoff volumes from site 2, runoff plots 1 and 2 during 2008, and rainfall in the antecedent period

Date	Rainfall (mm)	Site 1 Runoff plot 1 Runoff volume		Site 1 Runoff plot 2 Runoff volume	
		L/plot	mm	L/plot	mm
23-Jun-08	102	131*	2.93*	131*	2.93*
14-Jul-08	133	131*	2.93*	131*	2.93*
29-Jul-08	35	167.7	3.76	304.2	6.82
05-Aug-08	10	27.7	0.62	11.6	0.26
22-Aug-08	15	11.6	0.26	0	0
03-Sep-08	33	769.8	17.26	322.0	7.22
15-Sep-08	33	131*	2.93*	131*	2.93*

* denotes overflow from both tanks and no electronic measurement

3.5.5 Pesticide measurements – 2005

Measurements of pesticides in water samples collected during 2005 are presented in this section. The results of pesticide measurements in soil samples were not available because of problems experienced in the extraction of pesticides at the PPRI laboratory in Roodeplaat (ARC). This was due to the presence of other organic compounds masking the signal of methomyl and tebuconazole in the spectral analysis. The analyses of water samples are shown in **TABLE 12**. The dam water sample analyzed at the beginning of the 2005 rainy season (04/07/2005) served as baseline data for concentrations of tebuconazole and methomyl in dam water. In the absence of measurements on soil samples, the analyses performed on runoff water samples collected on 22/07/2005 and 18/08/2005 could serve as baseline data for concentrations of pesticides in top soil.

As very little rain occurred after application of Folicur on 21/08/2005 and no rain after application of Methomex on 21/10/2005, it was expected that the dam water sample analyses would provide a good idea of the degradation of these two pesticides in dam water.

Two days after application of Folicur (23/08/2005), the concentration of tebuconazole measured in dam water was relatively low (**Table 12**). A rainfall event just before 23/08/2005 caused a high concentration of tebuconazole in the runoff water sample (S1P1T1 collected on 23/08/2005) and the concentration in dam water increased to 10.8 µg L^{-1} on 08/09/2005. The concentration of tebuconazole in dam water decreased thereafter as the pesticide decayed.

The measured concentrations of tebuconazole in dam water after the runoff event on 23/08/2005 are shown in **FIGURE 11** as a function of time. The following decay function was fitted to the measurements in order to calculate the degradation rate constant (K):

$C_2 = C_1 \exp[-K (t_2-t_1)]$

where :

C_2 – Concentration at time t_2

C_1 – Concentration at time t_1

K – Degradation rate constant

This yielded a degradation rate constant for tebuconazole of 0.0293. The concentration as a function of time was plotted on the graph in **FIGURE 11** using the calculated value of K. Half-life ($T_{1/2}$) was then calculated as follows:

$T_{1/2} = \ln(2)/K = \ln(2)/0.0293$

This yielded a half-life of 23.6 days for tebuconazole.

The concentrations of methomyl in dam water as a function of time were plotted in **FIGURE 12** for measurements on samples taken on 28/10/2005 and 03/11/2005. The calculated degradation rate constant for methomyl was 0.1561 and the half-life was 4.4 days.

Half-lives of tebuconazole and methomyl measured in this study were compared to studies found in the literature.

Strickland *et al*. (2005: www.ars.usda.gov/research/publications/publications.htm, accessed on 2 March 2007) evaluated the potential for tebuconazole to degrade in a sandy loam soil with and without poultry litter amendments and the effect this fungicide may have on soil microbial activity. Results showed that the half-lives for tebuconazole were 41 days for the unamended and 46 days for the litter-amended soil. Tebuconazole had no effect on microbial activity. In this study, the half-life of tebuconazole determined in dam water was shorter (23.6 days).

Methomyl was reported to have a fairly short-medium half-life, resultantly it does not remain in the environment for long periods of time. One does not expect to find residues of methomyl in soil beyond the growing season during which it was applied. According to Johnson (2003: www.speclab.com/compound/c1675277.htm, accessed on 2 March 2007), the transformation rates in 3 greenhouse soils were reasonably high with half-lives from about 3 to 14 days. He also noted that half-lives of methomyl on cotton plants were found to be in the range from 0.4 to 8.5 days, 0.8 to 1.2 days on mint plants, and approximately 2.5 days on Bermuda grass. These values are in the range of the methomyl half-life determined in dam water in this study (4.4 days).

The HYDRUS-2D model (Simunek *et al*., 1999) was used to simulate pesticide concentrations on two hillslope soil profiles of the Goedertrou catchment using data collected in 2005. Simulation results confirmed that the two pesticides applied on wheat during 2005 may degrade relatively quickly in the soil, and therefore they do not represent a hazard to surface water and groundwater. The simulated concentrations of methomyl in soil water were higher due to the lower sorption coefficient compared to tebuconazole. Details of this simulation exercise can be found in Deliverable 5 (2006/07) of this project.

Both pesticides are therefore expected to have limited impact on water quality resources in the catchment. However, this will also depend on the amounts applied and management practices implemented.

TABLE 12: Analyses of pesticides measured in environmental samples during 2005

Date	Type of sample	Pesticide analysis ($\mu g\ L^{-1}$)	
		Tebuconazole	**Methomyl**
04/07/2005	Dam water	0.12	0.92
22/07/2005	S1P2T1 runoff	0.06	0.81
22/07/2005	S2P2T1 runoff	0.16	1.17
18/08/2005	S2P1T1 runoff	0.07	3.39
21/08/2005	***Application of fungicide – Folicur (active ingredient tebuconazole)***		
23/08/2005	Dam water	2.04	1.06
23/08/2005	S1P1T1 runoff	56.7	0.54
08/09/2005	Dam water	10.8	1.26

TABLE 12: Analyses of pesticides measured in environmental samples during 2005

Date	Type of sample	Pesticide analysis ($\mu g\ L^{-1}$)	
		Tebuconazole	Methomyl
14/10/2005	Dam water	5.2	5.2
21/10/2005	***Application of insecticide – Methomex (active ingredient methomyl)***		
28/10/2005	Dam water	4.62	2.5
03/11/2005	Dam water	2.09	0.98
08/12/2005	Dam water	Sample lost: bottle broken after freezing	
S1 – Site 1; S2 Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1			

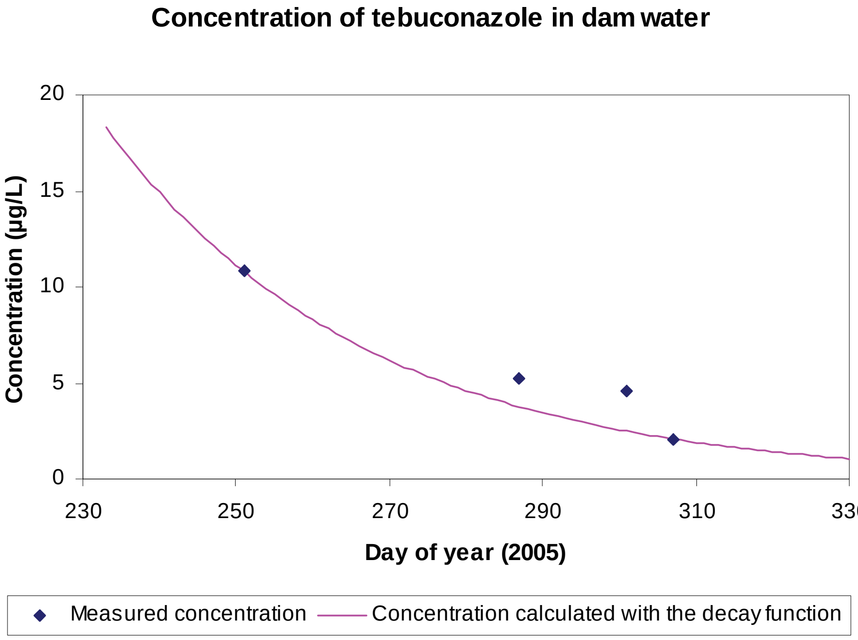


FIGURE 11: Measured and fitted concentrations of tebuconazole in dam water

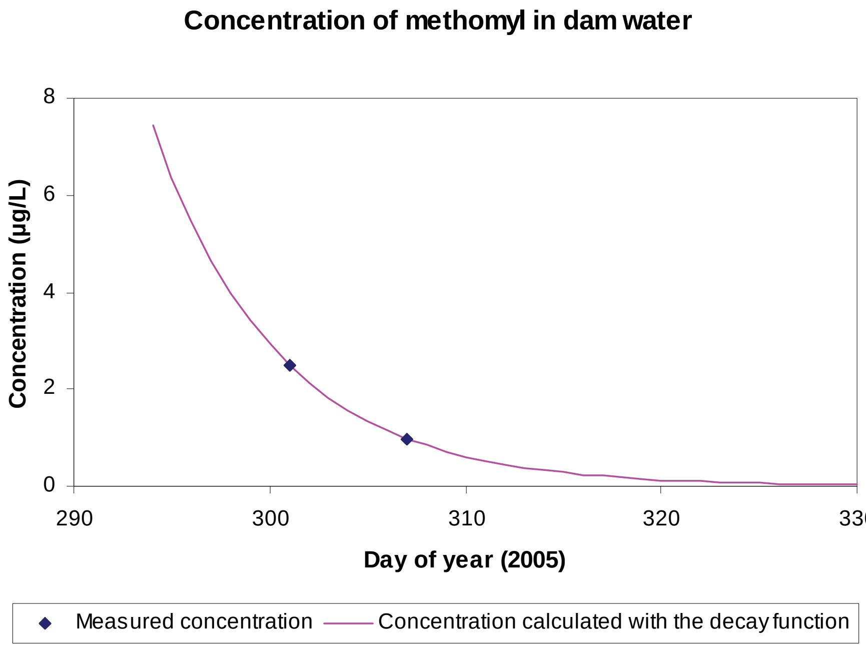


FIGURE 12: Measured and fitted concentrations of methomyl in dam water

3.5.6 Pesticide measurements – 2008

Samples of dam water were collected on five occasions during 2008 after application of herbicides (i.e. 29/07/2008, 05/08/2008, 22/08/2008, 03/09/2008 and 15/09/2008). The purpose was to analyze water samples for the presence of MCPA that could have been washed off via overland flow after spraying. The analyses were done by SABS according to standard methods and protocols. Recovery determinations of known concentrations of pesticide, carried out at a level of 1 µg L^{-1}, yielded a mean value of 105%. MCPA residue content was below detectable limits for all samples. Under the conditions of test employed, the lowest limit of quantification was 0.2 µg L^{-1}.

3.5.7 Measurements of nutrients – Soil

The results of soil analyses of N and P for 2005 are shown in **TABLE 13** per sampling site in chronological order. The data represent concentrations measured with Standard AutoAnalyzer methods in 1:5 soil:water extracts. Nutrient concentrations in soils are also shown as a function of time in **FIGURE 13** (site 1) and **FIGURE 14** (site 2). Fertilization took place on 08/05/2005 (DoY 128) and in the middle of July 2005 (around DoY 200).

Concentrations of NO_2 were generally very low throughout the season (**FIGURE 13** and **FIGURE 14**). The data showed a tendency of increase in concentrations of NO_3 after application of fertilizer. Some residual NO_3 and PO_4 were present at the beginning of the season as was evident from the baseline measurement done on 13/04/2005 (DoY 103), before planting. A slight increase in concentration of NO_3 and PO_4 was observed at the end of the season, possibly due to mineralization of residual plant material. Some NO_3 and PO_4 collected in contour soils at the end of the season, although the concentrations were relatively low.

TABLE 13: Analyses of n and p for soil samples collected during 2005

Date	Sample	NO_2 (mg L^{-1})	NO_3 (mg L^{-1})	PO_4 (mg L^{-1})
03/11/2005	S1, Contour	0	32.9	4.8
03/11/2005	S1, Contour	0	30.2	4.8
13/04/2005	S1P1, 10 cm	1.8	153.9	95.1
08/12/2005	S1P1, 10 cm	0	19.9	21.9
22/07/2005	S1P1 Bottom, 10 cm	0	118.5	17.4
04/07/2005	S1P1 Bottom, 40 cm	1.9	7.7	7.9
22/07/2005	S1P1 Bottom, 40 cm	0	59	5.2
04/07/2005	S1P1 Top, 10 cm	16.2	0	36
22/07/2005	S1P1 Top, 10 cm	0	40.9	21.9
08/09/2005	S1P1 Top, 10 cm	0	0	23.1
14/10/2005	S1P1 Top, 10 cm	0	0	22.3
04/07/2005	S1P1 Top, 40 cm	0	5.3	9.7
22/07/2005	S1P1 Top, 40 cm	0	5.1	60.8
08/09/2005	S1P1 Top, 40 cm	0	0	44.7
14/10/2005	S1P1 Top, 40 cm	0	0	60.5
14/10/2005	S1P2 Bottom, 10 cm	0	0.9	1.2
03/11/2005	S1P2 Bottom, 10 cm	0	13.4	10.3
04/07/2005	S1P2 Top, 10 cm	2.8	0.8	5
22/07/2005	S1P2 Top, 10 cm	0	0	9.4
23/08/2005	S1P2 Top, 10 cm	0.44	0	0
14/10/2005	S1P2 Top, 10 cm	0	0	4.2
03/11/2005	S1P2 Top, 10 cm	0	26.3	7.1
04/07/2005	S1P2 Top, 40 cm	0	2.4	3.5
22/07/2005	S1P2 Top, 40 cm	0	1.5	8
23/08/2005	S1P2 Top, 40 cm	0	3.3	0
14/10/2005	S1P2 Top, 40 cm	0	0.9	3
03/11/2005	S1P2 Top, 40 cm	0	34.6	8.9
13/04/2005	S2, 10 cm	0	64.6	46.3

TABLE 13: Analyses of n and p for soil samples collected during 2005

Date	Sample	NO_2 (mg L^{-1})	NO_3 (mg L^{-1})	PO_4 (mg L^{-1})
03/11/2005	S2, Contour	0	57	21
08/12/2005	S2P2, 10 cm	0	9.4	34.1
04/07/2005	S2P2 Top, 10 cm	0	0	37.9
22/07/2005	S2P2 Top, 10 cm	0	0	12.6
23/08/2005	S2P2 Top, 10 cm	0	0	32.5
14/10/2005	S2P2 Top, 10 cm	0	0	11.1
03/11/2005	S2P2 Top, 10 cm	0.3	25.2	38.8
04/07/2005	S2P2 Top, 50 cm	0	0	12.1
22/07/2005	S2P2 Top, 50 cm	0	1.6	5.9
30/01/2006	S1P2, 10 cm	0	57.4	22
30/01/2006	S2P2, 10 cm	0	11.7	30.5

S1 – Site 1; S2 – Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2;

Top – Top of the runoff plot; Bottom – Bottom of the runoff plot

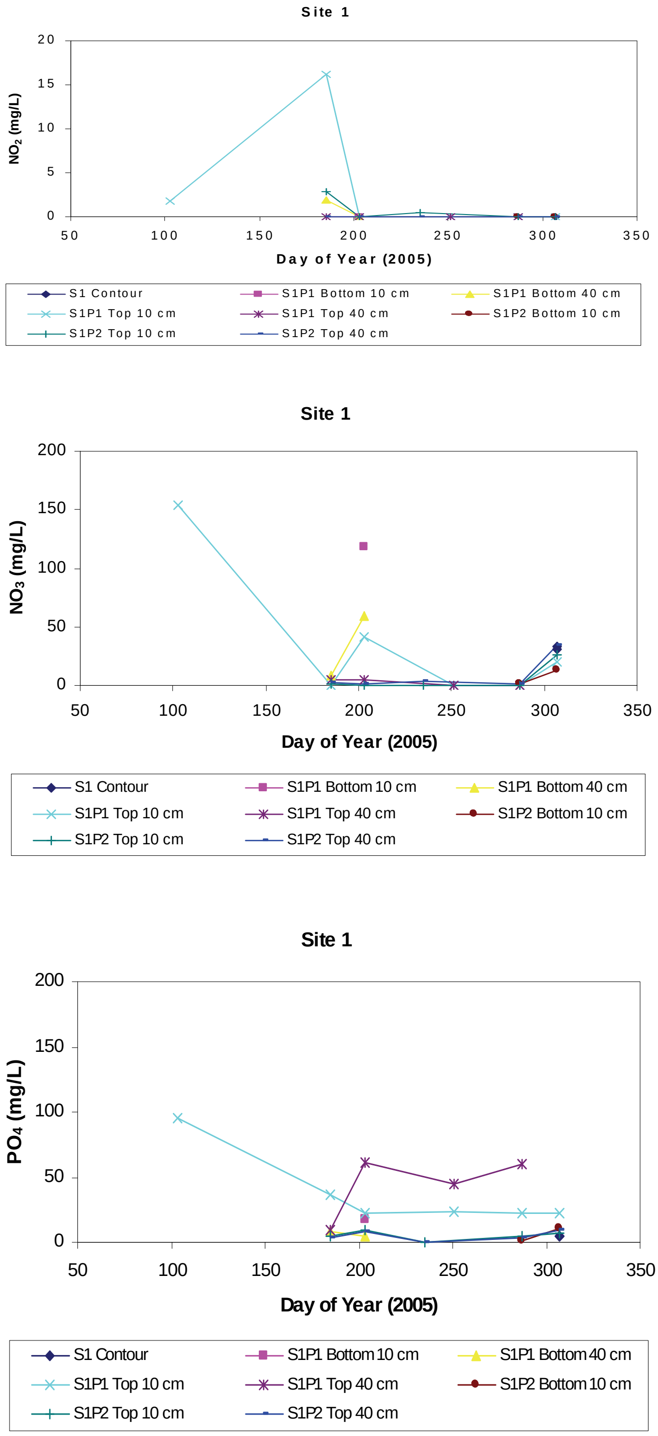


FIGURE 13: Concentrations of NO2, NO3 and PO4 measured in soil samples at Site 1 during 2005 (S1 – Site 1; P1 – Runoff plot 1; P2 – Runoff plot 2; Top – Top of the runoff plot; Bottom – Bottom of the runoff plot)

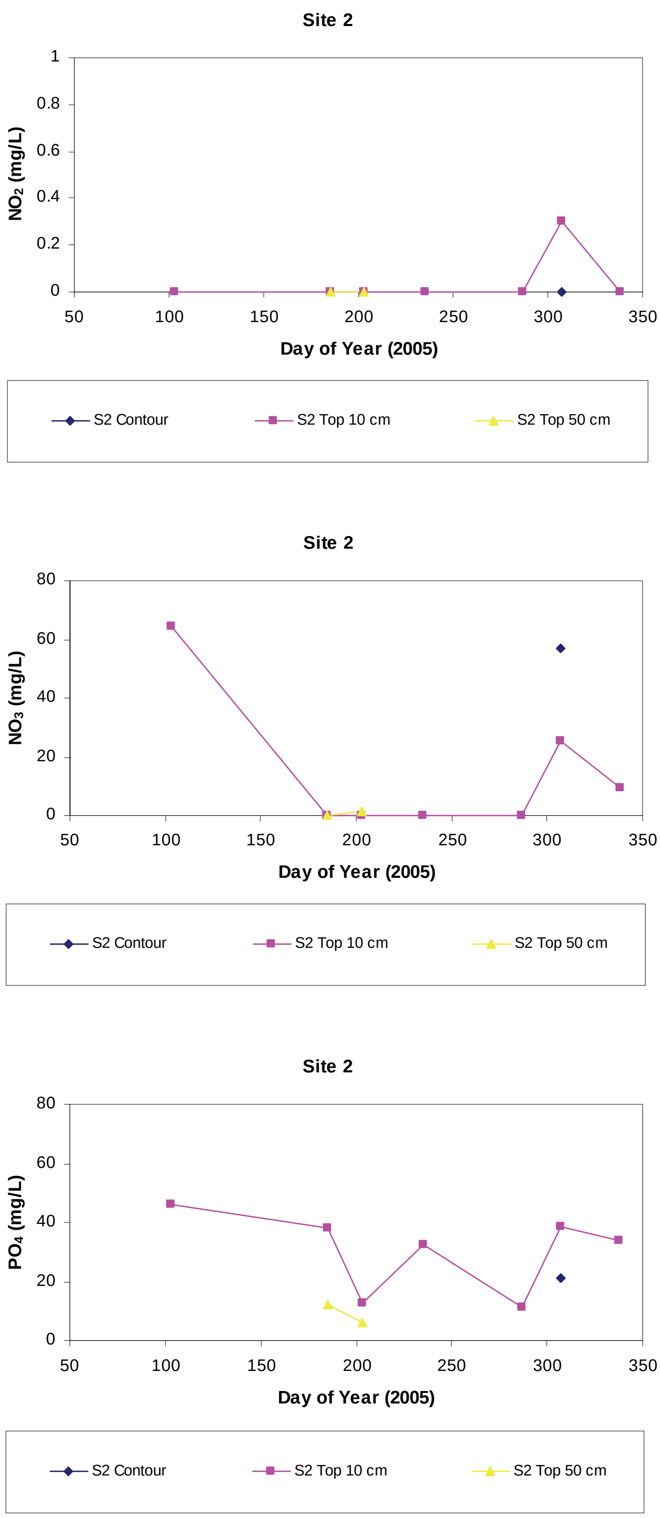


FIGURE 14: Concentrations of NO2, NO3 and PO4 measured in soil samples at Site 2 during 2005 (S2 – Site 2; Top – Top of the runoff plot)

The results of soil analyses of N and P, done as spot checks during 2006, are shown in **TABLE 14** for information purposes.

TABLE 14: Results of soil analyses of N and P done as spot checks during 2006

Sample			$N\text{-}NH_4$ ($mg\ kg^{-1}$)	$N\text{-}NO_3$ ($mg\ kg^{-1}$)	P ($mg\ kg^{-1}$)	Total N (%)	Total P ($mg\ kg^{-1}$)
Site	Date	Soil depth (m)					
1	21/03/2006	10	11.20	1.89	21.2	0.069	347.41
		40	8.28	23.28	39.4	0.102	364.56
	29/06/2006	10	7.08	1.45	6.61	0.038	267.33
		40	6.48	4.70	4.39	0.018	254.65
2	21/03/2006	10	6.81	1.50	41.5	0.078	161.46
		40	8.39	19.32	42.0	0.083	195.27
	29/06/2006	10	6.47	1.59	8.59	0.043	133.35
		40	6.35	5.21	6.80	0.051	95.83

3.5.8 Measurements of nutrients – Water

The results of water analyses of N and P for 2005 are shown in **TABLE 15** per sampling site in chronological order. Nutrient concentrations are also shown as a function of time in **FIGURE 15** (site 1) and **FIGURE 16** (site 2 and dam water). The data represent concentrations measured with Standard AutoAnalyzer methods. Fertilization took place on 08/05/2005 (DoY 128) and in the middle of July 2005 (around DoY 200).

Concentrations of NO_2 in runoff water were generally very low throughout the season (**FIGURE 15** and **FIGURE 16**) with one exception on 23/06/2005 at site 2, runoff plot 2 (41.3 mg L^{-1}). A time lag was observed between the time of fertilizer application and the increase in concentrations of NO_3 in runoff water, as nutrients were washed out by erratic events. Analyses of PO_4 were done only in the last two months of the season. Some NO_3 was detected in contour waters at the beginning of the season as it is evident from the measurement done on 13/04/2005 (DoY 103), before planting, both at site 1 and 2. NO_3 and PO_4 were also detected in contour waters at the end of the season at both sites. The concentrations of NO_3 and PO_4 in the dam were in the range of those measured in runoff water.

TABLE 15: Analyses of N and P for water samples collected during 2005

Date	Sample	NO_2 (mg L^{-1})	NO_3 (mg L^{-1})	PO_4 (mg L^{-1})
13/04/2005	Dam 1	0	17.9	-
13/04/2005	Dam 2	0	19.6	-
14/10/2005	Dam	0	6.2	43.3

TABLE 15: Analyses of N and P for water samples collected during 2005

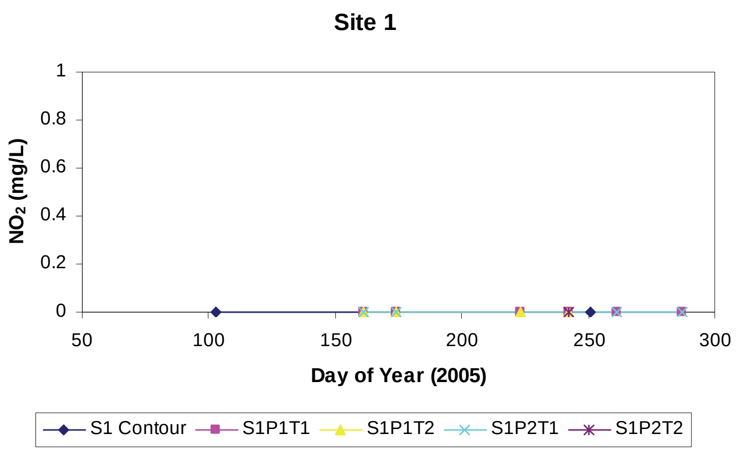
Date	Sample	NO_2 (mg L^{-1})	NO_3 (mg L^{-1})	PO_4 (mg L^{-1})
03/11/2005	Dam	0	6.9	42.5
13/04/2005	S1 Contour	0	51	-
08/09/2005	S1 Contour	0	12.6	22.2
10/06/2005	S1P1T1	0	49.3	-
23/06/2005	S1P1T1	0	86.1	-
23/06/2005	S1P1T1	0	9.68	-
11/08/2005	S1P1T1	0	8.7	-
30/08/2005	S1P1T1	0	12.5	-
18/09/2005	S1P1T1	0	0.6	0.4
14/10/2005	S1P1T1	0	7.1	45
10/06/2005	S1P1T2	0	8.4	-
10/06/2005	S1P1T2	0	9	-
23/06/2005	S1P1T2	0	44.4	-
11/08/2005	S1P1T2	0	2.3	-
30/08/2005	S1P1T2	0	18.4	-
10/06/2005	S1P2T1	0	10.3	-
23/06/2005	S1P2T1	0	2	-
18/09/2005	S1P2T1	0	88.9	41.6
14/10/2005	S1P2T1	0	1.6	10.2
30/08/2005	S1P2T2	0	0	-
13/04/2005	S2 Contour	0	22.3	-
13/04/2005	S2 Contour	0	26	-
08/09/2005	S2 Contour	0	15.7	72.6
23/06/2005	S2P1T2	0	136	-
11/08/2005	S2P1T2	0	3.8	-
23/06/2005	S2P2T1	41.3	12.2	-

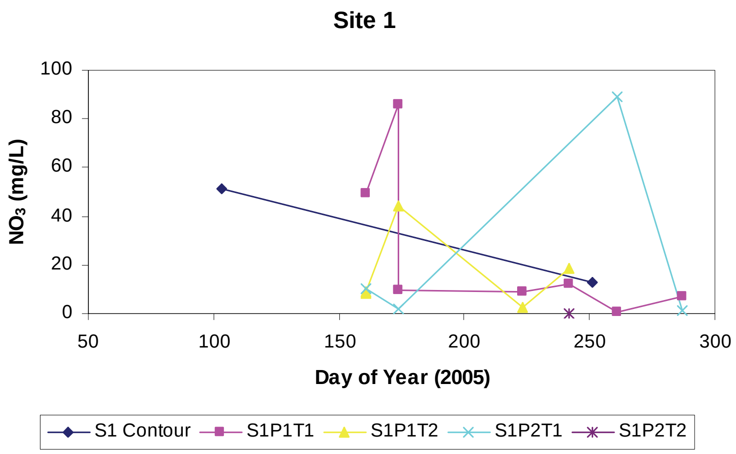
TABLE 15: Analyses of N and P for water samples collected during 2005

Date	Sample	NO_2 (mg L^{-1})	NO_3 (mg L^{-1})	PO_4 (mg L^{-1})
11/08/2005	S2P2T1	0	16.8	-

S1 – Site 1; S2 Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2;

T1 – Tank 1; T2 – Tank 2





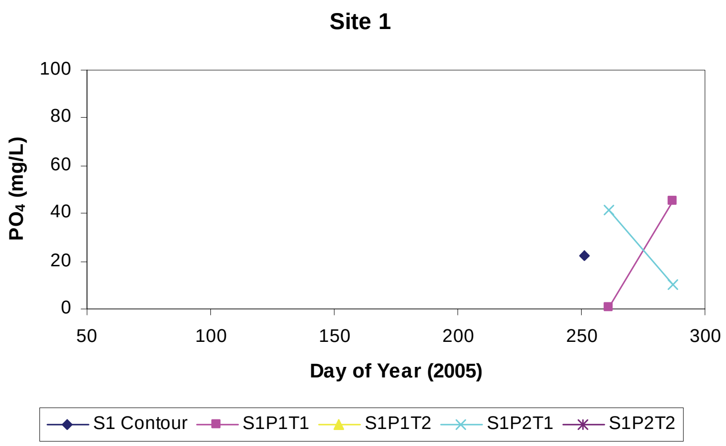


FIGURE 15: Concentrations of NO2, NO3 and PO4 measured in water samples at Site 1 during 2005 (S1 – Site 1; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1; T2 – Tank 2)

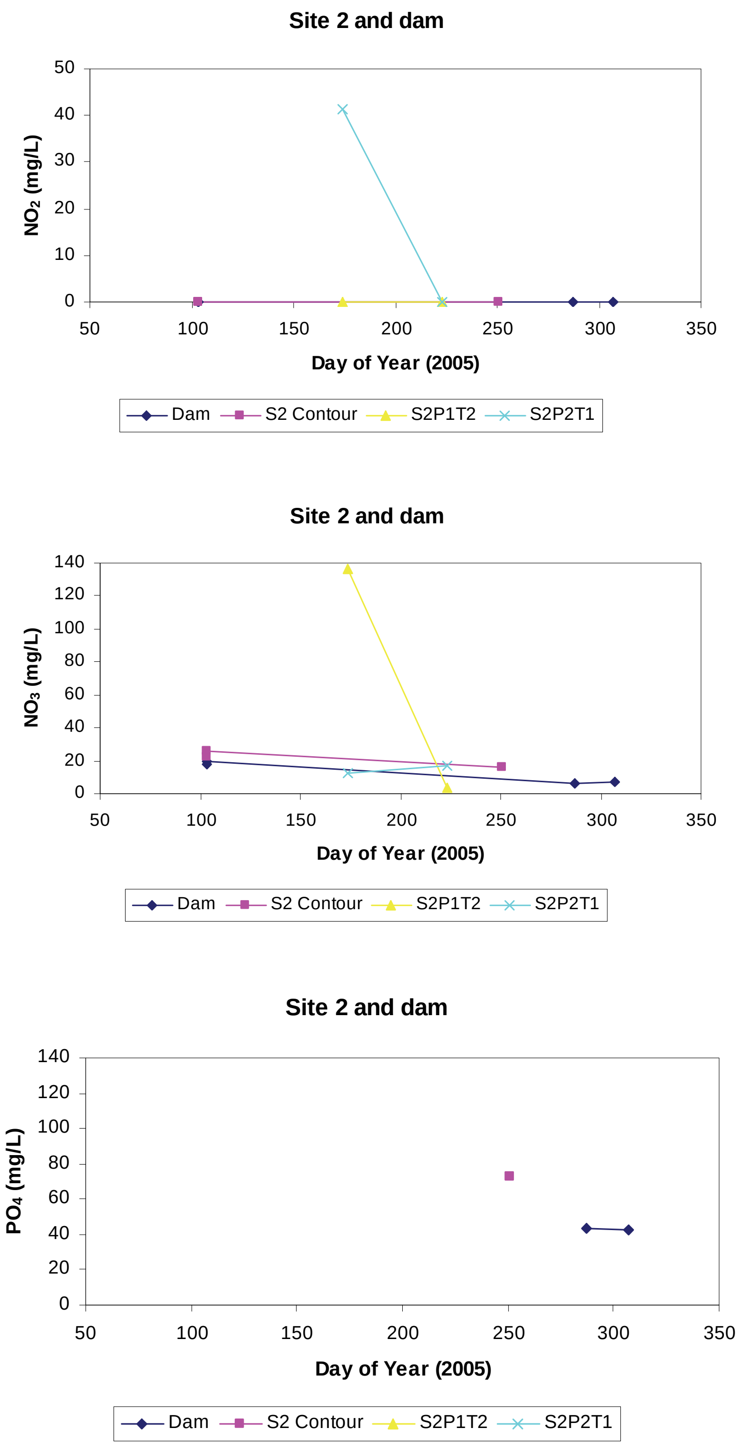


FIGURE 16: Concentrations of NO2, NO3 and PO4 measured in water samples at Site 2 and in the dam during 2005 (S2 – Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1; T2 – Tank 2)

3.5.9 Measurements of nutrients – Plants

The plant analyses done during 2006 are summarized in **TABLE 16** for two replicates at sites 1 and 2. These values should be indicative of the seasonal uptake of N and P by the vegetation on fallow land.

TABLE 16: Plant analyses of N and P on samples of fallow re-growth collected on 21/09/2006

Plant sample		Total N (%)	P (%)
Site 1	Repl. 1	1.50	0.219
	Repl. 2	1.36	0.175
Site 2	Repl. 1	1.33	0.252
	Repl. 2	1.30	0.233

3.5.10 Measurements of sediments

Water samples were taken from the sediment tanks at the runoff plots from 2006 to 2008 in order to determine the amounts of sediments mobilized from the runoff plots. The results of sediment content in water samples are presented in **TABLE 17** (2006), **TABLE 18** (2007) and **TABLE 19** (2008) in chronological order. The mobilization of sediments depended mainly on rainfall intensity and duration. For example, considerable amounts of sediments were measured in most samples during rain storms occurring between 03/07/2008 and 12/07/2008 (**TABLE 19**), when 132.6 mm of rain was recorded with a maximum intensity of 13.4 mm h^{-1} on 09/09/2008.

In general, high concentrations of sediments were measured when small runoff events occurred (low rainfall amounts and/or intensity). With high rainfall and runoff volumes, sediment concentrations were generally low due to dilution effects. This is a good representation of the nature of rainfall in the area, generally consisting of prolonged low-intensity drizzle, and it indicates that most sediment mobilization may occur at the beginning of a runoff event. Soil surface crusting is common in the study area due to naturally-occurring elevated concentrations of NaCl in the soil (De Clercq *et al*., 2010). Overland flow occurs on crusted soil surfaces without considerable generation of sediments even during long duration and high-intensity rainfall. In terms of total sediment load, more eroded material was mobilized from the runoff plots during heavy rainfall and runoff events at both sites. Site 2 generally produced lower sediment concentrations in runoff water, but more runoff and higher sediment loads when compared to site 1.

The results obtained with the LASER particle size analyzer, and analyzed with Saturn Digisizer 5200 software, are reported in Deliverable 12 (2008/09) of this project. Particle volume frequency percent and cumulative finer volume percent were measured for all sediment samples with the particle size analyzer. The bulk of mobilized particles had diameters in the range between 5 and 15 μm (silt range), depending on the soil texture (source of mobilized sediments) and slope (gravity force for transport), and regardless of rainfall and overland flow. The expected sediment particle size distribution in the catchment can be used in conjunction with sorption data to estimate transport of sorbed contaminants, e.g. nutrients and pesticides.

TABLE 17: Total sediment content in water samples collected during 2006

Date	Sample	Sediment content ($g\ L^{-1}$)	Date	Sample	Sediment content ($g\ L^{-1}$)
01/06/2006	Dam	1	01/06/2006	S2 Contour	2
29/06/2006	Dam	0	29/06/2006	S2 Contour	3
11/07/2006	Dam	0	11/07/2006	S2 Contour	1
23/05/2006	S1 Contour	1	25/07/2006	S2 Contour	1
01/06/2006	S1 Contour	1	25/04/2006	S2 P1 T1	-
13/06/2006	S1 Contour	1	09/05/2006	S2 P1 T1	1
29/06/2006	S1 Contour	1	23/05/2006	S2 P1 T1	2
11/07/2006	S1 Contour	0	01/06/2006	S2 P1 T1	0
25/07/2006	S1 Contour	1	29/06/2006	S2 P1 T1	1
25/04/2006	S1 P1 T1	0	18/07/2006	S2 P1 T1	1
09/05/2006	S1 P1 T1	1	25/07/2006	S2 P1 T1	0
23/05/2006	S1 P1 T1	2	03/08/2006	S2 P1 T1	1
01/06/2006	S1 P1 T1	235	10/08/2006	S2 P1 T1	1
13/06/2006	S1 P1 T1	1	23/05/2006	S2 P1 T2	22
29/06/2006	S1 P1 T1	2	29/06/2006	S2 P1 T2	2
18/07/2006	S1 P1 T1	1	25/07/2006	S2 P1 T2	1
25/07/2006	S1 P1 T1	1	03/08/2006	S2 P1 T2	0
10/08/2006	S1 P1 T1	3	10/08/2006	S2 P1 T2	1
09/05/2006	S1 P1 T2	5	09/05/2006	S2 P2 T1	1
23/05/2006	S1 P1 T2	6	23/05/2006	S2 P2 T1	2
13/06/2006	S1 P1 T2	1	29/06/2006	S2 P2 T1	0
25/07/2006	S1 P1 T2	1	18/07/2006	S2 P2 T1	1
10/08/2006	S1 P1 T2	1	25/07/2006	S2 P2 T1	1
09/05/2006	S1 P2 T1	1	10/08/2006	S2 P2 T1	0
23/05/2006	S1 P2 T1	2	23/05/2006	S2 P2 T2	98
10/08/2006	S1 P2 T1	0	29/06/2006	S2 P2 T2	0

TABLE 17: Total sediment content in water samples collected during 2006

Date	Sample	Sediment content ($g\ L^{-1}$)	Date	Sample	Sediment content ($g\ L^{-1}$)
10/08/2006	S1 P2 T2	-	25/07/2006	S2 P2 T2	0
23/05/2006	S2 Contour	1	10/08/2006	S2 P2 T2	0

S1 – Site 1; S2 Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1; T2 – Tank 2

TABLE 18: Total sediment content in water samples collected during 2007

Date	Sample	Sediment content ($g\ L^{-1}$)	Date	Sample	Sediment content ($g\ L^{-1}$)
05/03/2007	DAM	-	01/08/2007	S1P2T1	0
17/05/2007	DAM	2	08/08/2007	S1P2T1	1
17/05/2007	DAM	2	15/08/2007	S1P2T1	0
12/06/2007	DAM	1	28/08/2007	S1P2T1	-
27/06/2007	DAM	20	12/06/2007	S1P2T2	1
10/07/2007	DAM	15	01/08/2007	S1P2T2	4
17/07/2007	DAM	3	08/08/2007	S1P2T2	2
01/08/2007	DAM	4	15/08/2007	S1P2T2	0
15/08/2007	DAM	4	15/08/2007	S2 Contour	0
23/08/2007	DAM	-	21/02/2007	S2P1T1	3
28/08/2007	DAM	-	05/03/2007	S2P1T1	-
15/08/2007	S1 Contour	3	07/05/2007	S2P1T1	1
28/08/2007	S1 Contour	-	17/05/2007	S2P1T1	1
18/07/2007	S1P1	-	22/05/2007	S2P1T1	1
21/02/2007	S1P1T1	4	12/06/2007	S2P1T1	1
05/03/2007	S1P1T1	-	01/08/2007	S2P1T1	1
17/05/2007	S1P1T1	1	08/08/2007	S2P1T1	3
22/05/2007	S1P1T1	1	15/08/2007	S2P1T1	2
12/06/2007	S1P1T1	2	21/02/2007	S2P1T2	2

TABLE 18: Total sediment content in water samples collected during 2007

Date	Sample	Sediment content ($g\ L^{-1}$)	Date	Sample	Sediment content ($g\ L^{-1}$)
27/06/2007	S1P1T1	12	05/03/2007	S2P1T2	-
10/07/2007	S1P1T1	12	22/05/2007	S2P1T2	0
17/07/2007	S1P1T1	19	12/06/2007	S2P1T2	4
01/08/2007	S1P1T1	0	01/08/2007	S2P1T2	3
08/08/2007	S1P1T1	1	08/08/2007	S2P1T2	3
15/08/2007	S1P1T1	0	15/08/2007	S2P1T2	3
28/08/2007	S1P1T1	-	21/02/2007	S2P2T1	4
21/02/2007	S1P1T2	3	05/03/2007	S2P2T1	-
05/03/2007	S1P1T2	-	22/05/2007	S2P2T1	-
22/05/2007	S1P1T2	1	12/06/2007	S2P2T1	4
12/06/2007	S1P1T2	5	27/06/2007	S2P2T1	1
27/06/2007	S1P1T2	14	01/08/2007	S2P2T1	2
01/08/2007	S1P1T2	3	08/08/2007	S2P2T1	2
08/08/2007	S1P1T2	0	15/08/2007	S2P2T1	0
15/08/2007	S1P1T2	3	28/08/2007	S2P2T1	-
21/02/2007	S1P2T1	0	17/05/2007	S2P2T2	-
05/03/2007	S1P2T1	-	22/05/2007	S2P2T2	3
22/05/2007	S1P2T1	4	12/06/2007	S2P2T2	4
12/06/2007	S1P2T1	3	27/06/2007	S2P2T2	10
27/06/2007	S1P2T1	8	01/08/2007	S2P2T2	3
10/07/2007	S1P2T1	22	08/08/2007	S2P2T2	3
17/07/2007	S1P2T1	3	15/08/2007	S2P2T2	0

S1 – Site 1; S2 Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1; T2 – Tank 2

TABLE 19: Total sediment content in water samples collected during 2008

Date	Sample	Sediment content ($g\ L^{-1}$)	Date	Sample	Sediment content ($g\ L^{-1}$)
23/06/2008	S1P1T1	7.1	23/06/2008	S2P1T1	2.6
14/07/2008	S1P1T1	0	14/07/2008	S2P1T1	7.0
05/08/2008	S1P1T1	1.3	29/07/2008	S2P1T1	1.0
03/09/2008	S1P1T1	0.6	05/08/2008	S2P1T1	1.0
15/09/2008	S1P1T1	2.6	22/08/2008	S2P1T1	2.3
23/06/2008	S1P1T2	14.2	03/09/2008	S2P1T1	1.7
14/07/2008	S1P1T2	10.0	15/09/2008	S2P1T1	0.4
03/09/2008	S1P1T2	0.7	23/06/2008	S2P1T2	0.3
15/09/2008	S1P1T2	0.8	14/07/2008	S2P1T2	3.0
23/06/2008	S1P2T1	0.8	05/08/2008	S2P1T2	0.8
29/07/2008	S1P2T1	0	03/09/2008	S2P1T2	0.7
03/09/2008	S1P2T1	0.4	15/09/2008	S2P1T2	0.5
15/09/2008	S1P2T1	0.9	23/06/2008	S2P2T1	2.1
23/06/2008	S1P2T2	0.5	05/08/2008	S2P2T1	0.5
03/09/2008	S1P2T2	0.4	03/09/2008	S2P2T1	0.7
15/09/2008	S1P2T2	0.4	15/09/2008	S2P2T1	0.7
			23/06/2008	S2P2T2	3.0
			03/09/2008	S2P2T2	0.4
			15/09/2008	S2P2T2	0.4

S1 – Site 1; S2 Site 2; P1 – Runoff plot 1; P2 – Runoff plot 2; T1 – Tank 1; T2 – Tank 2

3.6 CONCLUSIONS

The following main conclusions were made based on the data collected from 2005 to 2009:

- Air temperature varied between 1.8°C and 42.8°C, average relative humidity for the recorded period was 63.9%, average wind speed was 3.0 m s^{-1}, and rainfall was about 330 mm a^{-1} with the highest recorded intensity of 27.8 mm h^{-1}.

- Wheat grain yield was between 2 Mg ha^{-1} (in 2005) and 3 Mg ha^{-1} (in 2008). Total biomass production from fallow land was between 2 and 2.7 Mg ha^{-1} (in 2006).

- Volumetric soil water content varied depending mainly on seasonal rainfall and the presence of vegetation. The South-oriented, clayey soil at site 2 retained more water than the North-oriented, lighter-textured soil at site 1. Soil water contents exhibited high spatial variability depending on soil properties and sensors' installation. Both types of sensors (EC-20 and Echo-TE) were highly sensitive to rainfall events.

- Overland flow was between 4 and 19% of annual rainfall, depending on vegetation, soil type, slope and orientation.

- Different land uses caused different volumes of runoff and different amounts of sediment mobilization. Uncultivated (bare) soil and less densely planted soil produced more runoff. Different soil properties, slopes and antecedent moisture conditions also caused different volumes of runoff. In general, more overland flow occurred from uncultivated land, and from land oriented towards the South, with steep slope and clayey soil.

- The maximum flux of pesticides measured in runoff water was 1.38 g ha^{-1} for tebuconazole (rainfall/runoff event 2 days after application in 2005). No rainfall occurred after application of methomyl in 2005. Both methomyl and tebuconazole, applied towards the end of the wheat 2005 season (end of rainy winter), degraded rapidly *in situ* and did not impact to a large extent surface waters in the absence of rainfall. Half-lives in dam water were 23.6 d for tebuconazole and 4.4 d for methomyl.

- No detectable traces of MCPA in dam water were observed after application of this herbicide in the first week of July 2008 and subsequent rains that occurred during the 2008 winter season.

- Based on overland flow volumes and NO_3 concentrations measured at the Wischmeier runoff plots, it was calculated that between 0.24 and 3.65 kg ha^{-1} a^{-1} of NO_3 were mobilized via overland flow during 2005. NO_3 and PO_4 concentrations in runoff water collected at the runoff plots varied widely depending mainly on the timing of fertilizer application and rainfall/runoff distribution.

- The temporal patterns of nutrient concentrations in both soils and waters followed mainly fertilizer applications. Very low concentrations of NO_2 were generally measured. A time lag was observed between the application of fertilizer and increase in concentrations of NO_3 in runoff water, as nutrients were washed out by erratic events. The concentrations of NO_3 and PO_4 in dam water were in the range of those measured in runoff water.

- Concentrations of sediments in runoff water were between 0 and 22.0 g L^{-1} (2.6 g L^{-1} on average), depending on rainfall distribution and intensity, slope and vegetation. Total seasonal sediment mobilization ranged between 0.02 and 0.85 Mg ha^{-1} a^{-1} (0.26 Mg ha^{-1} a^{-1} on average).

- High concentrations of sediments in runoff water were generally measured when small runoff events occurred (low rainfall amounts and/or intensity). With high rainfall and runoff volumes, sediment concentrations were generally low due to dilution effects. In terms of total sediment load, however, more eroded material was mobilized from the runoff plots during heavy rainfall and runoff events. The bulk of mobilized particles had diameters in the range between 5 and 15 µm (silt range), depending on the soil texture (source of mobilized sediments) and slope (gravity force for transport), and regardless of rainfall and overland flow volumes. The expected sediment particle size distribution in the catchment can be used in conjunction with sorption data to estimate transport of sorbed contaminants, e.g. nutrients and pesticides. In addition, sediment size distribution can be used in conjunction with chemical properties of mineral particles to trace the origin and history of sediment transport in catchments.

- Water levels in the dam at Goedertrou varied seasonally and responded within hours of rainfall events.

- It should be noted that NPS pollutant fluxes estimated in this study originated from Wischmeier runoff plot measurements. The effects of countour banks on mobility of nutrients, pesticides and sediments should be taken into account.

4 EXPERT SYSTEM FOR PESTICIDES

4.1 BACKGROUND

During the Research Team meeting on 10 April 2008 and the Reference Group meeting on 27 May 2008 for WRC project No. K5/1516, it was proposed that an expert system (guidelines) for modelling fate of pesticides at field-scale be developed by the Pesticide Task Team. This proposal emanated from the fact that there are many organic chemical species that are potential NPS pollutants, and it would be practically impossible to assess the impacts of each chemical through field trials.

An index for the estimation of environmental mobility of pesticides was therefore developed (including guidelines based on expert knowledge) as support to the integrated framework for modelling agricultural NPS pollution. This Chapter includes the following sections:

1) Literature review of expert systems and environmental indicators

2) Description of the Pesticide Environmental mobility indeX (PestEX)

3) Example of application of PestEX

The full report on guidelines for modelling fate of pesticides at field-scale and on the development of the pesticide environmental mobility index can be found in Deliverable 3 (2007/08) of this project.

4.2 LITERATURE REVIEW

Traditionally, from the agricultural production point of view, both farmers and the chemical industry consider the three main properties of pesticides as being selectivity, efficacy and persistence. In the last few decades, with the shift from agricultural production issues towards environmental issues, more attention is being paid to the environmental impacts of pesticide application (Shahane and Inman, 1987; Levitan *et al*., 1995; Van der Werf, 1996). Environmental impacts resulting from the use of pesticides can be predicted with process-based simulation models (Vanclooster *et al*., 2000). However, Boesten (1999) and Meinhardt (2003) pointed out difficulties in the application and validation of such models. Some of the problems are the complexity of the soil-plant-atmosphere system, large amount of input data required, lack of knowledge on pesticide behaviour and toxicity as well as spatial and temporal uncertainties.

An alternative to process-based models is the use of expert systems. This approach is particularly suitable when large databases of information exist that can to be applied to, and interpreted for specific cases. Expert systems are generally interactive computer programmes that include quantitative informational databases and qualitative knowledge, experience and judgement gained over many years of work and research. They can be used as support to both decision- and policy-making (Crowe and Mutch, 1990; Levitan, 2000; Rao, http://www.manage.gov.in/managelib/faculty/PanduRanga.htm, accessed on 28 July 2008). For this purpose, the output of the expert system is often expressed in the form of simple environmental performance indicators or indexes (Penrose *et al*., 1994; Giupponi, 1998; Reus *et al*., 2002; Stachetti Rodrigues *et al*., 2003; Juraske *et al*., 2007; Stenrod *et al*., 2008). The development of expert systems and the compilation of guidelines for the use of pesticides and their environmental impacts are not novelties (Lewis and Bardon, 1998; Van der Werf and Petit, 2002; Padovani *et al*., 2004). Due to the very dynamic market of chemical products and the wide range of research questions and environmental issues, there is constantly need to update databases, test the performance of new pesticides, perform toxicological tests on new products and determine the possible impacts on the environment (Donati *et al*., 1993).

Crowe and Mutch (1992) developed an expert system (EXPRES) as an aid to regulatory personnel in Canada in the assessment of the potential for pesticides to contaminate soil and groundwater. EXPRES includes a numerical model and guidelines to the user on how to select realistic input data for simulations. In this way, a complex model can be operated by non-experts without sacrificing the accuracy of predictions. Neumann *et al*. (2003a and b) developed LIMPACT, an expert system used to indicate whether a stream is contaminated with pesticides or not, based on macroinvertebrate indicators. The system was developed using standardized toxicities, as well as data on water quality and 39 taxa of benthic macroinvertebrate fauna obtained from 157 data sets (1992 to 2000) in 104 small headwater streams with agricultural catchment areas. Van der Werf and Zimmer (1998) proposed an agro-ecological indicator (Ipest) as a tool to assess the environmental effects of pesticides, based on a fuzzy logic expert system that uses pesticide properties, site-specific conditions and type of application as inputs. Their expert system is based on four modules, namely i) the presence of the pesticide reflected by the rate and method of application, ii) the risk of surface water contamination, iii) the risk of groundwater contamination, and iv) the risk of air contamination. Bues *et al*. (2004) tested the Ipest approach, as well as an approach called environmental impact quotient (EIQ) (Kovach *et al*., 1994) in several Mediterranean countries and recommended that the two methods be used together to provide a more complete analysis of the environmental impacts of pesticides. A similar approach was developed by Reus and Leendertse (2000), who recommended an indicator called environmental yardstick, based on the risks to water organisms, groundwater contamination and soil organisms. This approach was used by De Jong and De Snoo (2002) to evaluate the environmental impacts of pesticides in integrated and conventional potato cultivation. Ferraro *et al*. (2003) used fuzzy logic-based indicators to evaluate the environmental effects of pesticides and tillage in different cropping systems.

Environmental costs are not always considered in environmental studies because of the difficulties in assigning costs to indirect (external) economic values (e.g. ecological functions, opportunity costs etc.) (Barrow, 1999), in particular when data and resources are limited (Leach and Mumford, 2008). Wossink *et al*. (2001) highlighted that production, pollution and abatement are to be treated as non-separable, whilst spatial and temporal heterogeneity should be taken into account in economic and ecological attributes. In a study assessing the environmental impacts of agriculture in the United Kingdom, Skinner *et al*. (1997) considered the costs involved in reducing levels of pollutants in water bodies. Falconer and Hodge (2001) combined an economic model of land use and production with a set of environmental indicators to identify the most appropriate specification of a tax instrument to reduce environmental problems of agricultural pesticide usage. In an income analysis based on full cost principle and environmental life cycle assessment, Mouron *et al*. (2006) found that improved on-farm management can increase income of apple-growers in Switzerland without compromising environmental quality. The effects of on-farm management practices (conventional, low-input, and organic pest management in processing tomato and field corn) on economic efficiency and the environment were discussed by Clark *et al*. (1998). Van der Werf and Petit (2002), and Payraudeau and Van der Werf (2005) recommended that indicators of environmental impact should preferably be expressed in the form of values (e.g. impacts per unit area or per unit product), rather than in the form of rating scores. However, threshold values for these indicators are lacking (Van der Werf and Petit, 2002), and validation would be required at a large number of sites (Halberg *et al*., 2005). Existing environmental impact indicators also seldom include the effects of mitigation/management practices and seldom consider different scales of impact.

In this study, we developed a Pesticide Environmental indeX (PestEX) that accounts for the main factors affecting the contamination of surface- and groundwater, including the effects of mitigation/management measures. The novelty of the approach is that the factors were combined based on their occurrence at different scales. In addition, fuzzy logic normalization of the factors allows comparison and minimization of environmental and pollution abatement costs. The main purpose of PestEX is to assess the mobility of pesticides and their potential for reaching a water resource, and therefore the exposure potential to the aquatic environment.

4.3 PESTICIDE ENVIRONMENTAL MOBILITY INDEX (PestEX)

4.3.1 Conceptual model

The conceptual model of PestEX is shown in **FIGURE 17**. All factors considered in the assessment of the environmental mobility of pesticides are shown on the left side in **FIGURE 17**. The first group of factors includes local scale inputs related to site specific conditions and management practices. These include drift of pesticides at application (e.g. by tractor spraying or aircraft), position of application in relation to streams and groundwater, general slope of the area, dominant flow direction (horizontal or vertical) due to the presence of impervious layers in soils, tillage practices, soil hydraulic properties (saturated hydraulic conductivity), irrigation practices/rainfall distribution through overland flow and deep percolation, and the presence of anti-erosion contours. Each of these factors is assigned a rating and weighting to produce a score. The scores are then averaged into a combined local scale score (**FIGURE 17**).

The second group of factors, or catchment scale inputs, is represented by pesticide properties and the presence of wetlands/buffer strips. These factors are placed at a higher level compared to the local scale factors because the processes depending on pesticide properties (volatilization, sorption and decay) occur at both local and catchment scale (at any position along the pathways of chemicals towards water), whereas wetlands and buffer strips generally serve an area larger than individual farms and fields (local scale), and they are generally located in proximity of streams. Each catchment scale factor is assigned a rating and weighting to produce a score. The scores for catchment scale factors are then averaged together with the combined local scale score, to produce a combined local+catchment scale score (**FIGURE 17**).

The third group of factors is represented by overarching inputs. Pesticide application represents the source of contamination, whilst environmental sensitivity gives an indication of the sensitivity of the receiving environment. Regardless of all other inputs, high pesticide applications (expressed either as rate or volume) will tend to increase the effects on the environment, whilst no pesticide application will result in no effects. Similarly, the presence of organisms that are more sensitive to contamination will tend to increase the sensitivity of the receiving environment, whilst the presence of organisms that are tolerant to contamination will result in no sensitivity of the receiving water body. Pesticide application and environmental sensitivity are assigned a rating, weighted and combined with the scores of all other factors to produce a combined score (**FIGURE 17**).

Up to this point, rating and scoring is done separately for surface- and groundwater. Therefore, two combined scores are produced, the one for surface water and the other for groundwater. These are then weighted depending on water usage. A higher weighting is assigned to surface water if this is the dominant or the only water source for consumption, and vice versa. Finally, the scores for surface- and groundwater are combined to produce an environmental score (**FIGURE 17**). One of the overarching factors included in the environmental score, namely pesticide application, also affects the economic yield. A higher pesticide application results in a smaller yield reduction (the trade-off being a higher environmental cost) and vice versa (**FIGURE 17**).

All scores are normalized from 0 to 1. An environmental score of 0 indicates the pesticide is unlikely to reach and have an effect on water resources, whilst 1 corresponds to maximum environmental mobility. An economic score of 0 corresponds to maximum yield and profit, whilst an economic score of 1 represents total crop loss. The normalization was done in order to facilitate the comparison and optimization (minimization) of environmental and economic scores, as well as the translation of scores into real cost values.

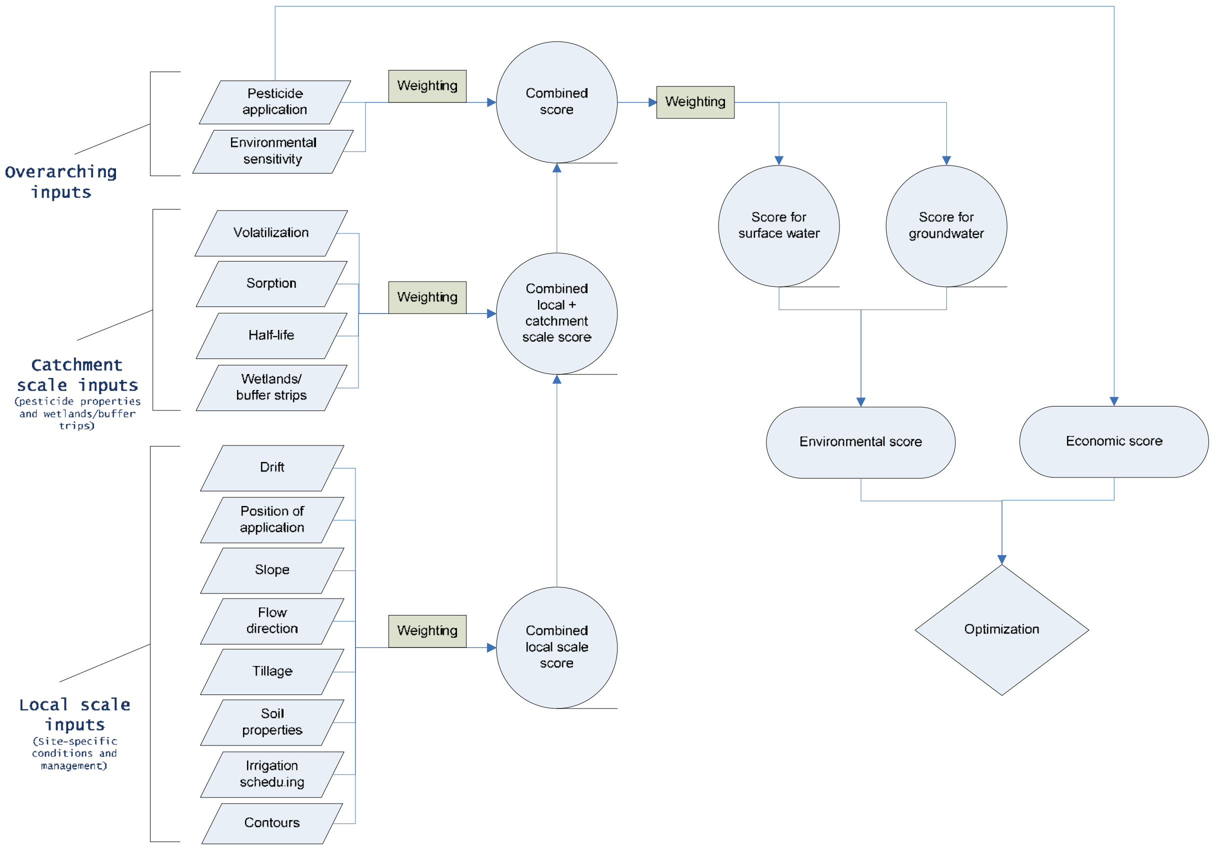


FIGURE 17: Flow diagram of the Pesticide Environmental indeX (PestEX)

4.3.2 Scoring system

The scoring system used for each factor affecting the environmental and economic scores of pesticide usage is summarized in **TABLE 20**. Each factor is represented by a numerical or boolean variable.

Numerical variables are assigned two values based on expert knowledge, the one corresponding to the maximum rating (1) and the other representing the minimum rating (0). Three categories of ratings are therefore defined for each variable, namely low, medium and high (**TABLE 20**). For example, the drift factor is expressed through the variable drift percentage, or the pesticide rate drifting and reaching surface water as a percentage of intended rate of field application (Van der Werf and Zimmer, 1998). The drift rating is applied only to surface water, and it depends on distance to stream, application technique (e.g. aircraft or spraying by tractor), crop structure and cover as well as wind speed. A drift of 0% causes no effects on waters (0), whilst a drift of 1% results in maximum rating (1). The rating of any drift between 0 and 1% is determined using fuzzy logic, based on the concept of partial truth. The concept of partial truth is commonly applied when categories of natural variables, rather than exact values, are used to deal with uncertainties (Zadeh, 1965). In conventional set theory, an element can be either member or non-member of a set. In fuzzy set theory, elements can have a degree of membership, or be partial members of one or more sets. For example, a drift of 0% belongs entirely to the low rating category, whilst a drift of 1% belongs entirely to the high rating category. A drift of 0.75% belongs partially to the high rating category (75%) and partially to the low rating category (25%). This can be described with a function, for this particular example the straight line in **FIGURE 18**. Under natural conditions, changes between categories of variables do not generally occur abruptly, so the straight line representing the degree of membership was smoothed out using a Beta-cumulative distribution function (**FIGURE 18**). A similar approach was used for the other variables and their rating categories in **TABLE 20**.

Amongst the other numerical variables, the impact of the position of application depends on how far the source of pesticide is located from the receiving environment (representing often the distance from the source to a monitoring point). Two variables are therefore used, namely the distance from a water course for surface water and the groundwater depth.

The general slope of land determines the amount of water and contaminants moving from fields through overland flow (along with other factors like land use and management, rainfall intensity, etc.). Steeper slopes will result in higher rating for surface waters, whilst gentler slopes will result in a higher rating for groundwater. For this reason, the rating for groundwater is calculated as 1 – rating for surface water.

Saturated hydraulic conductivity determines infiltration and it can be calculated from texture and bulk density. Typical saturated hydraulic conductivities are 7.128 m d^{-1} for sandy soil and 0.0048 m d^{-1} for clays (Van Genuchten *et al*., 1991). The logarithms of these values are used to assign the rating categories for soil properties, because of the logarithmic nature of saturated hydraulic conductivity. Other soil properties like organic matter content, texture and pH are implied in the organic carbon partition coefficient (variable of the sorption factor). As in the case of slope, ratings for surface- and groundwater are complementary.

Irrigation management and/or rainfall distribution determines overland flow, deep percolation and leaching. Two variables are therefore used for the irrigation scheduling factor. Estimated overland flow is used as variable for rating for surface water. Under poor irrigation management, most rainfall is lost through overland flow. Deep percolation is used as variable for rating for groundwater. Under irrigation with leaching fraction, water is lost through deep percolation and leaching occurs. In the absence of irrigation, rainfall amounts and distribution play a role in overland flow and leaching for this factor.

Pesticide properties like volatilization, sorption and decay play a role in the environmental score. Higher volatilization and sorption rates result in lowered effects on waters. Longer half-life of chemicals results in increased effects on waters. The maximum half-life of parent and daughter products is considered in the rating of decay. A database of properties of more than 2,000 chemicals was compiled by Usher *et al*. (2004) and linked to PestEX. The database also provides links to web sites where extensive information on individual chemicals is available. A link to an additional database of pesticide half-lives, developed in Deliverable 3 (2005/06) of this project, is also available in PestEX. The organic carbon partition coefficient can be found in the database, or it can be calculated as a function of soil organic matter content, texture and pH (Weber *et al*., 2004).

Wetlands and/or buffer strips trap/retard travel time of pesticides. Larger wetlands/buffer strips can trap/retard pesticides applied over larger areas. The ratio of area of pesticide application to area of wetlands/buffer strips is therefore used as a variable to determine the rating of wetlands/buffer strips. The minimum rating produced by either wetlands or buffer strips is considered. PestEX includes a link to literature case studies on wetlands and buffer strips. As in the case of drift, this input factor is not applied to groundwater.

A decrease in pesticide application leads to decreases in yield, but a lower environmental score (trade-off between environmental and economic scores). Optimal pesticide application rates are recommended by suppliers and consultants. Recommended rates of application (or higher) result in a maximum environmental score and a minimum economic score expressed as percent yield reduction.

The effects of pesticides depend on the type and intensity of the source as well as the sensitivity of the receiving environment. The sensitivity of the receiving environment depends on bio-speciation in the receiving water body and water usage. The sensitivity of macroinvertebrate species was rated in the South African River Health Programme SASS 5 from 1 (tolerant to pollution) to 15 (intolerant to pollution) (Dickens and Graham, 2002). In PestEX, the SASS 5 system is translated into a normalized rating for waters (from 0 to 1). A score of 15 (maximum rating) is recommended if the impacted water is used for human consumption.

Boolean variables in PestEX are flow direction, tillage practices and contours. The presence of impermeable layers in the soil tends to impede vertical drainage, resulting in the build-up of shallow temporary water tables and enhanced interflow. This creates conditions for dominant flow direction, either horizontal along slopes or vertical. Practices like conventional tillage, shallow tillage and no tillage are common in South Africa. Tillage practices enhance infiltration and reduce overland flow. Research in the Berg river catchment showed that bare soil generates more overland flow and contaminant transport compared to shallow-tilled soil (De Clercq *et al*., 2010). The establishment of anti-erosion contours retards the movement of pesticides via overland flow, but it may cause more infiltration and leaching. Categorization of boolean variables is opposite for surface water and groundwater. The magnitude of the effects can be adjusted through weighting.

TABLE 20: Rating categorization, ranges of variables and motivation for input factors in PestEX

Input factor	Variable	Ranges	Rating categories	Motivation and comments
Drift	Drift percentage (%)[1]	0	Low	Values of ranges after Van der Werf and Zimmer (1998). This input factor is not applied to groundwater.
		0-1	Medium	
		>1	High	
Position of application	Distance from stream (m) for surface water[1]	>1000	Low	-
		0-1000	Medium	
		Next to stream	High	
	Groundwater depth (m) for groundwater[1]	>30	Low	Categories can be refined based on the nature of the material in the unsaturated zone (Saayman *et al*., 2007).
		5-30	Medium	
		<5	High	
Slope	Slope (%)[1]	<2	Low	Categorization for surface water; complementary score is used for groundwater.
		2-5	Medium	
		>5	High	
Flow direction	Dominant flow[2]	Vertical	Minimum (0)	Categorization for surface

TABLE 20: Rating categorization, ranges of variables and motivation for input factors in PestEX

Input factor	Variable	Ranges	Rating categories	Motivation and comments
		Horizontal	Maximum (1)	water; the opposite is applied for groundwater. The magnitude of the effects can be adjusted through weighting.
Tillage	Tillage practice[2]	Yes	Minimum (0)	Categorization for surface water; the opposite is applied for groundwater. The magnitude of the effects can be adjusted through weighting.
		No	Maximum (1)	
Soil properties	Saturated hydraulic conductivity (m d^{-1}) [1]	>Log7.128	Low	Categorization for surface water; complementary score is used for groundwater. Values of ranges after Van Genuchten *et al*. (1991) for sandy and clay soil.
		Log0.0048-Log7.128	Medium	
		<Log7.128	High	
Irrigation scheduling/rainfall distribution	Overland flow (mm a^{-1}) for surface water[1]	<50	Low	-
		50-550	Medium	
		>550	High	
	Deep percolation (mm a^{-1}) for groundwater[1]	<50	Low	

TABLE 20: Rating categorization, ranges of variables and motivation for input factors in PestEX

Input factor	Variable	Ranges	Rating categories	Motivation and comments
		50-550	Medium	
		>550	High	
Contours	Presence of contours[2]	Yes	Minimum (0)	Categorization for surface water; the opposite is applied for groundwater. The magnitude of the effects can be adjusted through weighting.
		No	Maximum (1)	
Volatilization	Henry Law's constant[1]	>Log 2.65E-4	Low	Values of ranges after Van der Werf and Zimmer (1998). Chemical properties database is available (Usher *et al*., 2004).
		Log 2.65E-6-Log 2.65E-4	Medium	
		<Log 2.65E-6	High	
Sorption	Organic carbon partition coefficient[1]	> Log 634000	Low	Values of ranges are minimum and maximum recorded in the chemical
		Log 0.001-Log 634000	Medium	

TABLE 20: Rating categorization, ranges of variables and motivation for input factors in PestEX

Input factor	Variable	Ranges	Rating categories	Motivation and comments
		<Log 0.001	High	properties database (Usher *et al*., 2004).
Decay	Half-life (d) [1]	0-10	Low	Maximum half-life of parent and daughter products is considered. Chemical properties database (Usher *et al*., 2004) and pesticide half-lives database is available.
		10-100	Medium	
		>100	High	
Wetlands/buffer strips	Ratio of area of application to area of buffer strip[1]	No application	Low	Minimum of rating for wetlands or buffer strip is used. This input factor is not applied to groundwater.
		0-100	Medium	
		>100	High	
	Ratio of area of application to area of wetland[1]	No application	Low	
		0-2500	Medium	
		>2500	High	

TABLE 20: Rating categorization, ranges of variables and motivation for input factors in PestEX

Input factor	Variable	Ranges	Rating categories	Motivation and comments
Pesticide application	Percentage of recommended rate of application (%)[1]	No application	Low	Maximum rating is assigned to application rates equal to or bigger than the recommended rate. The economic rating is complementary to the environmental rating and expressed as percentage yield reduction.
		0-100	Medium	
		>100	High	
Environmental sensitivity	Score from SASS 5[1]	1	Low	The sensitivity of macroinvertebrate species was rated in the South African River Health Programme SASS 5 from 1 (tolerant to pollution) to 15 (intolerant to pollution) (Dickens and Graham, 2002).
		1-15	Medium	
		15	High	

[1] Numerical variable

[2] Boolean variable

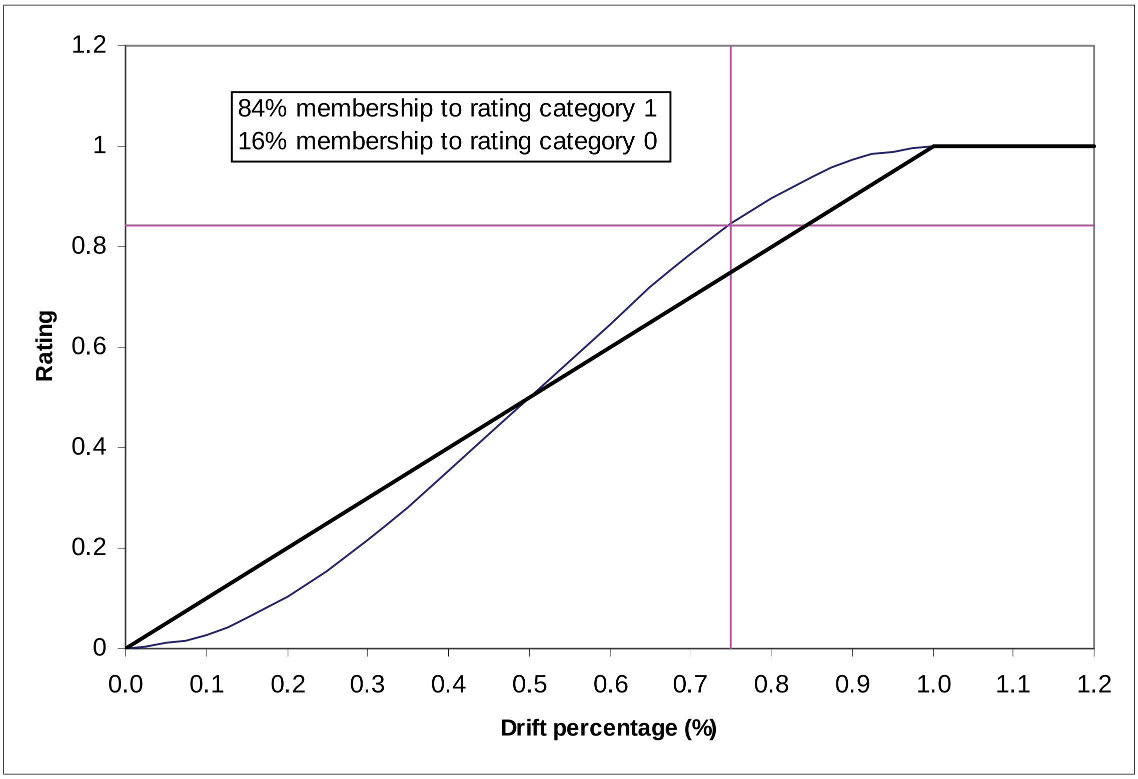


FIGURE 18: Example of fuzzy logic applied to rating for surface water as a function of percentage drift of pesticide at application. The curve is a Beta-cumulative distribution function used to smooth out the straight line of the fuzzy function

The rating for each factor is multiplied by a weighting fraction (from 0 to 1) in order to produce a score from 0 to 1. The weighting is meant to assign a relative importance of one factor compared to the others, given the environmental conditions, context and objectives of the calculation. The weighting is therefore a site-specific and subjective choice of the user. However, some recommendations can be made on selecting the weighting for each factor. For example, windy areas or windy conditions during pesticide application may require a higher weighting for drift. If the position of application is upstream of an area where there are no water users, the weighting for this factor can be decreased. The weighting for slope can be chosen depending on concave (higher weighting) or convex (lower weighting) shapes of the terrain. Weighting for flow direction (boolean variable) is useful in the presence of semi-impervious soil layers. The magnitude of the effects of tillage can be adjusted through weighting to account for mulching, conventional, shallow or other types of tillage. Soil properties (saturated hydraulic conductivity) require a higher weighting for groundwater in the presence of preferential flow paths. Irrigation scheduling/rainfall distribution can be weighted based on irrigation/rainfall intensity, length of dry periods between wetting, etc. Different shapes and sizes of contours result in different retardation times and attenuation of pesticides and this can be adjusted through weighting. Pesticide properties can be weighted depending on the importance of environmental compartments. For example, high volatilization of a chemical may be favourable in terms of surface- and groundwater quality, but less favourable if air quality needs to be preserved. Sorption can be increased with the addition of manure, mulching or use of other highly sorbing material; higher weighting for sorption is then required. Half-life of chemicals tends to be longer or shorter depending on moisture, temperature, pH, exposure to light etc. The positioning of wetlands/buffer strips in relation to source and receiving environment can affect pesticide mobility, and this can be adjusted through weighting. If the size of the application area is large, the weighting of the pesticide application factor can be increased. If the primary objective is to assess the effects on wildlife, the environmental sensitivity factor can be assigned a higher weighting. More examples can, of course, be made on the need to adjust the weighting for each factor.

After multiplying the rating by the weighting, if the score of all factors is unfavourable to the environment, the total environmental score is 1 (maximum score). This value may correspond to a threshold concentration for the most sensitive organism using the receiving water body. Threshold concentrations can be found in databases linked to PestEX, and they are related to the toxicity of a specific chemical (some pesticides are more or less toxic than others) to a specific aquatic organism. Higher levels than these threshold concentrations are unacceptable, so an environmental score of 1 may correspond to the cost of treating/replacing water, cost of rehabilitation, cost of human health deterioration, cost of replacing the cropping system with pest tolerant crops and similar. Any environmental score lower than 1 can therefore be translated into an environmental cost. A total environmental score of 1 could also be related to maximum allowable concentration of a chemical in water. Databases of maximum allowable concentrations can be accessed through the PestEX links.

The economic score is expressed as percent yield reduction. This can be translated into pollution abatement cost, or the cost to society of pollution reduction, if the economic loss per unit yield reduction is known. Abatement may involve a reduction in the activity that produces the emissions and/or the application of some emission-reducing measures. The total cost of pesticide application can then be expressed as the sum of the environmental and abatement costs.

4.3.3 Interface

PestEX is an Excel-based, interactive programme. A snapshot of the Main Menu of the programme is shown in **FIGURE 19**. One worksheet is dedicated to the input and calculation of each factor and it can be accessed by clicking on the relevant command button in the Main Menu. Any factor can be disabled by clicking on the tick-box (**FIGURE 19**). Caution should, however, be exercised in disabling some factors, because this may cause disproportionate weighting of factors that are not disabled. The input cells are clearly marked, for example the weighting cells in **FIGURE 19**. The programme makes extensive use of pop-up comments to facilitate the user in operating the programme as well as selecting the inputs. Links to databases, reviews and references are available within the programme. The graphs are interactive and they automatically show input data and ratings, as in the example in **FIGURE 18**.

Nearly-linear relationships described with fuzzy logic could be substituted with non-linear functions, should these be available. For example, the relationship between yield reduction and pesticide application cannot always be approximated with a straight line. Similarly, abatement costs increase as more pollution is abated. In practice, a certain level of pollution is permitted corresponding to the water quality standard. This reduces pollution to acceptable levels and keeps pollution abatement costs also within acceptable limits. In addition, farmers have other options to incorporate different means of abating pollution besides reducing pesticide usage, for example changing production practices, selecting pest tolerant crops, etc. This would also shift environmental and abatement cost functions from linearity.

It should be borne in mind that the PestEx index is not meant to give a measure of local or catchment processes. However, some of the factors considered may be more relevant to the local scale and others to the catchment scale. The relevant factors for a particular application can then be selected by checking the tick-box in the Main Menu of PestEx (**FIGURE 19**).

FIGURE 19: Snapshot of the Main Menu of PestEX

4.4 EXAMPLE OF APPLICATION

An example of application of PestEX was carried out using data from the Goedertrou catchment described in Chapter 3 of this report. The purpose of this application was to compare and interpret the mobility of two pesticides applied in 2005 on a wheat crop in relation to water collecting in the stock-watering dam and groundwater. The pesticides, applied according to the recommended rates, were Folicur (active ingredient tebuconazole) and Methomex (active ingredient methomyl). The input data used in the programme for the comparative analysis of pesticide mobility are summarized in **TABLE 21**.

A drift percentage of 2% was entered corresponding to maximum rating due to pesticide application by aircraft. A minimal distance from stream was entered because the area of application surrounds the dam. The groundwater depth at the site varies between about 2 and 20 m (De Clercq *et al.*, 2010). A groundwater depth of 2 m, occurring at the outlet of the catchment, was used. The average slope in the catchment is about 10% corresponding to maximum rating for surface water and minimum rating for groundwater. Whilst water in the dam originated both from overland flow and throughflow, vertical conductance is constrained by the presence of the impervious Malmesbury shale layer (dominant flow in the soil is horizontal along the slope). Land was shallow-cultivated producing a minimum rating for surface water and a maximum rating for groundwater. A very low saturated hydraulic conductivity of 0.001 m d^{-1} was entered due to the geological nature and compaction of the soil, and based on field measurements (De Clercq *et al*., 2010). This corresponded to maximum rating for surface water and minimum rating for groundwater. Overland flow was between 4% and 19% of annual rainfall (330 mm), based on measurements done at the runoff plots (Chapter 3 of this report). An average of 12% corresponds to about 40 mm of overland flow. It was assumed that minimal deep percolation occurs under dryland conditions, given the presence of an impermeable layer in the soil and depth of groundwater.

The presence of contours resulted in a maximum rating for groundwater and a minimum rating for surface water for this factor. Henry's Law constant and the organic carbon partition coefficient for methomyl were obtained from the PestEX database of chemical properties (Usher *et al*., 2004). Minimum volatilization and sorption were assumed for tebuconazole as a precaution, because its properties are not available in databases. Half-lives were determined from measurements of pesticide concentrations in dam water (**FIGURE 11** and **FIGURE 12**). No wetlands/buffer strips were present, so this factor was disabled. Pesticide application rate was equal to the recommended rate. No sensitive organisms are present in the dam water, so the rating for environmental sensitivity was disabled.

The output scores produced by PestEX are summarized in **TABLE 22** for all factors. All weightings were equal to 1 in this example. Given all factors and conditions were the same in the catchment, the output changed depending only on pesticide properties.

TABLE 21: Data inputs used in PestEX for the comparative analysis of mobility of Methomyl and Tebuconazole at Goedertrou (Western Cape)

Variable	Pesticide	
	Methomyl	**Tebuconazole**
Drift percentage (%)	2	2
Distance from stream (m) for surface water	0	0
Groundwater depth (m) for groundwater	2	2
Slope (%)	10	10
Dominant flow	Horizontal	Horizontal
Tillage practice	Yes	Yes
Saturated hydraulic conductivity (m d^{-1})	0.001	0.001
Overland flow (mm a^{-1}) for surface water	40	40
Deep percolation (mm a^{-1}) for groundwater	0	0
Presence of contours	Yes	Yes
Henry Law's constant	8.05E-10	0 (not available)
Organic carbon partition coefficient	0.01201	0 (not available)
Half-life (d)	4.4	23.6
Ratio of area of application to area of buffer strip	-	-
Ratio of area of application to area of wetland	-	-
Percentage of recommended rate of application (%)	100	100
Score from SASS 5	-	-

TABLE 22: Scores produced by PestEX in the comparative analysis of pesticide mobility				
Factors	**Methomyl**		**Tebuconazole**	
	Score for surface water	**Score for groundwater**	**Score for surface water**	**Score for groundwater**
Drift	1	-	1	-
Position of application	1	1	1	1
Slope	1	0	1	0
Flow direction	1	0	1	0
Tillage	0	1	0	1
Soil properties	1	0	1	0
Irrigation scheduling	0	0	0	0
Contours	0	1	0	1
Combined local scale score	**0.63**	**0.43**	**0.63**	**0.43**
Volatilization	1	1	1	1
Sorption	0.96	0.96	1	1
Half-life	0	0	0.06	0.06
Wetlands	-	-	-	-
Combined local scale + catchment scale score	**0.65**	**0.60**	**0.67**	**0.62**
Pesticide application	1	1	1	1
Environmental sensitivity	-	-	-	-
Combined score	**0.83**	**0.80**	**0.84**	**0.81**
Environmental score	**0.82**		**0.83**	

The model predicted moderate mobilities for these two pesticides in relation to the receiving water bodies, mainly due to the pesticides' properties (low volatilization and sorption). A slightly higher score was observed for tebuconazole compared to methomyl due to the different sorption coefficients and half-lives used in the calculation, consistently with the measurements presented in Chapter 3 (**FIGURE 11** and **FIGURE 12**). The score for surface water was greater compared to groundwater for both pesticides. The environmental scores of the pesticides were possibly exaggerated, given the area of the catchment was very small and no sensitive organisms are present in the small dam. This can be adjusted by changing the weighting factors.

4.5 CONCLUSIONS

A pesticide environmental mobility index was developed that accounts for the main factors affecting the contamination of surface- and groundwater, including the effects of mitigation/management measures. It should be noted that PestEX gives a normalized environmental index based on several input variables. Absolute values of contamination will depend on the total amounts of pesticide applied and the dilution capacity of the receiving water body. These can be obtained through measurements and/or predicted with transfer functions and process models.

Similar indicators of pesticide environmental impact have been developed worldwide and they are applied for different purposes. The advantages of PestEX compared to other indicators are seen to be the multi-level approach in the combination of factors (local scale, catchment scale and overarching level), the inclusion of mitigation/management measures and the possibility of linkages to economic models. Additional factors can be easily incorporated in the programme, for example solubility of chemicals or effects on air quality, providing some information is available on the behaviour of chemicals in the environment and depending on the specific objectives to be achieved.

The tool developed here serves mainly the purpose of this project. However, it is envisaged that potential users could also be the scientific community, farmers, pesticide consultants and the regulatory authority. Many applications are possible, but the main ones envisaged are comparative analyses of mobility and exposure potential (between two or more pesticides or factors), and sensitivity analyses (effects of changing one or a combination of factors). In particular, applications can be the comparison of environmental and pollution abatement costs of different chemicals for regulatory or marketing purposes, sensitivity analyses to assess the effects of different mitigation/management measures (e.g. size of wetlands to be constructed), the minimization of costs by changing mitigation/management practices, etc. For all purposes, a calibration and validation of the model is recommended by adjusting the weighting of each factor, and comparing the output to measured data. The sensitivity of PestEX should be calibrated and tested at different sites and for different pesticides.

The PestEX program written in Excel and the accompanying database files can be requested from the primary author, free of charge.

5 GENERAL CONCLUSIONS

The following priority processes for modelling pesticide NPS pollution were identified: overland flow and pesticide transport; vertical water and pesticide fluxes (including drainage and leaching); preferential flow (macropore or by-pass flow and funneling); throughflow (subsurface lateral water and pesticide fluxes); plant uptake of water and pesticides; processes linked to specific pesticide properties (volatilization, sorption and degradation). Several models were identified that are capable to simulate pesticide priority processes. These are FIRST, GENEEC, HYDRUS-2D, PELMO, PESTAN, PRZM, SWAP, SWAT and VS2DT.

Extensive environmental monitoring in a catchment in the Western Cape included all components of the system (atmospheric, soil and vadose zone, surface water and groundwater). These monitored data, along with comprehensive baseline information, generated a body of knowledge on the mechanisms of NPS fluxes that can inform field-scale modelling. The identification of priority processes and the knowledge gained from experimental work resulted in the compilation of an expert system in the format of a Pesticide Environmental indeX (PestEX) that assesses the mobility of pesticides and their potential for landing in a water resource.

In recent years, computer modelling, database handling and remote sensing capabilities increased to the point that integration of detailed information at local and field-scale into large catchment scale has now become realistic. Intensive monitoring at local/field-scale of water and nutrient fluxes can therefore serve the purpose of informing processes at regional scale. In order to achieve this, it is imperative that databases of detailed information be compiled in order to facilitate the set-up and parametrization of distributed hydrological models operating according to the principle of hydrological response units (e.g. ACRU). The database population and handling is crucial. The predictive capabilities of existing models/methods and those developed during the course of this project can be used to transfer knowledge to water managers. In particular, scenarios of land use and management can be simulated to recommend the most environmentally and economically acceptable practices. It is, however, essential that these scenarios be developed through a participatory process with stakeholders (scientists and modellers, farmers, Government officials and others) in order to facilitate technology transfer.

6 RECOMMENDATIONS

Three main recommendations emanated from the research. Firstly, there is a need to strengthen the monitoring network of pesticides nation-wide. Lack of good data sets for modelling pesticides at different scales and costs of measurements were expected shortcomings. Pesticides are chemicals with specific properties and new products are continuously being released on the market. Many of these chemical species represent a hazard to human health and the environment. It is known that many of the emerging contaminants, including some pesticide species, are endocrine disruptors and represent ecotoxicological hazards. Research on endocrine disruptors and ecotoxicology (effects of specific chemicals on specific organisms) needs to be strengthened. It is recommended that a target spectrum of pesticides be detected at key locations in catchments in order to identify priority species to be monitored.

Secondly, the effects of specific pesticides, their residuals and daughter products on soil fertility and food production are often not known. An anecdotal occurrence is worth mentioning. During the field campaigns for data collection in the Goedertrou catchment in 2005, soil samples were collected for laboratory analyses of pesticides. The laboratory at the PPRI at Roodeplaat (ARC) was not in the position to determine pesticides in those samples due to the presence of other organic compounds, possibly hydrocarbons, masking the pesticide signals in the spectral analysis (E. van De Walt, PPRI, Roodeplaat, personal communication). The suspected source of hydrocarbons could be machinery used on land. This occurrence triggers the question: What are all the unknown factors (e.g. residual pesticides, hydrocarbons etc.) that could affect food production and ultimately impact on sustainable use of soil and water resources? In that sense, it would be beneficial to initiate a soil quality research programme in order to define and quantify soil quality indicators and thresholds for different environmental conditions, as well as to describe and quantify interactions of soil physical, pedogenetical, chemical and biological processes, as these are likely to directly or indirectly affect water resources.

Thirdly, alternative methods of pest control like, for example, integrated pest management need to be investigated further.

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