NITRATE LEACHING FROM SOILS CLEARED OF ALIEN VEGETATION

REPORT TO THE

WATER RESEARCH COMMISSION

by

NZ Jovanovic¹, A Hon¹, S Israel¹, D Le Maitre¹, F Rusinga^{1*}, L Soltau, G Tredoux¹, MV Fey², A Rozanov² and N van der Merwe²

¹CSIR Natural Resources and the Environment, Stellenbosch ²Department of Soil Science, University of Stellenbosch ^{*}Currently Ninham Shand, Cape Town

WRC Report No. K5/1696 ISBN

MARCH 2008

page i

Acknowledgements

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

- Dr Innocent Msibi, Water Research Commission (Chairman in 2006)
- Dr Shafick Adams, Water Research Commission (Chairman from 2007 to 2008)
- Mr Ahmed Khan, Department of Water Affairs and Forestry, Working for Water Programme
- Dr Felix Dakora, Cape Peninsula University of Technology
- Dr Samson Chimpango, University of Cape Town
- Prof Dave Richardson, University of Stellenbosch
- Ms Christine Colvin, The Council for Scientific and Industrial Research

The authors also wish to thank the following individuals and organizations for their contributions to this project:

- Special thanks to Mr Ahmed Khan from the Working for Water Programme of the Department of Water Affairs and Forestry for funding the soil water sensors and Leveloggers.
- Ms Louise de Roubaix and Cape Nature Conservation for making the experimental site at Riverlands Nature Reserve available.
- Mr Peter Duckitt, owner of Burger Post farm, for making the experimental site available.
- Mr John Witbooi (Cape Nature Consrvation), Officer at Riverlands Nature Reserve, for supplying manual readings of rainmeters throughout the season.
- Prof Simon Lorentz (University of Kwa-Zulu Natal) who provided a licensed copy of the HYDRUS-2D model.
- Mr Peter Meyer and Mr Brian Lawrence, Technical Officers, as well as Mr Abdulkhader Ali and Ibrahim Harun, Hons students at the Department of Earth Sciences, University of the Western Cape, for their assistance with field work and data processing.
- Dr John Bean and Mr Ross Campbell (previously CSIR NRE) for leading the project at its early stages.
- Ms Chairman Smit and Mr Jan du Plessis (Water Research Commission) for the coordination of the project.
- The South African Weather Services for supplying weather data for Malmesbury.

Contributing organizations to the execution of this project were:

- The Council for Scientific and Industrial Research, Natural Resources and Environment
- Department of Soil Science, University of Stellenbosch
- Department of Earth Sciences, University of the Western Cape

Contents

Contentsiii
List of Files enclosed on CD
List of Figures
List of Tables
Executive Summaryix
1.INTRODUCTION 1
1 1Problem statement
1 2Project objectives
1.3Approach
1.0.1010001
2.LITERATURE REVIEW
2.1Nitrogen in catchments and its impact on water quality
2.2The soil nitrogen cycle
2.2.1 Nitrogen cycling within the plant-microorganism-soil system
2.2.21mpacts of forest clearing on the N-cycle: Case studies
2.2.3 Mechanisms of N cycling following forest clearing
2.3Review of nitrogen models
3.FIELD EXPERIMENT AND LABORATORY TESTING
3.1.1 Site selection
3.1.2 Borehole siting
3.1.2Borehole siting
3.1.2Borehole siting
3.1.2Borehole siting
3.1.2Borehole siting. 11 3.1.3Experimental treatments. 15 3.1.4V egetation and site description. 16 3.1.5Material and methods 18 3.1.6Experimental results. 19
3.1.2Borehole sitting
3.1.2Borehole stitug. 11 3.1.3Experimental treatments. 15 3.1.3Experimental treatments. 15 3.1.4V egetation and site description. 16 3.1.5Material and methods 18 3.1.6Experimental results. 19 3.2Unsaturated zone measurements. 25 3.2.1Material and methods. 25 3.2.1Material and methods. 25
3.1.2Borehole siting
3.1.2Borehole siting. 11 3.1.3Experimental treatments. 15 3.1.4V egetation and site description. 16 3.1.5Material and methods. 18 3.1.6Experimental results. 19 3.2Unsaturated zone measurements. 25 3.2.1Material and methods. 25 3.2.2Experimental results. 26 3.3Soil chemical analyses. 38 3.4 Material and methods. 38
3.1.2Borehole stitug. 11 3.1.3Experimental treatments. 15 3.1.3Experimental treatments. 15 3.1.4V egetation and site description. 16 3.1.5Material and methods 18 3.1.6Experimental results. 19 3.2Unsaturated zone measurements. 25 3.2.1Material and methods. 25 3.2.2Experimental results. 26 3.3Soil chemical analyses. 38 3.3.1Material and methods. 38
3.1.2Borehole stitug. 11 3.1.3Experimental treatments. 15 3.1.4Vegetation and site description. 16 3.1.5Material and methods 18 3.1.6Experimental results. 19 3.2Unsaturated zone measurements. 25 3.2.1Material and methods. 25 3.2.2Experimental results. 26 3.3Soil chemical analyses. 38 3.3.1Material and methods. 38 3.3.2Laboratory results. 38
3.1.2Borehole siting
3.1.2Borehole siting
3.1.2Borebole siting
5.1.2 Borebole string
3.1.2 Borebole sting
3.1.2 Borebole siting. 11 3.1.3 Experimental treatments. 15 3.1.4 Vegetation and site description. 16 3.1.5 Material and methods 18 3.1.6 Experimental results. 19 3.2 Unsaturated zone measurements. 25 3.2.1 Material and methods. 25 3.2.2 Experimental results. 26 3.3Soil chemical analyses. 38 3.3.1 Material and methods. 38 3.3.2 Laboratory results. 38 3.3.2 Laboratory results. 38 4.1 Nitrogen transport and transformation processes in the unsaturated zone. 45 4.1.1 Model description. 45 4.1.3 Model simulations. 47
3.1.2 Borebole siting. 11 3.1.3 Experimental treatments. 15 3.1.4 Vegetation and site description. 16 3.1.4 Vegetation and site description. 16 3.1.5 Material and methods 18 3.1.6 Experimental results. 19 3.2 Unsaturated zone measurements. 25 3.2.1 Material and methods. 25 3.2.2 Experimental results. 26 3.3Soil chemical analyses. 38 3.3.1 Material and methods. 38 3.3.1 Material and methods. 38 3.3.2 Laboratory results. 38 4.1 Nitrogen transport and transformation processes in the unsaturated zone. 45 4.1.1 Model description. 45 4.1.3 Model simulations. 47 4.2 Nitrogen transport and transformation processes in the saturated zone. 61
3.1.2Borebole sting

5.CONCLUSIONS	70
5.1Outcomes of the research 5.2Recommendations for further research	70 71
6.REFERENCES	72

List of Files enclosed on CD

Folder	File name	Description		
	Deliverable 1	Literature Review 1		
	Deliverable 5	Literature Review 2		
	Deliverable 4	Progress report		
Deliverables	Deliverables 2, 3 and 6	Sampling and laboratory testing (experimental set-up and saturated zone measurements, unsaturated zone measurements, top soil measurements)		
	Deliverables 7 and 8	Preliminary report and reactive transport model (nitrogen transport and transformation processes in the unsaturated zone, spatial distribution of nitrogen concentration in groundwater)		
	Final Report K5 1696	Final report		
Workshop	* *	Slide presentations at the technology transfer workshop		
Paper draft	* *	Draft paper		
	Rainfall.xls	Rainfall (manual readings at Riverlands Nature Reserve)		
	Soil chemistry data.xls	Raw soil chemistry data		
	EM3193.xls	Hourly soil water contents, temperatures and electrical conductivities in the Uncleared treatment at Riverlands		
	EM3194.xls	Hourly soil water contents, temperatures and electrical conductivities in the Fynbos treatment at Riverlands		
Data	EM3195.xls	Hourly soil water contents, temperatures and electrical conductivities in the Cleared treatment at Riverlands		
	Soil samples.xls	Soil water retention and root density distribution data		
	Soil textural analysis.xls	Soil textural analysis		
	Topography survey.doc	Ground level survey with RTK GPS		
	Coordinates of treatments.doc	Geographic coordinates of the areas of the three treatments		
Data\Groundw	ater chemistry*.*	Raw and processed groundwater chemical analyses		
Data\Acculink	* *	Canopy cover raw data		
Data\Groundwater level\Manual*.*		Manually collected groundwater level raw data		
Data\Groundwater Groundwater level raw data collected with Leveloggers level\Leveloggers*.*		Groundwater level raw data collected with Leveloggers		
Data\Borehole	Data\Borehole logs*.* Borehole logs			
Data\Slug tests*.* Pumping tests raw data		Pumping tests raw data		
Data\Weather	Data\Weather data*.* Weather data for the Malmesbury station obtained from SAWS			

List of Figures

Figure 1	Interactions of N processes in soils (adapted from Rosswall, 1976).	5
Figure 2	Hypothetical effects of clear-cutting on the internal N in deciduous forest (Vitousek, 1981).	9
Figure 3	Location of the Riverlands Nature Reserve on the Western Cape map of conservation areas. The white square in Google Earth indicates the experimental area.	12
Figure 4	Deep resistivity survey profile next to the existing 120 m deep borehole.	12
Figure 5	Map of experimental site (the coordinates are represented in the WGS 1984 reference positioning system, the projection is Transverse Mercator, the central meridian is 19.0, the linear units are expressed in m).	14
Figure 6	A view of the Fynbos treatment showing the restio dominated community of the lower-lying areas in the foreground and the taller shrubs of the higher- lying community in the background (top left); the Cleared treatment with the sparse cover and the Willdenowia in the left foreground (bottom left); the interior of the Acacia clump of the Uncleared treatment showing the high litter cover from a dead tree that was killed by the bio-control (right).	16
Figure 7	Groundwater levels measured manually at all boreholes in Riverlands during 2007.	21
Figure 8	Electrical conductivity (EC) in groundwater measured during 2007.	23
Figure 9	Nitrogen in nitrates and nitrites measured in groundwater boreholes at Riverlands during 2007.	23
Figure 10	Soil water release curves for soil samples collected at different soil depths at Riverlands.	29
Figure 11	Root density distribution in the three treatments at Riverlands.	30
Figure 12	Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Fynbos treatment at Riverlands.	32
Figure 13	Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Uncleared treatment at Riverlands.	32
Figure 14	Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Cleared treatment at Riverlands.	33
Figure 15	Rainfall data measured with manual rainmeters from May to December 2007 at Riverlands.	33
Figure 16	Soil temperatures measured with Echo-sensors at different soil depths and positions in the three treatments at Riverlands.	37
Figure 17	Concentrations of N in NOx in the soil solution at different depths in the soil profile of the Fynbos, Uncleared and Cleared treatments. The X-axis represents days after the beginning of the model simulation as the polynomial was used to calculate the input into HYDRUS-2D.	40
Figure 18	Descriptive statistical analysis of groundwater and soil nitrogen data (units are in mg L ⁻¹), showing maximum, minimum, 1 st and 3 rd quartiles, median and average (cross) values.	41
Figure 19	Flow diagram of the modelling exercise.	42
Figure 20	Simulated volumetric soil water contents in the Fynbos treatment during 2007. The observation nodes are: N1 $-$ 150 cm; N2 $-$ 5 cm; N3 $-$ 40 cm; N4 $-$ 80 cm.	48
Figure 21	Simulated volumetric soil water contents in the Uncleared treatment during 2007. The observation nodes are: N1 $-$ 150 cm; N2 $-$ 5 cm; N3 $-$ 40 cm; N4 $-$ 80 cm.	49

Figure 22	Simulated volumetric soil water contents in the Cleared treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.	49
Figure 23	Simulated NO_3^- concentrations in the soil solution in the Fynbos treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.	50
Figure 24	Simulated NO_3^- concentrations in the soil solution in the Uncleared treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.	50
Figure 25	Simulated NO_3^- concentrations in the soil solution in the Cleared treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.	51
Figure 26	Simulated cumulative water fluxes at the atmospheric boundary (top graph), potential evapotranspiration (middle graph) and actual evapotranspiration (bottom graph) of the Fynbos treatment.	53
Figure 27	Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Fynbos treatment.	54
Figure 28	Simulated cumulative potential evapotranspiration (top graph) and actual evapotranspiration (bottom graph) in the Uncleared treatment.	55
Figure 29	Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Uncleared treatment.	56
Figure 30	Simulated cumulative water fluxes at the atmospheric boundary (top graph), potential evapotranspiration (middle graph) and actual evapotranspiration (bottom graph) in the Cleared treatment.	57
Figure 31	Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Cleared treatment.	58
Figure 32	Spatial distribution of head equipotentials (water table elevations) in m calculated with Visual MODFLOW.	63
Figure 33	Spatial distribution of net recharge (recharge minus evapotranspration) in mm calculated with Visual MODFLOW.	64
Figure 34	Spatial distribution of N concentration in groundwater in mg L ⁻¹ calculated with Visual MODFLOW.	65
Figure 35	Spatial distribution of N concentration in groundwater in mg L ⁻¹ with saturated hydraulic conductivity equal to 0.000133 m s ⁻¹ (11.46 m d ⁻¹) calculated with Visual MODFLOW.	66
Figure 36	Spatial distribution of N concentration in groundwater in mg L^{-1} with initial N concentration in groundwater equal to 0.75 mg L^{-1} and recharge concentration equal to 41 mg L^{-1} in the Cleared treatment (same as for Fynbos treatment).	67

List of Tables

Table 1	Summary of processes and main factors involved in nitrogen cycling within the plant-microorganism-soil system.	5
Table 2	Detail of drilled and hand-augered monitoring points.	15
Table 3	Slug test analysis results.	20
Table 4	Common hydraulic conductivity for medium and fine sand.	20
Table 5	Correlation matrix (Pearson) for groundwater chemistry analyses.	24
Table 6	Factor loading on groundwater chemistry analyses.	24
Table 7	Description of predominant soil profile at Riverlands.	27
Table 8	Depth, colour and textural analyses of soil samples collected in three treatments at Riverlands.	28
Table 9	Bulk density and porosity of soil samples collected in the treatments at Riverlands.	29
Table 10	Rainfall measured with rainmeters under vegetation canopies and in the clear for each treatment at Riverlands.	36
Table 11	Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Fynbos treatment, volumetric soil water contents and calculated N concentration in the soil solution.	38
Table 12	Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Uncleared treatment, volumetric soil water contents and calculated N concentration in the soil solution.	39
Table 13	Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Cleared treatment, volumetric soil water contents and calculated N concentration in the soil solution.	40
Table 14	Output values obtained with HYDRUS-2D for the period from 15/05/2007 to 31/12/2007 and used in Visual MODFLOW.	60

Executive Summary

Introduction

The Working for Water Programme (WfW) initiated by the Department of Water Affairs and Forestry in October 1996 is aimed at controlling woody invading alien plants to reduce water use and preserve stream flow in South African catchments. Many alien invasive species that are being targeted by WfW are nitrogen-fixing legumes (Fabaceae family). The hypothesis in this study was that clearing invasive alien vegetation might disturb the vegetation-microorganism-soil N cycling system by producing a large episodic input of fresh litter rich in N and by eliminating a large N sink. In addition, changes to local microclimate as well as soil chemistry and physics may result in increased net N mineralization beyond the N requirements of the remaining biota. There is thus a distinct risk that clearing alien vegetation may lead to nitrate contamination of groundwater, with a consequent potential for negative health effects from consumed groundwater, and eutrophication of surface water bodies.

The general aim of this research project was to assess nitrogen reserves in soils under alien vegetation and nitrogen movement in soils, subsoils, groundwater and surface water after clearing. The main objectives were to:

- Quantify N accumulation in soils and subsoils under invasive vegetation, using undisturbed natural vegetated areas as baseline;
- Investigate the spatial distribution of N species (nitrate, ammonia, and organic N), within soil and subsoil profiles and across catchment landscapes, as well as groundand surface water; and
- Determine changes to the physical distribution and chemical speciation of N in catchment landscapes after clearing of alien vegetation and the impact on the quality of water resources.

The approach used in the study included:

- A literature review on the processes and mechanisms of the nitrogen cycle, case studies on the impacts of forest clearing on the N-cycle, as well as models that describe the N-cycle;
- The establishment of a one-year field experiment and laboratory testing aimed at collecting data to answer the research questions and for modelling; and
- Modelling of N leaching and spatial distribution of N concentration in groundwater.

Literature review

Nitrogen in catchments is present in reduced (ammonia NH_3 and ammonium NH_4^+) or oxidized forms (nitrite NO_2^- and nitrate NO_3^-). The main processes involved in the N-cycling were identified as:

- Inputs (gains): Dry and wet deposition; Biological N fixation; and Lightning.
- **Cycling (storage):** Plant organic N (plant uptake); Decomposition/mineralization (ammonification and nitrification) and immobilization (N in microorganisms or litter); and Adsorption/desorption.
- Losses: Denitrification; Ammonia volatilization; Runoff; Leaching; and Removal through harvest.

Case studies reported in the literature indicated that disturbance to the nutrient cycling through clearance of vegetation may manifest itself with increased N losses in some ecosystems and decrease in mineral N in others. Based on the literature review, this research focused on the following factors affecting processes and mechanisms of N-cycling:

- Climate
- Soil physical and chemical properties
- Land use and vegetation
- Time lag of the system in terms of N release and transport
- Temporal and spatial heterogeneity of the catchment
- Availability of different forms of nitrogen

Nitrogen models were screened for their availability/cost, dimensions/scale, processes simulated and main applications. As a result of the literature review on models, HYDRUS-2D satisfied most of the technical requirements for simulating processes in the unsaturated zone, whilst Visual MODFLOW, including MODFLOW and the MT3DMS code, satisfied the requirements for modelling the nitrogen distribution within the saturated zone.

Field experiment and laboratory testing

The experimental site located at the Riverlands Nature Reserve was suggested by WfW and it was selected according to the following criteria:

- It is within the boundaries planned for clearing by WfW;
- It is densely vegetated with homogenous alien vegetation;
- It is close to a weather station with sufficient records;
- It is underlain by a homogenous and isotropic sandy aquifer;
- It is free from human activities; and
- It is adjacent to a natural catchment.

Three experimental plots were delineated based on resistivity measurements, topography and expected groundwater flow direction. Each plot represented a treatment:

- A site invaded by alien species to be cleared (Cleared treatment)
- A site invaded by alien species to be used as control (Uncleared treatment)
- A site with natural vegetation to be used as background (Fynbos treatment)

The following measurements were carried out in each of the three treatments during 2007:

- Aquifer characteristics (elevation, hydraulic conductivity and borehole logs)
- Groundwater level, temperature and quality
- Soil physical and hydraulic properties
- Volumetric soil water content and soil temperature
- Root density distribution
- Canopy cover
- Soil chemical analyses
- Weather

The main results obtained from field experiments and laboratory testing are summarized below:

- The hydraulic conductivity of the aquifer was calculated to be between 0.173 and 0.784 m d⁻¹ based on slug tests.
- Groundwater levels changed in response to mainly vertical recharge events.

- Electrical conductivity (EC) in groundwater was generally below 200 mS m⁻¹ at all borehole sites. Higher EC values, alkalinity and hardness were measured in the presence of a laterite layer.
- Oxidized forms of N (NO₃⁻ and NO₂⁻) were dominant in groundwater. Values of total nitrogen (nitrate plus nitrite) in groundwater of the Cleared and Uncleared treatments were not significantly different (4.40 and 2.72 mg L⁻¹ on average respectively), they were dependent on rainfall and leaching, and significantly higher than those measured in the Fynbos treatment (0.66 mg L⁻¹ on average).
- The texture of the soils is sandy (>98% sand, mainly fine grained), which results in relatively high bulk densities, low porosities and a quick release of water in the wet range of soil moisture.
- Root density measurements indicated that both *Acacia* and fynbos may display phreatophytic behaviour, but more data are required in order to confirm this.
- Generally, soil water content tended to increase over time from the onset of the rainy season until mid-September 2007, it decreased thereafter.
- Generally, soil temperature tended to decrease over time from May to the beginning of August 2007, it increased thereafter. Strong daily oscillations of soil temperature were recorded in shallow soil layers.
- Considerable interception of water by the *Acacia* canopy was measured (18% of total rainfall). This water may have been lost through evaporation or may have reached the soil through stem flow paths.
- Higher concentrations of oxidized N in soils were generally measured in the invaded Uncleared and Cleared treatments compared to the Fynbos treatment due to N fixation associated with *Acacia saligna*. Higher N concentrations were generally measured in the top soil compared to deeper soil layers in all three treatments.
- The pattern of oxidized N concentrations in the soil solution appeared to be sinusoidal depending on the season (higher concentrations during the dry summer due to mineralization of organic matter and lower concentrations during the rainy winter due to dilution and leaching). Peaks of high N concentrations were measured occasionally from August to October 2007, possibly due to dry spells with high temperatures that sped up the mineralization processes. Inorganic N was then leached by rains after these dry spells, possibly through preferential flow paths along plant roots.

Modelling

The step-wise procedure followed in the modelling exercise included:

- 1) Interpretation of soil nitrogen analysis and **development of algorithms** to describe transport and transformation processes of nitrogen in soils to be used as input in HYDRUS-2D.
- 2) **Simulation of nitrogen transport in the unsaturated zone** using HYDRUS-2D. The model was used to simulate actual evapotranspiration, recharge and nitrogen leaching to groundwater to be used as input in MODFLOW.
- 3) Simulation of spatial distribution of nitrogen concentration in groundwater using Visual MODFLOW.

Field data of nitrogen concentrations in the soil solution at 5, 40 and 80 cm soil depth were collected every two weeks during 2007. A polynomial fit was drawn through the measured data points representing N concentrations in the soil solution at 5 cm soil depth. These polynomials were used in the HYDRUS-2D model to represent concentrations at the atmospheric boundary condition, e.g. the source of N salts.

Simulations with HYDRUS-2D were run for the 2007 season for all three treatments of the Riverlands experiment. Measured and simulated data of soil water contents and N concentrations were compared. The model's prediction of soil water contents and N concentrations were generally satisfactory for a relatively long period of simulation.

Once the refinement of the model's inputs was completed and a reasonable simulation of soil water content and N concentrations was obtained, HYDRUS-2D was used to predict cumulative water fluxes (evapotranspiration and recharge) and cumulative solute fluxes at the bottom nodes (N leaching) for the three treatments. The output data obtained with HYDRUS-2D are summarized in the table below. Seasonal rainfall was 454 mm.

	Treatment				
Variable	Fynbos	Uncleare d	Cleared		
Potential evapotranspiration (mm)	1080	1300	85		
Actual evapotranspiration (mm)	770	850	82		
Soil evaporation (mm)	-	-	162		
Recharge (mm)	85	60	210		
Solutes leached (mg cm ⁻²)	0.35	0.61	3.80		
Average recharge concentration (mg L ⁻	41	102	181		

Simulated recharge, evapotranspiration and recharge concentrations were used as input in Visual MODFLOW in order to predict the nitrogen spatial distribution occurring in the shallow sandy aquifer at Riverlands.

Steady-state simulations were run with Visual MODFLOW. The main outputs that were analysed were spatial distribution of groundwater heads in order to determine groundwater flow, net recharge (recharge minus evapotranspiration) and N concentrations in groundwater. The groundwater flow direction was predicted to occur from the North-West to the South-East. Net recharge was > 150 mm in the Cleared treatment, and between -250 and 50 mm in the vegetated treatments, depending mainly on water table depth and topographic effects. Predicted N concentrations in groundwater were about 1.0 mg L⁻¹ in the Fynbos treatment, about 2.0 mg L⁻¹ in the Uncleared treatment, and about 4.0 mg L⁻¹ in the Cleared treatment. These simulated values of N concentrations in groundwater approached the seasonal average values measured in boreholes within each treatment.

Conclusions

The main outcome of the research was that, by clearing alien invasives, a fast release of nitrogen is induced due to high residual N reserves in the rooting zone of invasive legumes, decreased evapotranspiration and increased recharge. However, in the long run, the increased N concentrations in groundwater underlying cleared land will occur only until all the leachable nitrogen has been depleted from the soil. A decrease in N concentration in groundwater can be expected thereafter. Clearing land of alien invasive legumes may therefore have a beneficial effect on reduced groundwater contamination from nitrate, besides reducing water use in catchments. The trend of decrease in N concentration will depend on weather conditions, in particular rainfall being the main leaching agent, soil moisture and temperature being the main factors for mineralization, as well as the speciation in the secondary succession process of re-colonization.

The modelling exercise and the comparison between measurements and simulations gave confidence in the predictive capabilities of the models. Model scenario simulations indicated that, in the long run, N concentrations in groundwater underlying land cleared from alien legumes will decrease because of the absence of N fixation and the depletion of N from the soil. However, it will be beneficial to confirm this through measurements and, in particular, to determine how long it takes for all nitrogen to be leached from the soil. A continuation of field measurements is also recommended to fully describe the seasonal patterns of nitrogen mineralization and leaching. Further research will also be needed in order to measure evapotranspiration of fynbos and *Acacia saligna*, and to investigate the impacts of different practices, like for example burning and pesticide application, on the effectiveness of clearance, resilience of invasives and the environment (groundwater and surface waters). It is likely to be appropriate to expand the scope of this research to include catchments across the country and to develop appropriate methods for managing risks to water resource quality posed by clearing invasive alien vegetation.

1. INTRODUCTION

1.1 Problem statement

It is recognized that invasive alien plants have become a threat to biodiversity and ecosystem services, including water purification, soil generation, waste decomposition and nutrient cycling (Le Maitre et al., 2004). Alien invasives in South Africa are species that are well adapted to climatic conditions, grow fast, they are high water users and they impact on stream flow reduction through incremental water use (additional water use compared to natural vegetation) (Le Maitre et al., 2000). As a result, the Working for Water Programme (WfW) was initiated by the Department of Water Affairs and Forestry in October 1996 with the aim of controlling woody invading plants (DWAF, 1997). Extensive areas of land are currently being cleared under this programme.

The nitrogen-fixing invasive alien plants cause the N-cycling regimes within ecosystems to shift from low to high N-cycling (Yelenik et al., 2004). It is known that changes to ecosystems such as those resulting from clearing vegetation also alter patterns of nutrient cycling in soils (Vitousek and Melillo, 1979). The hypothesis in this study was that clearing invasive alien vegetation might disturb the alien vegetation-microorganism-soil N cycling system by producing a large episodic input of fresh litter rich in N and by eliminating a large N sink (Yelenik et al., 2004). In addition, changes to local microclimate as well as soil chemistry and physics may result in increased net N mineralization beyond the N requirements of the remaining biota (Conrad et al., 1999). Many alien invasive species that are being targeted by WfW are nitrogen-fixing legumes (Fabaceae family). For example, Port Jackson (*Acacia saligna*), Black wattle (*Acacia mearnsii*) and rooikrans (*Acacia cyclops*) are commonly found in Western Cape landscapes. There is thus a distinct risk that clearing alien vegetation may lead to nitrate contamination of groundwater and eutrophication of surface water bodies.

While it is generally accepted that clearing invasive alien vegetation in South Africa will have significant benefits in enhancing runoff from catchments, thus increasing the volumes of water available to people and ecosystems, there have been no studies on the impact on groundwater and surface water quality associated with clearing alien vegetation. The leaching of nitrate from cleared areas into groundwater and surface water is likely, but its true extent is unknown. This study aimed at assessing nitrogen stocks in soils under alien vegetation and nitrogen movement in soils, subsoils, groundwater and surface water after clearing.

1.2 **Project objectives**

The main objectives of this project were to:

- Quantify N accumulation in soils and subsoils under invasive vegetation, using undisturbed natural vegetated areas as baseline;
- Investigate the spatial distribution of N species (nitrate, ammonia, and organic N), within soil and subsoil profiles and across catchment landscapes, as well as ground- and surface water; and
- Determine changes to the physical distribution and chemical speciation of N in catchment landscapes after clearing of alien vegetation and the impact on the quality of water resources.

1.3 Approach

Key scientists were selected representing the following research disciplines: soil chemistry and soil nitrogen cycle (Department of Soil Science, University of Stellenbosch); soil physics, hydrology, hydrogeology and hydrogeochemistry (CSIR, Natural Resources and Environment, Stellenbosch). The Department of Earth Sciences, University of the Western Cape, also participated in the research.

The approach used in this study in order to answer the research question and to meet the specific project objectives included:

- A literature review
- The establishment of a field experiment and laboratory testing
- Modelling

The literature review included i) an overview of the extent of nitrogen in South African catchments and its impacts, ii) the nitrogen cycle, with particular reference to vegetation clearing, in order to identify the dominant processes, and iii) a review of nitrogen models in order to identify the most suitable models to be used in this research.

A one-year field experiment was established in a suitable small catchment in the Western Cape within and adjacent to the Riverlands Nature Reserve, in the vicinity of Malmesbury. Experimental treatments were a site cleared of alien vegetation, a site invaded by alien plants to be used as control, and a nearby site with natural indigenous vegetation to be used as background. The field experiment and laboratory measurements served to collect data related to nitrate leaching to groundwater, interpret them and use them as inputs for modelling.

Modelling consisted of the development of a spatial model for simulating and predicting nitrate leaching and contamination of groundwater due to clearing of alien invasive legumes.

The Chapters of this report are organized accordingly.

2. LITERATURE REVIEW

2.1 Nitrogen in catchments and its impact on water quality

Nitrogen in catchments is present in the following forms:

- Reduced ammonia (NH₃) and ammonium (NH₄⁺)
- Oxidized nitrite (NO₂⁻) and nitrate (NO₃⁻)

The total inorganic nitrogen is given by the sum of NH_3 , NH_4^+ , NO_2^- and NO_3^- . Nitrogen is seldom present in unimpacted surface waters because it is readily taken up by plants. Typical concentrations in unimpacted aerobic surface waters are < 0.5 mg L⁻¹ (Cullis, 2004).

Nitrogen and other nutrients are generally associated with non-point source pollution (Hoffman, 2005). The main sources of nitrogen contamination are natural, agriculture and urban waste. Nitrogen originating from agricultural land is seen as a major source of non-point source pollution. Cullis (2004) supplied first order estimates for nitrogen loads in three South African catchments, namely the Breede, Middle Vaal and Mgeni rivers. The sources can be diffuse and intermittent, originating from storm wash-off and drainage (flushing events), or concentrated, originating from localized activities like for example feedlots, landfills, mining and industrial sites (Pegram and Görgens, 2001). Pegram and Görgens (2001) also indicated that the main non-point source pollution processes in catchments are runoff (overland flow), precipitation, atmospheric deposition, drainage, interflow, seepage, and groundwater flow or river course modification. Some of these processes also represent the pathways of nitrogen transport. The clearing of alien legumes, which is the problem dealt with in this project, could be an additional source of nitrogen contamination in groundwater (Conrad et al., 1999) and its impact needs to be investigated. Clearing of alien legumes could be seen as a point- or non-point source of nitrogen depending on the size and hydrological characteristics of the area.

Contamination of water resources and sustainable use of resources were singled out as the two main concerns in terms of management of the nitrogen cycle in natural systems. Excess of nitrogen may cause a number of unwanted impacts to the environment, in particular:

- Health impact
- Eutrophication problems in surface water

Colvin and Genthe (1999) indicated that methaemoglobinaemia or blue baby syndrome may become a risk for infants when N concentrations are > 10 mg L⁻¹ (45 mg L⁻¹ NO₃⁻) in drinking water, causing miscarriages and death in infants. High nitrogen concentrations may also represent a problem to livestock (Sigma Beta, 2004).

Eutrophication represents a common problem in South African surface waters. Excess nitrogen as a key plant nutrient causes water quality deterioration, increased growth of plants and algae with resulting oxygen depletion, algal toxin production and reduced biodiversity, as well as taste and odour problems. The mobility of nitrate is constrained in soil, sub-soil and aquifers by the microbially-mediated process of denitrification, biological uptake, sorption etc. For nitrate to have any toxic or eutrophing effects, it has to be transported to sensitive consumers or surface water bodies more rapidly than it can be transformed by biochemical processes. The outcome of these competitive processes will control nitrate's impact.

Van Ginkel (2002) reviewed the trophic status of selected South African dams during the period from 1990 to 2000. The results of the investigation indicated that dams draining water from

urban areas were generally the most impacted (hyper-eutrophic). Amongst the different forms of nitrogen, nitrate (NO_3^{-}) is the most mobile in water and it has therefore a better chance to contaminate groundwater. Simonic (1999) compiled a national map of nitrogen concentrations in groundwater using national water quality databases. Tredoux (1993) pointed out some particular regions where elevated levels of nitrate in groundwater were recorded. In particular, groundwaters in the Gordonia District and Prieska are naturally rich in nitrogen, whilst groundwaters in the Springbok Flats and in the Crocodile river catchment are impacted by human activities.

2.2 The soil nitrogen cycle

This research is concerned with the fate of N following clearing invasive alien vegetation. Therefore, this section includes aspects related to (i) the nitrogen cycle within plant-soilmicroorganism systems; (ii) case studies that reported impacts of forest clearing on N-cycling; and (ii) the mechanism of processes that control N inputs, outputs and the internal transformations following plant felling. These relevant aspects are intended to provide a broad understanding of the fate of N following clearing invasive alien vegetation.

2.2.1 Nitrogen cycling within the plant-microorganism-soil system

The plant-microorganism-soil system constitutes the major proportion of the global N cycle, with only minor exchanges taking place within the atmosphere and the hydrosphere. It is estimated that, on a global scale, 95% of the total annual N flows in the terrestrial system occurs between soil and vegetation and only 5% of the total annual N flows is exchanged between the atmosphere and the hydrosphere (Rosswall, 1976). The individual components of the nitrogen cycling in the plant-microorganism-soil system were widely discussed in review publications by Stevenson (1982), Haynes (1986) and Havlin et al. (1999). Table 1 summarizes these components and the main factors involved, whilst their interactions are shown in the flow chart in Figure 1.

The major additions of N to soils are through wet and dry deposition, the action of microorganisms that fixate atmospheric N_2 gas and lightning (Table 1). Human activities such as industrial processes, the use of internal combustion engines, burning of coal and agricultural activities also add N to soils. In many areas, most of the nitrates in precipitation originates from human activities (Haynes, 1986).

Within the plant-soil system, N is one of several macronutrients essential to plant survival and growth. In soils, organic N exists in large quantities (2,000 to more than 4,000 kg ha⁻¹); however, seldom more than 1% is in an available inorganic (mineral) form at one time (Melillo 1981; Gosz, 1981). The availability of N to plants relies heavily on the conversion of organic N to mineral N and on the exchanges of mineral N between plants and soil (i.e. flow of N from soil to plant and back to the soil). The conversion of organic N into different forms of inorganic N (NH₃, NH₄⁺, NO₂⁻ and NO₃⁻) is performed through microbially-mediated processes occurring above and/or within the soil. The processes related to nitrogen cycling within the plant-soil system (storage) include plant uptake, litter production, mineralization (ammonification and nitrification) and immobilization, adsorption and desorption (Table 1).

Losses of nitrogen from the soil may occur in the form of denitrification, ammonia volatilization, runoff, leaching and through harvest (Table 1). Other factors that are not listed in Table 1, but may play a role, are allelopathic substances, limited supply of ammonium under vegetation, nutrient deficiencies of bacteria, trace element toxicity and pesticides.

Table 1: Summary of processes and main factors involved in nitrogen cycling within the plantmicroorganism-soil system.

	Processes	Main factors		
	Dry and wet deposition	N load, precipitation and human activities		
Input (gains)	Biological N fixation	Vegetation and microbial speciation, moisture and aeration, pH and temperature		
,	Lightning	Climatic conditions		
	Plant organic N (plant uptake)	Form of N (preferential uptake of NO ₃ ⁻ by plants), vegetation type and growth stage, soil water content		
Cycling (storage)	Decomposition/mineralization (ammonification and nitrification) and immobilization (N in microorganisms or litter)	Quality of substrate/litter (N content, C:N ratio, lignin content, polyphenol content), environmental factors (moisture and aeration, pH and temperature) and microbia speciation		
	Adsorption/desorption	Soil properties, form of N and soil mineralogy (NH ₄ ⁺ fixation in clay minerals)		
	Denitrification	Moisture and aeration, pH, temperature, redox and O ₂ content, C:N ratio and microbial speciation		
	Ammonia volatilization	Free ammonia near surface, pH, temperature, moisture content and wind speed		
Losses	Runoff	N load, precipitation, land use, sediment transport and sorption capacity		
203363	Leaching	N load, soil physical properties, C:N ratio, type of vegetation (plant uptake), precipitation or irrigation, depth of water table and form of N (NO_3^- is more soluble and less adsorbed in soils than NH_4^+)		
	Removal through harvest	Human activities		



Figure 1: Interactions of N processes in soils (adapted from Rosswall, 1976).

The invasion of plants that support symbiotic N-fixers has a large effect on N-cycling. Invasive species tend to have higher standing crop biomass, net primary production, shoot-root ratio (i.e. greater allocation of C to above-ground tissues) and faster growth rates than the native species that they displace. Litter of invasive species normally decays faster than that of native species. Larger amounts of extractable inorganic N are therefore found under invasive species may cause changes in the timing of nutrient fluxes and the spatial distribution of soil pools, even when no changes occur in absolute quantities of nutrients in the cycle. Soil pools of C, N and water often respond to invading species, but the direction of change cannot be predicted. It is important to note that invading species may result in different impacts depending on the environment (e.g. sandy soil/low temperature vs. clay loam soil/high temperature) (Ehrenfeld, 2003).

Once leached into groundwater, NO_3^- can be transported along with groundwater flow posing a serious threat to the quality of drinking water supplies for both humans and livestock. Denitrification or reduction to NH_4^+ is the primary processes that can remove nitrate from groundwater. The majority of denitrifying bacteria can survive with or without dissolved oxygen, i.e. they are facultative anaerobes (Firestone, 1982). It is when O_2 is in limited supply that facultative anaerobes begin to use nitrate as an electron acceptor. However, ammonia can be converted back to nitrate when aerobic conditions are achieved. The reduction potential of the aquifer depends on the availability and concentration of electron donors, O_2 , organic matter and/or reduced inorganic species. Organic carbon (e.g. CH_4) present in sediments (Smith et al., 1991), organic matter, pyrite, H_2S and Fe(II)-silicates are the most common electron donors during denitrification reactions. The reaction between NO_3^- and Fe^{2+} can be catalysed by Feoxyhydroxide, Cu^{2+} or microbes (Postma et al., 1991).

2.2.2 Impacts of forest clearing on the N-cycle: Case studies

Hubbard Brook Experiment Forestry, New Hampshire, USA

The Hubbard Brook Experiment Forestry consisted of a campaign of intensive monitoring of nutrient dynamics for a number of watersheds, which started two years before felling trees. The fallen trees were left on the watershed and herbicides (Bromacil and 2,4-D) were applied to inhibit growth for a period of three years. After five years, the watersheds were allowed to revegetate naturally (Likens et al., 1978 in Vitousek and Melillo, 1979). Monitoring of nutrient losses from the watershed continued throughout the five years and extended into the revegetation period.

The observed streamwater NO_3^- concentration increased 57 times, with concomitant increase in losses of potassium, aluminium, calcium and magnesium cations from the watershed. Likens et al. (1978, in Vitousek and Melillo, 1979) ascribed the increases in cation losses to increase in nitrate losses since the nitrification process supplies mobile anions and hydrogen ions to the soil solution (Nye and Greenland, 1960 in Vitousek and Melillo, 1979). The NO_3^- losses from the disturbed watershed to streamwater dropped within four years of re-vegetation.

Coweeta Hydrologic Laboratory, North Carolina, USA

Intensive experimental studies of the same order of detail as the Hubbard Brook study were also carried out by the Coweeta Hydrologic Laboratory in North Carolina (Vitousek and Melillo, 1979). The Coweeta studies investigated a wide range of land management strategies, which included the effects of clear-cutting, forest de-vegetation, fertilization, species conversions, grazing and natural disturbances such as insect outbreaks.

The main conclusions from these studies were that NO_3^- concentration in Coweeta stream increased more than those of other ions after forest clear-cutting, the most recently cleared

watersheds had the highest NO_3^- losses, and NO_3^- leaching into streams remained elevated up to twenty years after clear-cutting (Swank and Douglass, 1977 in Vitousek and Melillo, 1979). Subsequent results from a cleared watershed at Coweeta, reported by Swank (1980, in Vitousek and Melillo, 1979), showed that nitrate losses from the watershed increased substantially in the second year after clearance. However, the absolute magnitude of N losses remained low in relation to N inputs and to the amount of N cycling in the system.

H. J. Andrews Experimental Forest, Oregon, USA

The effects of timber harvesting on forest hydrology, nutrient budgets and slope stability were investigated at the H.J. Andrews Experimental Forest. Fredriksen (1971, in Vitousek and Melillo, 1979) reported increases in nitrate and total N losses following forest cutting and slash burning.

Clear-cutting of 67-year-old Douglas fir, France

A more recent study investigated the effects of a clear-cut on the *in situ* N mineralization and N cycle in a 67 year-old Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) plantation in the Beaujolais mountains of France (Jussy et al., 2004). Measurements of *in situ* net mineralization, deposition, uptake and leaching fluxes were performed during five years before and two years after the clear-cut.

Deposition and mineralization of N decreased after harvest, as the under-storey vegetation took over following the clear-cut and this counteracted the drastic decrease in tree N uptake. The net decrease in mineralization of N was probably caused by microbial immobilization, which was favoured by the input of organic matter and the increase in temperature following the clear-cut.

Deforestation in inter-tropical zones of Cote d'Ivoire

The study of Faillat and Rambaud (1999) investigated the source of NO_3^- found in groundwater from wells in inter-tropical zones of Côte d'Ivoire. These wells supply potable water to rural villages. The wells tapped into fractured zone groundwater. The fractured zone is isolated from the overlying weathered rock and thus eliminated the chances of a strong interaction between the upper weathered zone and the lower fractured zone. A total of 230 boreholes were monitored for nitrate, 69 (30%) of which displayed NO_3^- contents greater than or equal to 6.2 mg L⁻¹. There were no important sources of nitrogen in the area of study.

A statistical approach on a regional scale was employed to investigate the cause of nitrogen contamination of groundwater. The inflow of nitrogen into groundwater in fractured rock was attributed to the anthropogenic effect of deforestation.

Acacia spp. At Riverlands Nature Reserve, South Africa

A study by Yelenik et al. (2004) attempted to establish whether invading *Acacia spp.* increased the rates of N cycling and whether clearing of *Acacia spp.* would further increase the net N mineralization rate in soils. In the same study, the probability of weedy grass species growth being enhanced by higher levels of N in soils was also investigated. The field work was performed in the Riverlands Nature Reserve, where acid sand plain lowland fynbos was a broad classification used for the native vegetation. Areas with invasive alien vegetation, pristine areas and areas cleared of alien vegetation were compared.

Nitrogen-fixing alien species (*Acacia* spp.) were able to alter N-cycling regimes through long term (31 years) invasions within the low nutrient fynbos region. However, mineralization rates did not differ between cleared and uncleared areas as optimum temperatures for NH_4^+ and NO_3^- mineralization were not reached and N-mineralization was water-limited across the study site.

The high availability of N in *Acacia*-covered soils leads to growth of weedy grass. This was believed to potentially cause a problem for restoration of native plant species in the area.

2.2.3 Mechanisms of N cycling following forest clearing

Vegetation clearing affects the local microclimate, soil chemistry and physics. It also removes a large N sink and produces large episodic inputs of fresh litter (Vitousek, 1981). Consequently, the N cycling is disturbed. The disturbance to the nutrient cycling manifested itself with increased N losses in some ecosystems (Vitousek and Melillo, 1979; Swank et al., 2001; Yelenik et al., 2004; Fukuzawa et al., 2006) and decrease in mineral N in others (Jussy et al., 2004). Vitousek and Melillo (1979) and Vitousek (1981, 1982) ascribed these variable responses to factors that stimulate N mineralization and factors that inhibit N loss. These factors are biotic (e.g. vegetation and microorganisms) or abiotic (e.g. climate, geology, hydrology). Forest management practices also affect the ecosystem's response to clear-cutting (Vitousek and Melillo, 1979).

Hypotheses to explain why particular systems lose (or do not lose) nutrients following forest clear-cuts have been outlined by a number of authors. Typical examples are Rice and Pancholy (1972), Todd et al. (1975), and Vitousek and Reiners (1975, 1976). The suggested hypotheses explained only partially the patterns of nitrate losses. They did not account for the variability in observed N losses across disparate environments. Vitousek and Melillo (1979) and Vitousek (1981) suggested process-level mechanisms, which systematically examined how clear-cutting affects the processes controlling N inputs, outputs, and internal transformations in forest ecosystems. These mechanisms have formed the basis for interpreting the effects of clear-cutting on the N cycle in most of later studies (e.g. Browaldh, 1997; Yelenik et al., 2004). The mechanisms are outlined below.

Vegetation clearing removes the canopy covering the soil and enhances the input of radiant energy to the ecosystem. Clear-cutting also decreases water uptake by plants (Stone, 1973) causing soil moisture content to increase. The magnitude of fluctuations in soil temperature increases too. The effect of increases in soil temperature and moisture is increased N mineralization (Dominski, 1971; Stone, 1973; Aber et al., 1978) in most catchments. The competition for nutrients between decomposers and root/mycorrhizae complexes is reduced, substantially promoting the activities of the decomposers. The C:N ratio of the pioneer plants and detritus is one of the factors that affects the rate of mineralization. Where pioneer plants with low C:N (high N content and low lignin content) remain abundant on a site after clearing, processes of decomposition and mineralization may remain elevated due to additional litter content at the site (Vitousek, 1981). The mineralized pools of reduced and oxidized N represent an amount that could potentially be lost to stream or groundwater, driven by a number of transforming processes and associated factors (Table 1). The hypothetical effects of clear-cutting on the internal N in deciduous forest is illustrated in Figure 2.

Given the outcomes of the literature review and the objectives of this project, particular attention was dedicated to the following factors related to the soil nitrogen cycling:

- Climate. Given the climatic conditions of the study area (winter rainfall), limited wash-off and/or leaching were expected in summer. Dynamic behaviour of nitrogen was expected during the rainy winter season. Cullis (2004) reported that a "first flush" of contaminants may occur in some catchments at the beginning of the rainy season, followed by additional wash-off and/or leaching during the period of highest rainfall (June and July in the Western Cape). Air and soil temperature, oxygen diffusion, moisture conditions and evapotranspiration also play an important role in the nitrogen balance.
- **Soil physical and chemical properties**. Shallow and sandy soils in the Western Cape could cause fast release of nitrogen into groundwater. Soil chemical properties, such as pH, have limited buffering capacity and effect on nitrogen forms and solubility. The

organic matter content plays an important role in terms of C:N ratios, mineralization and immobilization. Soil mineralogy (trapping of NH_4^+ in clay minerals like vermiculite and illite) and N adsorption are expected to be negligible components of the nitrogen balance in sandy soils.

- Land use and vegetation. Plant species, rooting depth and density influence nitrogen uptake as well as evapotranspiration and the soil water balance. Plant species create positive feedbacks to nutrient cycling, directly through uptake, use and loss of nutrients and indirectly through influences on microbial activity (Hobbie, 1992). Important plant traits and attributes influencing the nitrogen cycle were reported by Ehrenfeld (2003). These include canopy structure, life history, tissue type, physiology, symbionts, vegetative spread, roots, tissue chemistry and photosynthetic pathway. Alien plants with traits and attributes similar to those of native plants result in a small impact, whilst a bigger difference results in a larger impact.
- **Time lag.** A lag in time in the system may occur in terms of leaching and groundwater contamination. In some catchments, N losses were immediate following clear-cutting, whilst longer lag times were encountered in other catchments (Vitousek, 1981).
- **Temporal and spatial heterogeneity**. Variability of soil properties, vegetation (e.g. canopy cover and density) and geohydrological properties control catchment landscape patchiness and may influence the nitrogen balance (Beaujouan et al., 2001).
- Availability of different forms of nitrogen as source. Nitrogen loads generated from litterfall (Stock and Lewis, 1984; Yelenik et al., 2004) coupled with higher tissue N concentrations result in large amounts of N from the above-ground biomass being returned to the soil. Along with microbiological activity, this represents the main source of mineralized nitrogen available for wash-off and leaching.



Figure 2: Hypothetical effects of clear-cutting on the internal N in deciduous forest (Vitousek, 1981).

2.3 Review of nitrogen models

The nitrogen balance is very complex and is influenced to a large extent by microorganisms in the soil, which mediate the reactions taking place in the cycle. Various methods have been developed in order to quantify the various components of the nitrogen balance, where extensive measurements can be time-consuming and difficult. The modern alternative to measurements is represented by simulation models. By simulating nitrogen transport and dynamics, it is possible to track the pathways of nitrogen in the environment.

An extensive literature and web-database search was carried out in order to identify suitable unsaturated and saturated zone models for the purpose of this project. The main sources of information were:

- Register of Ecological Models (REM) of the University of Kassel and the National Centre for Environment and Health, Germany (eco.wiz.uni-kassel.de/ecobas.html)
- U.S. Environmental Protection Agency, USA (<u>www.epa.gov/ada/csmos</u>)
- Scientific Software Group, Sandy, Utah, USA (www.scisoftware.com/environmental_software)
- University of Wageningen, The Netherlands (<u>www.alterra.wur.nl/models</u>)
- Modelling review of Ma and Shaffer (2001)

The screening criteria for selecting suitable models were:

- **1.** Availability/Cost of the model.
- 2. Dimensions/Scale.
- **3. Processes**. The models were screened for their ability to simulate processes that were identified to be relevant to this research (water and nitrogen fluxes, leaching, source/sink terms etc.).
- **4. Main applications**. The main purpose of a specific model was noted. Several models were found to be adaptable/applicable to a wide range of problems.

A complete overview of the screened models is available in Deliverable 5 on the enclosed CD. A brief summary is also given in Deliverable 5 for each screened model, including a brief theoretical description, main applications as well as main input requirements and output data. Both dedicated nitrogen models and models simulating generic contaminants were considered. The models that simulate generic contaminants were screened based on their ability to simulate processes like sorption, zero- or higher order kinetics and multi-phase equilibrium. The models were also screened for their main applications. These ranged from nitrogen transformation to soil water and solute transport, non-point source pollution, nitrate leaching, soil nitrogen cycling, crop response and fertilization management. Forestry and grassland ecosystem models were also considered.

Amongst the models for the unsaturated zone, HYDRUS-2D (Simunek et al., 1994) satisfied most of the technical requirements. Visual MODFLOW, including MODFLOW (McDonald and Harbaugh, 1988) and MT3DMS code, (Zheng and Wang, 1999; Zheng et al., 2001) satisfied the requirements for modelling the nitrogen distribution within the saturated zone. A description of these models can be found in Chapter 4 of this report.

3. FIELD EXPERIMENT AND LABORATORY TESTING

This Chapter deals with the experimental set-up, field measurements and laboratory analyses carried out in order to investigate the impact of clearing alien vegetation on groundwater. The Chapter includes measurements related to the saturated zone, unsaturated zone and soil chemistry.

3.1 Experimental set-up and saturated zone measurements

3.1.1 Site selection

A meeting was held between representatives of CSIR and the WfW Programme of the Department of Water Affairs and Forestry (DWAF) on 10 August 2006 to:

- Inform WfW of the project objectives;
- Get assistance with site selection; and
- Solicit assistance with vegetation clearing.

The criteria for site selection were discussed and the following were the main factors considered. The site had to be:

- Within the boundaries planned for clearing by WfW;
- Densely vegetated with homogenous alien vegetation;
- Close to a weather station with sufficient records;
- Underlain by a homogenous and isotropic aquifer (preferably sandy aquifer);
- Free from human activities; and
- Near or preferably adjacent to a natural catchment.

WfW suggested Riverlands Nature Reserve, managed by Cape Nature Conservation and located about 10 km South of Malmesbury (Western Cape) as potential site which closely met the criteria for site selection above. The research team visited the nature reserve and a site across the boundary between the Burger Post Farm and the nature reserve was chosen (Figure 3).

3.1.2 Borehole siting

In order to select the experimental plots for detailed investigations, a good knowledge of the underlying geologic framework and direction of groundwater flow was necessary. A resistivity survey adjacent to an existing 120 m deep livestock water supply borehole located at the Burger Post Farm was conducted to determine the underlying geologic framework. The survey was carried out with a LUND imaging system. Figure 4 shows the deep resistivity survey profile next to the existing 120 m deep borehole. It was expected that the borehole log of the existing borehole was available for comparing with the subsurface resistivity changes in order to infer the hydraulic properties and hence the underlying geologic framework. However, the log for this borehole is non-existent and no useful correlations could be made. Two shallow hand augered well points were then installed adjacent to the borehole to infer clues of aquifer system connectivity by comparing the water levels in the augered wells to that of the deep borehole. The water level in the 120 m deep borehole was 18 m below ground level and the water levels in the augered well points were levels suggested that the aquifer system is multi-layered with a superficial sand aquifer.



Figure 3: Location of the Riverlands Nature Reserve on the Western Cape map of conservation areas. The white square in Google Earth indicates the experimental area.



Figure 4: Deep resistivity survey profile next to the existing 120 m deep borehole.

From these observations, it was decided to drill four pairs of boreholes (one shallow and one deep adjacent to each other) and five shallow boreholes across the study site. The shallow boreholes, which represent the superficial sand aquifer, were ended at the top of clay beneath the sand layer. Deep boreholes were drilled to approximately 8 m below the top of the clay. Drilling was done by Roburgh Geotechnical Engineering CC under the supervision of the CSIR. The drilled boreholes were named RVLD1 to RVLD14, in which the first three letters stand for the name Riverlands, D implies that it was a drilled monitoring point and the numeric digit was a unique identification number used to distinguish the boreholes. At the four locations with a pair set of shallow and deep boreholes, shallow boreholes were even-numbered (RVLD2, RVLD4,

RVLD6 and RVLD8), and deep boreholes were odd-numbered (RVLD1, RVLD3, RVLD5 and RVLD7). The remaining drilled boreholes (RVLD9 to RVLD14) were all shallow. A clay layer was consistently observed at depths between 5 and 7 m below ground level. Since the boreholes were evenly spread, it was concluded that the underlying clay layer is continuous underneath the sand layer across the study site. A comparison of water levels in each set of boreholes showed that the water level in the upper sandy layer was consistently higher than that of the underlying clay layer suggesting possible downward flux across the clay layer into the underlying aquifer(s). The hydraulic conductivity of clay is orders of magnitude lower than that of sand, and the clay layer can be rightly classified as an aquitard forming a relatively impermeable base of the upper sandy aquifer.

The drilling of boreholes RVLD1 to RVLD4 commenced on 12 and was completed on 14 December 2006. The drilling of boreholes RVLD5 to RVLD8 commenced on 10 and was completed on 12 January 2007. The location of the remaining boreholes RVLD9 to RVLD14 required knowledge on groundwater flow direction. A good estimation of groundwater flow direction requires accurate information of ground surface levels. Tritan Survey CC were contracted to carry out the ground level survey and this was completed on 2 February 2007. The levels were observed using Real-Time Kinematic (RTK) Geographical Positioning System (GPS) on E-W lines 100 m apart. A plot of the ground levels is presented in Figure 5, whilst the surveyed ground levels can be found on the CD appended to this report (file "Topography survey.doc").

After the completion of land surveying, groundwater levels were calculated at the four shallow drilled points (RVLD2, RVLD4, RVLD6 and RVLD8). However, measurements at these four locations were insufficient to infer conclusively groundwater direction. Further six well points were hand augered bringing the total number of shallow aquifer water level monitoring points to 10. The hand augered well points were named RVLWP1 to RVLWP6 (Figure 5), in which the symbol D for drilled boreholes was substituted by WP, which stands for augered well point. Table 2 presents the details for both drilled and hand-augered monitoring points. A water table elevation map (as at 28 February 2007) was then produced based on the measurements at these 10 monitoring points and is shown in Figure 5. Groundwater flow direction is generally North-West to South-East.



Figure 5: Map of experimental site (the coordinates are represented in the WGS 1984 reference positioning system, the projection is Transverse Mercator, the central meridian is 19.0, the linear units are expressed in m).

Borehole (BH) ID	Treatment	Drill Date	GPS Positions (Cape LO 19/WGS84)		Total BH Depth (m)	Screen length (m)	Ground level (estimated from surveyed	Height of stand pipe above ground
			х	Y		. ,	levels) (m amsl)	ground (m) 0.49 0.42 0.65 0.50 0.17 0.20 0.19 0.17 0.20 0.19 0.17 0.20 0.19 0.17 0.02 0.17 0.02 0.19 0.17 0.02 0.17 0.02 0.17 0.02 0.35 0.47 0.47
RVLD1	Uncleared	2006/12/12	-39636	-3706991	15	6	113.46	0.49
RVLD2	Uncleared	2006/12/13	-39640	-3706990	7	6	113.49	0.42
RVLD3	Cleared	2006/12/13	-39657	-3707125	12	6	112.94	0.65
RVLD4	Cleared	2006/12/14	-39660	-3707120	6	6	112.94	0.50
RVLD5	Fynbos	2007/01/10	-39547	-3707154	21	12	110.50	0.17
RVLD6	Fynbos	2007/01/10	-39547	-3707155	3	3	110.46	0.20
RVLD7	Uncleared	2007/0112	-39725	-3706974	15	6	113.34	0.19
RVLD8	Uncleared	2007/01/12	-39733	-3706982	7	5	113.32	0.17
RVLD9	Fynbos	2007/03/15	-39560	-3707097	5	3	111.40	1.02
RVLD10	Cleared	2007/03/17	-39681	-3707128	6	4	112.80	0.35
RVLD11	Cleared	2007/03/16	-39688	-3707111	7	5	112.90	0.47
RVLD12	Uncleared	2007/03/15	-39627	-3707057	5	4	112.80	0.76
RVLD13	Uncleared	2007/03/16	-39663	-3707013	6	4	113.35	0.47
RVLD14	Cleared	2007/03/17	-39710	-3707094	6	4	112.90	0.54
RVLWP1	-	-	-39502	-3707198	-	-	110.47	1.10
RVLWP2	-	-	-39499	-3707100	-	-	110.72	1.18
RVLWP3	-	-	-39503	-3707003	-	-	111.63	1.18
RVLWP4	-	-	-39901	-3707001	-	-	113.50	1.10
RVLWP5	-	-	-39809	-3707107	-	-	112.86	0.95
RVLWP6	-	-	-39595	-3706998	-	-	113.42	1.10

Table 2: Detail of drilled and hand-augered monitoring points.

3.1.3 Experimental treatments

Upon site visits, the research project team decided to establish monitoring sites in three treatments, namely:

- A site invaded by alien species to be cleared. This site was cleared of alien invasives by the Working for Water Programme (Department of Water Affairs and Forestry) on 18 June 2007, and it will be further referred to as Cleared treatment.
- A site invaded by alien species to be used as control, further referred to as Uncleared treatment.
- A site with natural vegetation to be used as background, further referred to as Fynbos treatment.

A map of the area where the three treatments were established is shown in Figure 5. The geographic coordinates of the areas of the treatments can be found on the CD appended to this report. (file "Coordinates of treatments.doc")

The remaining boreholes RVLD9 to RVLD14 were then located based on the groundwater flow direction depicted in Figure 5. Boreholes RVLD4, RVLD10, RVLD11 and RVLD14 were located and closely spaced in the Cleared treatment. The groundwater quality in RVLD14 was meant to represent the quality of water entering the Cleared treatment. Borehole RVLD11 located at the centre of the plot was meant to capture the effect of clearing alien vegetation on water quality. Boreholes RVLD10 and RVLD4 were placed to monitor the quality of exiting water. The groundwater quality in the Uncleared treatment (alien species control site) was monitored in

boreholes RVLD2, RVLD8, RVLD13 and RVLD12, while that of the Fynbos treatment (natural vegetation background site) was monitored in boreholes RVLD6 and RVLD9. Monitoring in the shallow hand-augered well points, which depths were only as far as the water table elevation measured in February 2007, was limited to water level monitoring only (there was no water quality monitoring). The drilling technique and borehole logs can be found in Deliverable 6 on the enclosed CD.

3.1.4 Vegetation and site description

The background information for vegetation description was taken primarily from Rebelo et al. (2006), and supplemented with information from Yelenik et al. (2004). Botanical terminology follows Rebelo et al. (2006), and Manning and Goldblatt (1996). The study is based on a comparison of three states: a fynbos treatment, a treatment cleared of invasive *Acacia saligna* and a control treatment with clumps of sapling and mature *Acacia saligna* trees (Figure 6).



Figure 6: A view of the Fynbos treatment showing the restio dominated community of the lowerlying areas in the foreground and the taller shrubs of the higher-lying community in the background (top left); the Cleared treatment with the sparse cover and the *Willdenowia* in the left foreground (bottom left); the interior of the *Acacia* clump of the Uncleared treatment showing the high litter cover from a dead tree that was killed by the bio-control (right).

Distribution and status

The Riverlands Nature Reserve is situated on deep, well-leached, generally acidic and coarse sandy soils of marine and aeolian origin. The dominant vegetation type of the reserve is Atlantis Sand Plain Fynbos (FFd4, Rebelo et al. 2006), one of the 11 forms of sand plain fynbos that occurs on the coastal plains of the western and southern coast of the Western Cape Province. Atlantis Sand Plain Fynbos occurs as a series of islands in renosterveld, being confined to areas with deep sandy soils from about Kleindrif Station on the Berg River to Philadelphia in the South-West and Atlantis to Blouberg on the west coast. Riverlands is situated in the catchment of the Groen River, which drains into the Diep River. The vegetation type is classified as vulnerable with only about 6% conserved, mainly at Pella, Riverlands (1,111 ha) and Paardeberg. About 40% of the vegetation type has been transformed for agriculture, urban and industrial development and plantations of eucalypts (for firewood and windbreaks) and pines (windbreaks). Large areas have been invaded by Acacia saligna and A. cyclops which were used to control drift sands from the mid-1800s up to the 1950s, often in areas that were denuded of vegetation by grazing and excessive burning. Some 42 bird species have been recorded in the reserve but only four were recorded as breeding during two surveys (BIRP 1999). The reserve has at least 400 plant species, a number of which are only known from the area.

Climate

The mean annual rainfall for this vegetation type is 444 mm, ranging from 290 mm (in the North) to 660 mm (in the South) with a mean annual coefficient of variation of about 28% (Rebelo et al. 2006). Most of the rainfall occurs from May to August. The mean daily temperature varies from about 7.0°C in July to 27.9°C in February, and there are about 3 days of frost per year. The mean annual evaporation is about 2150 mm and daily evaporation exceeds the rainfall for about 70% of the time. Mist and fog are common in the winter, especially close to the coastal area, and probably account for the growth of lichens on the stems of the older *A. saligna* trees.

General vegetation structure

The vegetation is dominated by 1-1.5 m tall, emergent shrubs with a dense mid-storey of other shrubs and Restionaceae and a ground layer of recumbent shrubs, herbaceous species, geophytes and grasses with occasional succulents. The vegetation structure is strongly controlled by the depth to the water table, both in areas where it is shallow and where it is deep (Rebelo et al. 2006). Where the water table is very deep, the community is dominated by drought-hardy Restionaceae and, as the depth decreases, the incidence and cover of shrubs of the Asteraceae increases. Where the water table is shallower, and shows little seasonal variation, the Proteaceae comprise the dominant shrubs and the canopy cover is higher. Where water tables become shallower, albeit seasonally, the community is dominated by Restionaceae and Cyperaceae (sedges). At a local scale, the water table tracks elevation of the terrain and is generally shallow or rises to near or above the surface in localized depressions and lower lying areas during the winter. This results in marked topographically-related patterning of the vegetation in line with the general trends described above.

Fynbos treatment

The Atlantis Sand Fynbos at Riverlands is characterized by a relatively high cover of shrubs of the Proteaceae, Ericaceae and Rutaceae. Shrubs of *Euclea racemosa* and *Diospyros glabra* are also reasonably frequent. The vegetation of the fynbos site has two different communities that seem to be controlled by the micro-topography (Figure 6). Slightly higher lying areas are dominated by *Protea scolymocephala*, *Leucadendron salignum*, *Leucadendron cinereum* and

Leucospermum calligerum with Erica mammosa, Erica species A, Euclea, Diospyros, Phylica cephalantha, Staavia radiata and shrubs in the Rutaceae. In the lower lying areas the dominant species were from the Restionaceae – Chondropetalum tectorum, Willdenowia incurvata, Staberoha distachyos, Thamnochortus spicigerus - with Diastella proteoides, Berzelia abrotanoides, Serruria decipiens and S. fasciflora. The prostate, spreading shrub Leucospermum hypophyllocarpodendron (subspecies canaliculatum) occurred in both communities, but was more common in the higher lying areas. The difference in elevation was of the order of 0.3-0.5 m, which suggests that the distribution of the two forms is delicately controlled by the depth to the water table. The ground layer included a wide variety of geophytic species in the Liliaceae and Iridaceae, seasonal herbs and a few grass species. The weedy indigenous grass Ehrharta calycina occurred in open patches, particularly in the tracks made by the drilling rig that made the boreholes for the piezometers. Cynodon dactylon occurred in the track along the boundary. No Avena sativa was seen in the fynbos plot.

A map of the reserve on the wall in the Riverlands Nature Reserve office shows that most of the reserve is young following fires in 2004 (53 ha, CWCFPA 2005) and 2005 (206 ha) but the study area is situated in a section shown as being 11-15 years old. This compared well with an estimated age of 12-13 years based on counts of shoot growth increments on *Protea scolymocephala* shrubs. The average canopy cover masured with an AccuPar (Decagon Inc., USA) was 0.69 in the range of photosynthetically active radiation. The maximum reading was 0.94, the minimum was 0.19 and the standard deviation was 0.20.

Acacia saligna – Cleared and Uncleared treatments

Both Acacia stands are situated on the adjacent Burger Post property and separated by a barbed wire and track from the fynbos site on Riverlands. The Acacia trees on the control plot occurred in clumps with open space in between them, the average cover over the whole plot being about 45% (34% standard deviation), but with a maximum of 95% canopy cover within the clump (Figure 6). The mature Acacia trees were about 4-7 m tall with a large proportion of the branches carrying the galls formed by the biocontrol fungus (Uromycladium tepperianum). There were also a number of dead trees. Younger trees and saplings were present, particularly in the intensive sampling area of the control plot, but seedlings appeared to be absent. The ground layer within the clump was characterized by a high percentage of Acacia litter with sparse seasonal grasses and herbaceous species. The under-storey between the Acacia clumps, and in the cleared plot, was dominated by seasonal grasses and herbaceous species, notably the invasive alien Avena fatua and the weedy Ehrharta calycina. Common seasonal herbaceous species included Ursinia anthemoides, Selago corymbosa, Senecio species, Helichrysum species and Heliophila africana, and an unknown species of geophyte. There were some clumps of Willdenowia incurvata and Asparagus rubicundus in the areas between the shrubs. A single plant of Leucospermum hypophyllocarpodendron occurred between the control and cleared plots, but none of the other perennial shrubs were seen.

3.1.5 Material and methods

Groundwater level and temperature monitoring

Manual measurements of groundwater levels were made bi-weekly, during each site visit. Groundwater levels and temperature were also measured with Solinst Leveloggers (model 3001). When submerged, Leveloggers record the total of barometric pressure and water pressure below the water table. The Levelogger converts the total pressure reading to its corresponding water level equivalent. Actual water level is obtained by compensating for barometric pressure. The best method to compensate for barometric pressure is to employ a Barologger above the water level, somewhere on site, to obtain records of barometric pressure and one such logger was installed in RVLD9.

Estimation of aquifer hydraulic conductivity

During purging of the boreholes, it was observed that the boreholes would pump dry in a few minutes (less than 2 minutes) of pumping with a submersible pump (11 L min⁻¹). It was concluded from these observations that a normal pump test for the low yielding aquifer would be difficult. Under such circumstance, a slug test can be used. In a slug test, a known volume of water is displaced by lowering an object into the piezometer, instantaneously raising the water level in the piezometer. The test can also be conducted in the opposite manner by instantaneously removing a "slug" or volume of water (bail test). The water level changes can be analysed to derive the hydraulic conductivity of the aquifer. However, with the slug test, the portion of the aquifer "tested" for hydraulic conductivity is small compared to a pumping test, and is limited to a cylindrical area of small radius immediately around the well screen. Due to the fairly uniform aquifer formation underlying the study site, the slug test results were assumed to represent the greater aquifer.

There are two commonly used approaches for analysing slug tests to determine hydraulic conductivity of unconfined aquifers, namely the Hvorslev (1951) and Bouwer-Rice (1976) methods. The methods can be implemented manually or preferably through the use of dedicated software. One such software adopted in this study was the AQUIFER TEST Pro 3.5 developed by Waterloo Hydrogeologic, Inc.

The water level changes during a slug test are fast necessitating an automatic approach of recording the water levels. In this case, the Leveloggers, set to record the water levels at 2 seconds time interval, were used. Slug tests were carried out using a 2 m long PVC pipe (40 mm diameter). The tests were carried out in boreholes RVLD2, RVLD4 and RVLD8 (Figure 5). Both methods (Hvorslev, 1951; and Bouwer-Rice, 1976) were implemented with the aid of the AQUIFER TEST software.

Groundwater quality

The following groundwater chemistry parameters were measured approximately monthly:

- Calcium as Ca mg L⁻¹
- Magnesium as Mg mg L⁻¹
- Ammonia as N mg L⁻¹
- Nitrate plus Nitrite as N mg L⁻¹
- Sulphate as SO₄ mg L⁻¹
- Chloride as CI mg L⁻¹
- Alkalinity as CaCO₃ mg L⁻¹
- Iron as Fe mg L⁻¹
- Dissolved organic carbon (DOC) mg L⁻¹
- Electrical conductivity mS m⁻¹ (25°C)
- Kjeldahl Nitrogen as N mg L⁻¹
- pH (20°C)
- Hardness as CaCO₃ mg L⁻¹

These parameters were analysed at the CSIR laboratory. The methods used in carrying out the analyses were according to the 18th Edition of Standard Methods for the Examination of Water and Wastewater (1992).

3.1.6 Experimental results

Aquifer hydraulic conductivity

The results of the slug tests are presented in Table 3. For comparative purposes, the ranges of hydraulic conductivity for fine and medium sand reported in the literature are shown in Table 4.

Borehole	Hydraulic Conductivity (m d ⁻¹)				
Name Hvorslev (1951) analysis		Hvorslev (1951) analysis Bouwer-Rice (1976) analysis			
RVLD2	0.784	0.552	0.668		
RVLD4	0.246	0.173	0.210		
RVLD8	0.450	0.300	0.375		

Table 3: Slug test analysis results.

Table 4: Common hydraulic conductivity for medium and fine sand.

Aquifer material	Extreme minimum K _{min} (m d ⁻¹)	Likely minimum K _{min} (m d ⁻¹)	Likely maximum K _{max} (m d ⁻¹)	Extreme maximum K _{max} (m d ⁻¹)	Rock type	References
Medium sand	0.305	6.096	21.336	60.960	Unconsolidate d Sedimentary Rock	Bouwer (1978); Domenico
Fine sand	0.015	0.914	6.096	6.096	Unconsolidate d Sedimentary Rock	and Schwartz (1990)

Groundwater levels

Figure 7 presents groundwater levels measured manually during 2007. Groundwater levels tended to increase with the onset of the rainy season and reached their highest levels during the months of August and September 2007. The range of increase in groundwater level was about 1 m. Groundwater levels started decreasing after September 2007.



Figure 7: Groundwater levels measured manually at all boreholes in Riverlands during 2007.

Groundwater quality

Electrical conductivity in groundwater was below 200 mS m⁻¹ at all sites, with the exception of borehole RVLD10 in the cleared treatment, where EC values of about 450 mS m⁻¹ were recorded in July 2007 (Figure 8). Total dissolved solids (TDS) were generally below 1000 mg L⁻¹, except values in borehole RVLD10 of about 3000 mg L⁻¹ during July 2007. Higher EC values in borehole RVLD10 compared to other boreholes could be due to the presence of a laterite layer (see borehole logs in Deliverable 6 on enclosed CD), and corresponding higher alkalinity, hardness and concentrations of Ca, Mg and Cl. Similarly, higher EC values were observed in boreholes RVLD6, RVLD9, RVLD13 and RVLD14, all characterized by the laterite layer, but to a lesser extent than borehole RVLD10. An EC value of about 1000 mS m⁻¹ in the manually augered borehole RVLWP1 was measured at the beginning of the season (8 May 2007) with corresponding high TDS (6400 mg L⁻¹) due to high alkalinity, hardness and concentrations of Ca, Mg and Cl. This was the only measurement taken at borehole RVLWP1, which is located in the low-lying surface water drainage area (Figure 5).

Total nitrogen in nitrates plus nitrites measured in groundwater boreholes during 2007 is shown in Figure 9. Data represent averages of N in NOx measured in boreholes located within or adjacent to the treatment plots. These boreholes were RVLD2, RVLD 8, RVLD12 and RVLD13 for the Uncleared treatment, RVLD4, RVLD 10, RVLD11 and RVLD14 for the Cleared treatment, and RVLD6, RVLD 9, RVLWP1 and RVLWP2 for the Fynbos treatment (Figure 5). Average water quality data are therefore represented for groups of boreholes, each grouping representing a treatment. The standard deviations of the data are also represented on the graph with error bars. It is evident that total N in groundwater increased mainly during the rainy winter period, although the average values were always < 7 mg L⁻¹. Leaching occurred mainly from the Cleared and Uncleared treatments. Concentrations of N in groundwater of the Cleared treatment were generally higher compared to the Uncleared treatment, especially after clearing occurred on 18 June 2007. The large extent of the standard deviation (error bars), however,

indicates that these differences may not be statistically significant. Total nitrogen measured in the Fynbos treatment, used as background, was always low, and significantly lower in the latter part of the season compared to the invaded sites. The highest background value recorded was 3.3 mg L^{-1} in borehole RVLD9 on 17 July 2007.

The data in Figure 9 indicated that the contributions of total nitrates and nitrites to groundwater from the Cleared and Uncleared plots were similar and dependent on rainfall and leaching. Due to the lack of nitrogen fixation and turnover on land cleared from alien legumes, one could expect a reduction of nitrogen leaching over time, but this needs to be investigated further. It appears, however, that clearing alien invasive legume trees may also be beneficial in terms of reduction of groundwater contamination from nitrates, besides the reduction in water use in the catchment.

Oxidized forms of N were dominant in groundwater. Concentrations of Kjeldahl N (reduced nitrogen as ammonia plus nitrogen derived from organic matter) were always < 4.5 mg L⁻¹, whilst N in ammonia was always < 2.5 mg L⁻¹ for all boreholes. On several occasions, Kjeldahl N and N in ammonia were below detectable levels. Values of pH in groundwater ranged between 4 and 8 depending on the chemical speciation, whilst DOC decreased with the onset of the rainfall season. All groundwater chemistry data can be found on the CD appended to this report.

A full descriptive statistics and factor analysis were performed on groundwater data using XLSTAT, an add-on software package to Excel. Some representative data are presented here. Table 5 lists the results of the correlation test (Pearson) between anions, cations, EC, pH and DOC. Sixty data points were used for the analysis. A good correlation (>0.8) was found between EC, TDS, hardness, CI and Mg (shaded cells in Table 5). Dissolved organic carbon and alkalinity were also moderately correlated, as well as Ca and Mg (between 0.6 and 0.8).

Factor analysis was used to minimize the number of common and specific factors with XLSTAT. Eigen-values were used to determine the number of factors (internal attributes) that influence groundwater chemistry variables. Three major factors accounted for 93.25% of variability, with the first factor accounting for 62.75%. The factor loading is presented in Table 6, where a high loading of factor to variable is considered for values > 0.4. Factor F1 (salinity) had high loading on hardness, EC, TDS, CI, Mg and Ca; F2 (organic matter) had high loading on DOC, whilst F3 (gypsum in solution) had high loading on sulphate and Ca (shaded cells in Table 6). The communality is the proportion of the variance in the variable that is explained by the factors. Communality values were close to 1 for most variables except pH, nitrate + nitrite and sulphate, which were incidentally the variables that were not well accounted for by the factors.


Figure 8: Electrical conductivity (EC) in groundwater measured during 2007.



Figure 9: Nitrogen in nitrates and nitrites measured in groundwater boreholes at Riverlands during 2007.

								Nitrate			
Variables	Hardness	TDS	рН	EC	DOC	Alkalinity	CI	+	Sulphate	Mg	Са
								Nitrite			
Hardness	1	0.78	0.09	0.84	0.45	0.56	0.90	-0.36	0.48	0.99	0.72
TDS	0.78	1	0.11	0.95	0.15	0.30	0.81	-0.17	0.21	0.80	0.39
рН	0.09	0.11	1	0.16	0.14	0.57	0.18	-0.01	-0.09	0.15	-0.28
EC	0.84	0.95	0.16	1	0.16	0.39	0.86	-0.22	0.40	0.87	0.44
DOC	0.45	0.15	0.14	0.16	1	0.68	0.32	-0.27	0.21	0.43	0.38
Alkalinity	0.56	0.30	0.57	0.39	0.68	1	0.55	-0.17	0.25	0.58	0.25
CI	0.90	0.81	0.18	0.86	0.32	0.55	1	-0.19	0.28	0.91	0.52
Nitrate +	0.26	0.17	0.01	0.22	0.27	0.17	0 10	1	0.26	0.26	0.25
Nitrite	-0.30	-0.17	-0.01	-0.22	-0.27	-0.17	-0.19	I	-0.20	-0.50	0.25
Sulphate	0.48	0.21	-0.09	0.40	0.21	0.25	0.28	-0.26	1	0.45	0.48
Mg	0.99	0.80	0.14	0.87	0.43	0.58	0.91	-0.36	0.45	1	0.62
Ca	0.72	0.39	-0.28	0.43	0.38	0.25	0.52	-0.25	0.48	0.62	1

Table 5: Correlation matrix (Pearson) for groundwater chemistry analyses.

Table 6: Factor loading on groundwater chemistry analyses.

Variables	F1	F2	F3	F4	F5	Initial communality	Final communality	Specific variance
Hardness	0.995	0.056	0.021	0.067	0.031	0.992	0.999	0.001
TDS	0.853	-0.500	0.006	-0.115	-0.100	1.000	1.000	0.000
рН	0.029	0.033	-0.718	-0.092	-0.147	0.464	0.547	0.453
EC	0.853	-0.500	0.006	-0.115	-0.100	1.000	1.000	0.000
DOC	0.505	0.700	-0.031	-0.131	-0.018	0.707	0.763	0.237
Alkalinity	0.584	0.463	-0.512	-0.020	0.027	0.707	0.819	0.181
CI	0.909	-0.191	-0.140	0.172	0.193	0.920	0.949	0.051
Nitrate + Nitrite	-0.307	-0.218	-0.131	0.138	0.076	0.003	0.184	0.816
Sulphate	0.353	0.208	0.522	-0.276	-0.070	0.435	0.521	0.479
Mg	0.988	-0.004	-0.066	0.000	0.045	0.992	0.984	0.016
Ca	0.675	0.302	0.401	0.240	-0.021	0.719	0.765	0.235
Rainfall	0.084	0.087	0.026	0.383	-0.257	0.214	0.228	0.772

3.2 Unsaturated zone measurements

3.2.1 Material and methods

Laboratory analyses of soil physical properties and root distribution

Physical and hydraulic properties of Riverlands soils were determined in the laboratory, in particular colour, texture, bulk density, porosity and soil water retention characteristics. Soil profiles were described for colour and thickness of horizons during the installation of Echo-TE soil water sensors (Decagon Inc., USA). Soil texture of samples collected at different depths in profiles of each treatment was determined by sieving. One sample was taken from each soil horizon displaying different characteristics. Due to the nature of the soil (>98% sand fraction and coarser), it was not necessary to do settling tests to determine the silt and clay fractions in order to classify the soils' texture.

Water retention characteristics were obtained using an Eijkelkamp soil water retention system (sand box and clay box) on undisturbed soil samples that were collected in ring corers by augering at the locations and depths were the Echo-TE sensors were installed. Bulk density was determined by measuring the mass of the samples after drying in the oven at 105 °C, and dividing by the volume of the ring corer (100 cm³). Porosity was assumed to be equal to the volumetric soil water content at saturation.

Root density was determined in soil samples collected at different depths in the soil profiles of each treatment. One soil sample (about 5 kg) was taken from each soil horizon displaying different characteristics, at distances of 1 to 2 m from tree trunks and bushes. The soil samples were sieved and washed to separate roots from the mineral particles. The roots were then dried in the oven at 40°C for at least two days. Root density was expressed as mg of dry roots per kg of soil.

All these variables were essential inputs for modelling water fluxes and solute transport in Chapter 4. The details of the methodologies used can be found in Deliverable 6 in the enclosed CD.

Measurements of soil water content and temperature

In each of the treatments, continuous measurements of volumetric soil water content, soil temperature and electrical conductivity were carried out with an Echo-system (Decagon Inc., USA, www.decagon.com/echo/). The Echo-system consists of an Em50 logger and five Echo-TE sensors that were buried at different depths in the soil to measure volumetric soil water content, soil temperature and electrical conductivity of the soil solution. In this experiment, volumetric soil water content data were essential for modelling the soil water fluxes and transport of nitrogen. Soil temperature was essential for nitrogen transformation processes. Electrical conductivity data were not used in this research, but they were recorded with the Echo-TE sensors.

The Echo-TE sensors use an oscillator running at 70 MHz to measure the dielectric permittivity of the soil in order to determine the water content. Average temperature of the probe prongs is measured with a thermistor. The data collection and management system includes the DataTrac computer interface software. The DataTrac software is used to program the time, date and measurement interval times of the Em50 logger, as well as to download and chart data.

Five sensors were installed and connected to one Echo logger at representative sites in each treatment. Three sensors were installed in a profile adjacent to the stem of bushes/trees (close

to the main root system and below the bulk of the vegetation canopy), at depths of 5, 40 and 80 cm. The other two sensors were installed in a profile 1 to 2 m away from the stem of bushes/trees and on patches clear of vegetation canopy, at depths of 5 and 80 cm. The purpose was to get an idea of differences in water fluxes close and away from the bulk root system of vegetation and canopy in each treatment. Before installation, 30 cm diameter holes were augered. The sensors were inserted horizontally at the given depth into the wall of the hole in order to avoid the disturbed portion of the profile. Attention was paid to provide good contact between the probes and the soil. Air gaps, roots and any other inconsistencies were avoided as this may have skewed the sensors' readings. The soil was re-packed and compacted in the hole in the order it was dug, in order to regenerate a soil profile as close as possible to the original one.

All sensors were set to record volumetric soil water content, soil temperature and electrical conductivity every hour. The calibration supplied by the manufacturer for mineral sandy soils was used and data were downloaded with the DataTrac software. The point measurements obtained with the Echo-sensors were deemed suitable for the purpose of this experiment, where negligible overland flow was expected due to the sandy nature and spatial uniformity of the soil.

Rainmeters were installed in the vicinity of the soil sensors in each treatment, both under dense vegetation canopy and in the clear. The purpose was to measure the amount of rainfall intercepted by the canopy. Weather data were obtained from the Malmesbury station managed by the South African Weather Services. Manual rainfall measurements were also taken with rainmeters on a daily basis by Riverlands Nature Reserve.

3.2.2 Experimental results

Soil physical properties and root distribution

Soil profiles at Riverlands were described as Vilafontes 1120/10 or Lamotte 1100 (Soil Classification Working Group, 1991). The detailed description of the predominant soil profile is shown in Table 7. Soil textural properties are summarized in Table 8. Colour, textural classification and particle size analyses according to the classification system of the United States Department of Agriculture (USDA) were determined for soils in each treatment. All samples analyzed fell in the category of sandy soil.

The largest portion of particle sizes is in the range of medium sand (between 19.0 and 39.2%) and fine sand (between 19.6 and 56.1%). In some instances, a large fine gravel fraction (up to 31.3 %) was measured in layers deeper than 1.3 m. The portion of clay and silt was between 0.3 and 1.9%. The top soils (down to ~ 80 cm depth) in the Cleared and Uncleared treatments have a somewhat different texture from the top soil in the Fynbos treatment. The predominant particle fraction in the Cleared and Uncleared top soils is fine sand (45.6% and 45.0% on average for the profile respectively), whilst the predominant fraction in the Fynbos treatment is medium sand (40.9% on average for the profile).

Bulk density and porosity data are shown in Table 9. Bulk density values varied between 1.42 and 1.58 g cm⁻³, whilst porosity varied between 0.26 and 0.36. Bulk density tended to be slightly lower in the Uncleared and Cleared treatments (1.48 and 1.51 g cm⁻³ on average for the profile) compared to the Fynbos treatment (1.53 g cm⁻³ on average for the profile). This is due to the slightly coarser sandy texture of the Fynbos treatment top soil (Table 8). The values of porosity did not show any particular trends. No particular trends of bulk density or porosity were observed for different depths.

Master horizon	Diagnostic horizon	Depth (cm)	Soil Description	Photo
A1	Orthic A	0-30	Dry; light grey colour; med-fine sand; weak structure, apedal; loose in the dry and moist state, non- sticky and non- plastic when wet	
E	E	30-90	Dry-moist; grey with yellow and grey mottles; med-fine sand; weak structure, apedal; loose in the dry and moist state, non- sticky and non- plastic when wet	
В	Neocutanic B, or podzol B	90+	Slightly moist; non- uniform yellow; med-fine sand; weak structure, apedal; loose in the dry and moist state, non-sticky and non- plastic when wet	
¹ Concave matter.	footslope, ma	iny large	pores and root canals	s in the topsoil, surrounded by organic

Table 7: Description of predominant soil profile at Riverlands.

Table 8: Depth, colour and textural analyses of soil samples collected in three treatments at Riverlands.

	%										
Troatmont	Depth	Colour								Sand	Silt
Heatment	(cm)	Colour	FG	VCS	CS	MS	FS	VFS	Sand	+	+
										Gravel	Clay
	5	Light-brown	0.0	0.5	11.6	43.7	38.4	4.8	98.9	98.9	1.1
	20	Light-yellow	0.0	0.2	8.6	36.5	47.0	6.3	98.6	98.6	1.4
	40	Brown	0.0	0.2	9.5	41.9	43.2	4.8	99.6	99.6	0.4
	80	Light-yellow	0.0	0.3	9.8	44.5	35.6	7.9	98.1	98.1	1.9
Fynbos	85	Brown	0.0	0.2	8.5	38.0	45.8	6.1	98.6	98.6	1.4
	109	Brown	0.0	0.3	5.3	31.1	56.1	6.0	98.8	98.8	1.2
	139	White	0.1	0.4	3.4	31.7	57.4	5.8	98.6	98.7	1.3
	145	Light-yellow	24.6	2.0	11.1	26.0	32.7	3.1	74.8	99.4	0.6
	151	Yellow	22.7	1.4	12.3	25.0	34.9	3.0	76.6	99.3	0.7
	5	White	0.0	0.9	8.3	33.8	50.4	5.3	98.7	98.7	1.3
	23	White	0.0	0.4	12.9	42.7	39.0	4.0	99.0	99.0	1.0
	59	Light-yellow	0.0	1.3	11.8	42.4	39.5	3.9	99.0	99.0	1.0
Cleared	83	White	0.0	0.2	6.8	30.6	53.5	7.3	98.3	98.3	1.7
Cleareu	90	White	0.0	0.3	7.8	37.3	48.6	5.2	99.1	99.1	0.9
	100	Light-yellow	0.0	0.6	6.9	34.4	50.8	6.2	98.9	98.9	1.1
	172	Yellow	0.1	1.5	14.8	35.0	42.2	5.2	98.7	98.8	1.2
	190	Yellow	31.2	2.1	19.6	25.2	19.5	2.0	68.3	99.5	0.5
	5	Light-brown	0.0	0.6	11.1	41.6	40.9	4.9	99.0	99.0	1.0
	40	Yellow	0.0	0.5	8.6	35.7	48.5	5.5	98.7	98.7	1.3
	59	Yellow	0.8	0.5	8.5	34.1	47.8	6.9	97.9	98.7	1.3
Uncloared	82	Brown	0.0	0.0	11.3	40.1	42.7	5.0	99.1	99.1	0.9
Uncleared	106	White	0.0	1.9	16.6	35.0	40.1	5.2	98.9	98.9	1.1
	120	White	0.0	1.7	16.2	39.2	38.0	4.0	99.0	99.0	1.0
	138	White	18.5	4.0	19.3	33.8	22.7	1.4	81.2	99.7	0.3
	171	White	0.8	7.4	23.4	38.3	27.7	1.9	98.7	99.6	0.4
FG – Fine g	ravel										
VCS - Very	coarse s	and									
CS – Coarse	e sand										
MS – Mediu	m sand										
FS – Fine sa	and										
VFS – Verv	fine sand	d									

Treatment	Depth (cm)	Bulk density (g cm³)	Porosity
	5	1.51	0.26
	20	1.58	0.32
Fynbos	40	1.55	0.27
-	80	1.46	0.30
	85	1.57	0.32
	5	1.49	0.29
Cleared	23	1.48	0.30
Cleareu	59	1.43	0.30
	83	1.51	0.27
	5	1.42	0.31
Uncloared	40	1.53	0.32
Uncleared	59	1.59	0.36
	82	-	0.30

Table 9: Bulk density and porosity of soil samples collected in the treatments at Riverlands.

Water potential pressures in the range between 0 and 100 cm applied to undisturbed soil samples using the Eijkelkamp system were plotted against volumetric soil water content. The water release curves are shown in Figure 10. It is visible from these graphs that the soil in the Fynbos treatment releases rapidly water at water potential values close to saturation (between 20 and 60 cm of water pressure). The water release from the soils in the Cleared and Uncleared treatments is slower and more gradual. This is due to the slight differences in soil texture, where the predominant fractions are medium sand in the Fynbos treatment and fine sand in the Cleared and Uncleared treatments (Table 8). The sand in the Fynbos treatment is therefore slightly coarser and water is held with smaller adsorption forces compared to the soils in the other two treatments. No particular trends were observed for different soil depths. Deliverable 6 on the appended CD includes the raw data obtained for the determination of soil water characteristics.

The results of the root density measurements are shown in Figure 11. Although the patterns of root density profiles are typical for the top soil (higher root density close to the surface compared to deeper layers), high readings of root density were recorded at about 80 cm soil depth for the Fynbos and Uncleared treatments. This may indicate phreatophytic behaviour of both fynbos and *Acacia* species, with enhanced root development close to the water table. These results, however, need to be confirmed by collecting and measuring more samples, given the high spatial variability of plant rooting systems. At the time of sampling, it was not possible to auger deeper than 80 cm due to the occurrence of water tables.



Cleared treatment



Uncleared treatment



Figure 10: Soil water release curves for soil samples collected at different soil depths at Riverlands.





Cleared treatment



Uncleared treatment



Figure 11: Root density distribution in the three treatments at Riverlands.

Volumetric soil water content, rainfall and soil temperature

Volumetric soil water content data measured with the Echo-TE sensors were used in order to calibrate the HYDRUS-2D model for the unsaturated zone (see Chapter 4). The measurements are shown in Figures 12 to 14 for each treatment. Daily rainfall data measured by Riverlands Nature Reserve (Figure 15) were used as input in HYDRUS-2D. Total rainfall for the period of measurement from 15 May 2007 to 31 December 2007 was 454 mm.

It is clear from the data that all soil water content sensors responded to rainfall. This is visible from the trends of water contents in Figures 12 to 14 compared to rainfall data in Figure 15. In particular, shallow sensors installed at 5 cm soil depth showed large increases of volumetric soil water content after rainfall. The response of the sensors installed at 40 and 80 cm was less pronounced depending on the amount of rainfall and the depth of wetting. The increases in volumetric soil water content after rainfall in the Uncleared treatment were less pronounced compared to the Cleared and Fynbos treatments. This could be due to the positioning of the sensors under dense vegetation in the Uncleared treatment. It can also be noted that water drained more rapidly and the soil water content dropped faster after rainfall events in the Fynbos treatment compared to the other two treatments. This rapid release of water from soils in the Fynbos treatment was also observed in water release curves obtained in the laboratory (Figure 10) due to the coarser texture of the soil in this treatment (Table 8). In general, volumetric soil water content had a tendency to increase during the winter months at all depths and in all treatments, due to rainfall and the reduced water use by vegetation (May to mid-September 2007). From mid-September on, volumetric soil water content started decreasing sharply, first in the top soil layers followed by deeper layers. It is also evident from the data collected in the Fynbos treatment (Figure 14) that a water table built up above the deepest measurement point (80 cm depth) during the period from mid-August to the end of September 2007.

Soil temperature may have an effect on nitrogen transformation processes in soils and this was also measured with Echo-TE sensors. Soil temperatures had a general tendency to decrease over time during the period from May to the beginning of August 2007 (Figure 16). During this period, they were consistently higher in deeper soil layers compared to shallow ones, indicating inverse temperature profiles that are typical in winter. From the beginning of August 2007 on, soil temperatures started increasing and they became higher in shallow soil layers compared to deeper layers. Large daily oscillations of soil temperatures were observed at 5 cm soil depth. These oscillations were most pronounced in the Fynbos treatment, where the soil is covered by bushy vegetation and it is more exposed to weather conditions compared to the other two treatments located in, or surrounded by tree stands. More pronounced oscillations in daily temperature were also recorded by sensors located in the clear compared to those installed under the vegetation canopy. Weak daily oscillations in soil temperature were observed at 40 cm, whilst no effect of variations in daily air temperature was observed at 80 cm soil depth. Oscillations in soil temperature were larger during summer compared to the winter months.



Figure 12: Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Fynbos treatment at Riverlands.



Figure 13: Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Uncleared treatment at Riverlands.



Figure 14: Volumetric soil water contents measured with Echo-sensors at different soil depths and positions in the Cleared treatment at Riverlands.



Figure 15: Rainfall data measured with manual rainmeters from May to December 2007 at Riverlands.



Figure 16: Soil temperatures measured with Echo-sensors at different soil depths and positions in the three treatments at Riverlands.

A comparison between readings obtained from manual rainmeters below and clear of vegetation canopy was done in order to estimate canopy interception. The results of these rainmeter readings are summarized in Table 10. They represent the cumulative rainfall between two site visits. In the Uncleared treatment, *Acacia* trees intercepted a considerable amount of rainfall. Rainfall readings were consistently lower under the canopy of the dense Acacia stand (82% on average) compared to readings taken in the clear. This water may have been lost through evaporation or may have reached the soil through stem flow paths. The readings obtained under the fynbos canopy were not consistent, indicating that the nature of rainfall and wind conditions may determine the amount of rainfall intercepted by this bushy type of vegetation.

Table 10: Rainfall measured with rainmeters under vegetation canopies and in the clear for each treatment at Riverlands.

	Cleared t	reatment	Uncleared	treatment	Fynbos treatment		
Date	Under canopy Clear		Under canopy	Clear	Under canopy	Clear	
06/06/2007							
12/06/2007	29	28	25	34.5	39	31.5	
19/06/2007	-	5	3	5	5.5	5	
27/06/2007	-	19	12	19	12	18	
17/07/2007	-	22	19	22	20	22	
01/08/2007	-	78	63	77	70	70	
08/08/2007	-	24	24	19	24	18	
15/08/2007	-	40	31	38	30	38	
23/08/2007	-	8.5	6	8	10	8	
28/08/2007	-	15	12	16	12	15	
04/09/2007	-	8	8	8	10	9	
18/09/2007	-	20	18	20	22	22	
09/10/2007	-	8	4	8	-	10	
25/10/2007	-	1	0	1	0	1	
06/12/2007	-	28	31	36	-	28	

3.3 Soil chemical analyses

3.3.1 Material and methods

Soil samples were collected at the experimental site approximately every two weeks during 2007. Three soil profiles (representing three replications) were augered manually in each treatment and soil samples were collected at 5, 40 and 80 cm depth. The following soil properties were analyzed at the Soil Chemistry Laboratory of the Department of Soil Science, University of Stellenbosch: pH, exchangeable acidity, basic cations, extractable AI, carbonates and alkalinity, organic matter (carbon), NO₃⁻, NO₂⁻ and NH₄⁺. Inorganic analyses were done on 1:5 soil:water ratio extracts that were prepared by shaking 10 g of air-dried soil in 50 mL of distilled water for 15 minutes and filtering through a Whatman's filter paper.

3.3.2 Laboratory results

All results of the soil chemical analyses are reported on the CD attached to this report. In this document, focus is given to the results of NO_3^- and NO_2^- analysis. Tables 11 to 13 summarize NO_2^- and NO_3^- concentrations measured at different depths in the soil profiles of the three treatments during 2007. The concentrations of NO_2^- and NO_3^- were measured in mg L⁻¹ of 1:5 soil:water ratio extracts. These were firstly converted into N in NO_2^- and NO_3^- and the total N in NOx was calculated. The values were then converted into N in NOx in the soil solution using soil water content values measured with the Echo-TE soil water sensors (Tables 11 to 13). The soil water content values represented the average for the two sites where the sensors were installed in each treatment (see Section 3.2 for experimental set-up and sensors' siting). On the first day of soil sampling (08/05/2007), the soil water sensors were not installed yet. Other missing data of soil water content were due to malfunctioning of the sensors. It should be noted that the concentrations of NO_2^- in the soil were generally measured to be one order of magnitude smaller than the concentrations of NO_3^- .

From the data in Tables 11 to 13, it is visible that peaks in N concentrations in the soil solution occurred occasionally during the rainy season. In particular, peaks were measured on 28/09/2007 and 10/10/2007 in the Fynbos treatment, 10/08/2007 and 28/09/2007 in the Uncleared treatment and 10/08/2007 and 28/09/2007 in the Cleared treatment. These data are indicated in brackets in Tables 11 to 13. The possible cause of these peaks were dry spells with high temperatures that sped up the mineralization processes. Inorganic nitrogen was then leached by rains after these dry spells.

The dominant trends of N concentrations over time are visible in the graphs in Figure 17. A polynomial fit was drawn through the measured data points representing N concentrations in the top soil (5 cm soil depth, Figure 17). The polynomial fit was found to be the most suitable trendline depicting changes in N concentrations over time. The polynomial excluded the peaks in N concentration (values in brackets in Tables 11 to 13), because these were considered localized occurrences due to micro-climatic conditions. Data of N concentrations were used as input in the HYDRUS-2D model. In particular, initial concentrations at the three depths of measurement in the soil profile were used for each treatment. The polynomials describing N concentrations at 5 cm soil depth over time were used in the HYDRUS-2D to represent concentrations at the atmospheric boundary condition, e.g. the source of N salts.

Table 11: Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Fynbos treatment, volumetric soil water contents and calculated N concentration in the soil solution.

Soil depth (cm) Date (2007)		Day of Year/Day of	N coi 1:5 so	ncentratie il:water e (mg 1 ⁻¹)	ons in extracts	Soil water	N concentration in the soil
		simulation	N in	N in	N in	content (%)	solution (mg L ⁻¹)
	00/05	100	NO ₂	NU ₃		()	
	08/05	147/12	1.0	0.0	1.0	- 70	- 70.9
	27/05	147/13	0.1	1.0	1.1	1.0	70.0
	10/00	101/27	0.0	0.0	0.0	17.1	23.0
	24/00	175/41	0.0	1.1	1.1	10.1	00.Z
	29/00	100/40	0.0	0.0	0.0	12.7	33.1
	10/07	190/02	0.0	0.3	0.3	13.0	9.4
5 cm	10/00	222/00	0.0	0.4	0.4	<u> </u>	0.9
	01/09	244/110	0.0	0.5	0.5	18.9	12.5
	14/09	247/123	0.0	0.2	0.2	10.2	4.9
	28/09	2/1/13/	0.0	0.4	0.4	10.1	(105.4)
	10/10	283/149	0.0	0.0	0.0	10.0	(195.4)
	27/10	300/166	0.0	0.0	0.0	0.0	3.4
	09/11	315/181	0.0	0.2	0.2	10.1	8.3
	09/12	343/209	0.0	0.2	0.2	3.4	30.4
	08/05	128	0.7	0.0	0.7	-	-
	27/05	147/13	0.0	0.8	0.8	14.1	28.9
	10/06	101/27	0.0	0.6	0.6	23.8	12.5
	24/06	175/41	0.1	1.1	1.1	14.0	40.8
	29/06	180/46	0.0	0.4	0.4	18.4	11.0
	15/07	196/62	0.0	0.1	0.1	18.0	1.7
40 cm	10/08	222/88	0.0	0.1	0.1	18.0	4.1
	01/09	244/110	0.0	0.2	0.2	17.7	5.5
	14/09	247/123	0.0	0.4	0.4	17.3	12.3
	28/09	2/1/13/	6.0	137.1	143.1	13.7	(5212.2)
	10/10	283/149	0.0	5.7	5.7	11.7	(242.3)
	27/10	300/166	0.0	0.0	0.0	8.0	2.4
	09/11	315/181	0.0	0.2	0.2	12.7	8.5
	09/12	343/209	0.0	0.2	0.2	6.9	17.8
	08/05	128	0.0	0.4	0.4	-	-
	27/05	147/13	0.0	0.5	0.5	8.6	29.1
	10/06	161/27	0.0	0.5	0.5	12.1	19.2
	24/06	175/41	0.0	0.3	0.3	9.6	16.2
	29/06	180/46	0.0	0.3	0.3	10.7	14.0
	15/07	196/62	0.0	0.1	0.1	11.2	4.0
80 cm	10/08	222/88	0.0	0.1	0.1	26.1	2.2
	01/09	244/110	0.0	0.1	0.1	40.7	1.1
	14/09	247/123	0.0	0.0	0.0	44.8	0.5
	28/09	271/137	5.3	121.8	127.1	38.9	(1633.6)
	10/10	283/149	0.0	2.9	2.9	32.2	(44.6)
	27/10	300/166	0.0	0.0	0.0	23.7	0.0
	09/11	315/181	0.0	0.0	0.0	21.7	0.7
	09/12	343/209	0.0	0.2	0.2	13.2	7.4

Table 12: Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Uncleared treatment, volumetric soil water contents and calculated N concentration in the soil solution.

		N concentrations in		ons in			
Sail		Daviof	1:5	i soil:wa	ter	Soil	N concentration
501	Date	Day of		extracts		water	in the soil
depth	(2007)	Year/Day of		(ma 1 ⁻¹)		content	solution
(cm)	(2007)	simulation	Nin	Nin	Nin	(0/)	(mg 1 -1)
. ,			NO ₂ -	NO ³ .	NOx	(70)	(ing L)
	08/05	128	0.1	4.3	4.4	_	-
	27/05	147/13	0.0	2.8	2.8	4.3	328.8
	10/06	161/27	0.0	2.5	2.5	11.9	103.6
	24/06	175/41	0.1	3.5	3.6	10.0	180.4
	29/06	180/46	0.0	4.1	4.1	13.6	152.1
	15/07	196/62	0.0	5.2	5.2	15.5	166.9
-	10/08	222/88	0.0	2.9	2.9	22.2	65.3
5 cm	01/09	244/110	0.0	1.2	1.2	19.8	31.0
	14/09	247/123	0.0	0.9	0.9	18.8	24.4
	28/09	271/137	0.0	7.2	7.2	7.8	(463.5)
	10/10	283/149	0.0	0.1	0.2	4.6	16.6
	27/10	300/166	0.0	0.1	0.2	-	-
	09/11	315/181	0.0	0.3	0.3	1.7	96.4
	09/12	343/209	0.0	0.5	0.5	-	-
	08/05	128	0.0	1.3	1.3	-	-
	27/05	147/13	0.0	1.9	1.9	9.1	103.6
	10/06	161/27	0.0	0.8	0.8	13.5	31.3
	24/06	175/41	0.0	0.7	0.7	9.7	33.6
	29/06	180/46	0.0	0.3	0.3	11.3	14.4
	15/07	196/62	0.0	1.4	1.4	11.3	60.0
10 om	10/08	222/88	0.0	1.3	1.3	13.3	47.2
40 CIII	01/09	244/110	0.0	0.4	0.4	13.5	12.9
	14/09	247/123	0.0	0.3	0.3	12.8	13.0
	28/09	271/137	0.0	2.1	2.1	9.4	(112.5)
	10/10	283/149	0.0	0.2	0.2	6.9	12.8
	27/10	300/166	0.0	0.2	0.2	4.6	20.1
	09/11	315/181	0.0	0.2	0.2	3.8	31.8
	09/12	343/209	0.0	0.4	0.4	3.4	59.2
	08/05	128	0.0	0.4	0.4	-	-
	27/05	147/13	0.0	0.9	0.9	7.8	56.9
	10/06	161/27	0.0	0.6	0.6	8.8	35.1
	24/06	175/41	0.0	0.3	0.3	8.4	17.2
	29/06	180/46	0.0	0.2	0.2	8.7	13.3
	15/07	196/62	0.0	0.6	0.6	8.8	33.2
80 cm	10/08	222/88	6.1	4.5	10.6	15.4	(344.5)
80 cm	01/09	244/110	0.0	0.1	0.1	19.1	2.4
	14/09	247/123	0.0	0.2	0.2	20.0	6.0
	28/09	271/137	0.0	1.0	1.0	16.5	29.6
	10/10	283/149	0.0	0.1	0.1	13.6	3.9
	27/10	300/166	0.0	0.1	0.1	11.2	4.6
	09/11	315/181	0.0	0.1	0.1	10.3	4.5
	09/12	343/209	0.0	0.3	0.3	7.6	16.7

Table 13: Measured N concentrations of 1:5 soil:water ratio extracts at different depths in the soil profile of the Cleared treatment, volumetric soil water contents and calculated N concentration in the soil solution.

	N concentrations in		ons in				
Soil		Daviof	1:5	i soil:wa	ter	Soil	N concentration
501	Date	Day of		extracts		water	in the soil
depth		Year/Day of		(ma 1 ⁻¹)		content	solution
(cm)	(2007)	simulation	Nin	N in	Nin	(9/)	(mg -1)
			NO ₂ -	NO. ⁻	NOx	(70)	(ing L)
	08/05	128	0.1	4.3	44		
	27/05	147/13	0.0	2.8	2.8	4.3	328.8
	10/06	161/27	0.0	2.5	2.5	11.9	103.6
	24/06	175/41	0.0	6.7	6.7	10.3	324.6
	29/06	180/46	0.0	0.6	0.6	13.1	23.3
	15/07	196/62	0.0	1.3	1.3	13.1	49.5
F	10/08	222/88	0.0	34.1	34.1	20.4	(837.9)
5 cm	01/09	244/110	0.0	0.7	0.7	13.0	26.7
	14/09	247/123	0.0	1.3	1.3	12.5	50.7
	28/09	271/137	0.0	3.5	3.5	-	-
	10/10	283/149	0.0	0.2	0.2	-	-
	27/10	300/166	0.0	0.1	0.1	-	-
	09/11	315/181	0.0	0.4	0.4	5.6	39.9
	09/12	343/209	0.0	0.5	0.5	-	-
	08/05	128	0.0	1.3	1.3	-	-
	27/05	147/13	0.0	1.9	1.9	9.1	103.6
	10/06	161/27	0.0	0.8	0.8	13.5	31.3
	24/06	175/41	0.0	0.9	0.9	8.8	48.4
	29/06	180/46	0.0	0.4	0.4	12.9	16.2
	15/07	196/62	0.0	0.5	0.5	13.5	19.0
40 cm	10/08	222/88	0.0	16.7	16.7	13.3	(627.9)
40 CIII	01/09	244/110	0.0	0.3	0.3	11.9	11.2
	14/09	247/123	0.0	0.2	0.2	11.6	9.0
	28/09	271/137	0.0	8.6	8.6	10.6	(407.6)
	10/10	283/149	0.0	0.2	0.2	8.5	12.3
	27/10	300/166	0.0	0.1	0.1	2.4	30.1
	09/11	315/181	0.0	0.6	0.6	3.1	98.9
	09/12	343/209	0.0	0.4	0.4	6.5	33.3
	08/05	128	0.0	0.4	0.4	-	-
	27/05	147/13	0.0	0.9	0.9	7.8	56.9
	10/06	161/27	0.0	0.6	0.6	8.8	35.1
	24/06	175/41	0.0	0.7	0.7	10.1	32.3
	29/06	180/46	0.0	0.1	0.1	13.3	4.2
	15/07	196/62	0.0	0.4	0.4	14.0	13.5
80 cm	10/08	222/88	0.0	5.5	5.5	14.7	(187.9)
	01/09	244/110	0.0	0.2	0.2	13.4	6.6
	14/09	247/123	0.0	0.2	0.2	12.6	6.6
	28/09	271/137	0.0	2.7	2.7	9.3	(144.7)
	10/10	283/149	0.1	0.1	0.2	6.2	17.2
	27/10	300/166	0.2	0.1	0.3	2.1	64.4
	09/11	315/181	0.0	0.3	0.3	14.2	9.0
	09/12	343/209	0.0	0.4	0.4	6.0	29.4



Figure 17: Concentrations of N in NOx in the soil solution at different depths in the soil profile of the Fynbos, Uncleared and Cleared treatments. The X-axis represents days after the beginning of the model simulation as the polynomial was used to calculate the input into HYDRUS-2D.

Descriptive statistics was performed using XLSTAT both on groundwater and soil N data. In the statistical analysis, we omitted days when N concentrations in groundwater were missing for some boreholes. Concentrations of N at 5 cm soil depth were calculated using the polynomials in Figure 17 for days when groundwater N concentrations were analyzed for all boreholes. The resultant graphs (box plots) are shown in Figure 18. There was no significant difference between the means of N concentrations in both groundwater and soil for the Cleared and Uncleared treatments. However, the maximum and average N concentrations in groundwater were larger for the Cleared treatment, whilst the concentrations in soil were larger for the Uncleared treatment, indicating enhanced leaching from the Cleared treatment. Nitrogen levels in both soil and groundwater were significantly lower in the Fynbos treatment compared to the Cleared and Uncleared treatments.





Figure 18: Descriptive statistical analysis of groundwater and soil nitrogen data (units are in mg L⁻¹), showing maximum, minimum, 1st and 3rd quartiles, median and average (cross) values.

4. MODELLING NITROGEN LEACHING AND IMPACT ON GROUNDWATER

The step-wise procedure followed in the modelling exercise is described below (Figure 19):

- Interpretation of soil N analyses. This first step was aimed at developing algorithms to describe transport and transformation processes of N in soils using field measurements. Soil N represents the source of nitrogen in the system and the input to the unsaturated zone model (initial concentrations of N in soils and polynomials in Figure 17).
- Modelling N transport processes in the unsaturated zone with HYDRUS-2D. Model simulations of water and nitrogen fluxes were compared to field measurements. The model was then used to simulate nitrogen leaching to groundwater.
- Nitrogen concentration in the saturated zone. Visual MODFLOW was used to predict the spatial distribution of nitrogen concentration in groundwater, based on input data of recharge and nitrogen leaching obtained with HYDRUS-2D.



Figure 19: Flow diagram of the modelling exercise.

4.1 Nitrogen transport and transformation processes in the unsaturated zone

4.1.1 Model description

Amongst the unsaturated flow and transport models available in the literature, HYDRUS-2D was considered suitable for application in this study (see Deliverable 5 on enclosed CD). The HYDRUS-2D model (Simunek et al., 1999) includes algorithms for water and solute fluxes and it can simulate important processes like sorption, plant uptake and transformation. In addition, it automatically generates nodes for the calculation of soil fluxes in an unstructured triangular mesh, and it allows the user to set up boundary conditions (e.g. constant or variable heads and fluxes). These features were deemed to be suitable for simulating a system of predominantly rapid vertical fluxes in the unsaturated zone of the sandy soil at Riverlands.

HYDRUS-2D is computer software that can be used to simulate two-dimensional water flow, heat transport and movement of solutes in unsaturated, partially saturated and fully saturated porous media (Simunek et al., 1999). It uses Richards' equation for variably-saturated water flow and the convection-dispersion equations for heat and solute transport, based on Fick's Law. The water flow equation accounts for water uptake by plant roots through a sink term. The heat transport equation considers transport due to conduction and convection with flowing water, whilst the solute transport equation considers convective-dispersive transport in the liquid phase, as well as diffusion in gaseous phase. The solute flux equations account for non-linear, non-equilibrium reactions between the solid and liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions. A dual-porosity system can be set up for partitioning of the liquid phase into mobile and immobile regions and for physical non-equilibrium solute transport. A database of soil hydraulic properties is included in the model.

The HYDRUS-2D model does not account for the effect of air phase on water flow. Numerical instabilities may develop for convection-dominated transport problems when no stabilizing options are used, and the programme may crash when extremely non-linear flow and transport conditions occur.

The HYDRUS-2D model allows the user to set up the geometry of the system. The water flow region can be of more or less irregular shape and having non-uniform soil with a prescribed degree of anisotropy. Water flow and solute transport can occur in the vertical plane, horizontal plane or radially on both sides of a vertical axis of symmetry. The boundaries of the system can be set at constant or variable heads or fluxes, driven by atmospheric conditions, free drainage, deep drainage (governed by a prescribed water table depth) and seepage. The version of HYDRUS-2D used includes a CAD programme for drawing up general geometries and the MESHGEN-2D mesh generator that generates automatically a finite element unstructured mesh fitting the designed geometry.

The HYDRUS-2D model can be used for a wide range of applications: water and solute movement in the vadose zone and/or groundwater; specific laboratory or field experiments involving water flow and/or solute transport; field experiments involving different soil, crop, climatic and management conditions.

The HYDRUS-2D software runs in Microsoft Windows 95, 98, and NT with an interactive graphics-based user interface (GUI) to facilitate data input and interpretation of model results. The code is written in FORTRAN, whilst the interface in C++. The package requires a MS-DOS compatible system running Microsoft Windows 95 (or later), 16 Mb of RAM memory, VGA (SVGA is recommended), and at least 10 Mb of available disk space. Extensive on-line context-sensitive Help is available through the interface.

4.1.2 Input data

Simulations with HYDRUS-2D were run for the 2007 season for all three treatments of the Riverlands experiment. The water fluxes and transport processes of nitrogen were simulated and compared to measurements. The simulations were run from 15 May (DoY 135) to 31 December 2007 (DoY 365).

Detailed input data used in the simulations are included in Deliverables 7 and 8 on the enclosed CD. The main processes simulated were water flow, solute transport and root water uptake. A vertical plane in rectangular geometry was simulated with a homogeneous profile. The initial condition in water pressure head was established by setting pressure head = 0 at the bottom nodes with equilibrium from the bottom nodes upwards. The hydraulic properties model was van Genuchten-Mualem with no hysteresis. The hydraulic parameters (water flow parameters) were obtained from textural analyses, soil water retention properties and average bulk density (1.53 g cm⁻³) (see Section 3.2). The Feddes' water uptake reduction model incorporated in HYDRUS-2D was used with no solute stress, and parameters from the database of vegetation characteristics were chosen to be the closest possible to the type of vegetation in the three treatments. In this study carried out on very sandy soils, the bulk of the solute transport occurred by convection and the molecular diffusion coefficient in free water was chosen to be negligible in the very sandy soil.

The vertical rectangular dimension of the simulated geometry was 1.5 m, which corresponded approximately to the depth of water table at the beginning of the simulation (DoY 135). The boundary conditions were therefore:

- i) Atmospheric top boundary flux (rainfall, transpiration and evaporation).
- ii) No flux at all other boundaries. The bottom boundary was also set at no flux to simulate the build-up of the water table during the rainy season.

Root distribution was set down to the water table, as such root densities in the soil profile were measured (see Section 3.2). Observation nodes were set at 5, 40 and 80 cm soil depth to record soil water contents and N concentrations during simulations. These were also the depths of installation of soil water sensors and the depths of soil sampling for chemical analyses. Observation nodes were also set at 150 cm (bottom of profile) to record the simulated values of N concentration at this depth.

The time variable boundary conditions linked to the atmospheric boundary were rainfall, potential evapotranspiration and N concentrations.

In order to calculate potential evapotranspiration (PET), grass reference evapotranspiration (ETo) was first calculated from weather data obtained for Malmesbury from the South African Weather Services. ETo was calculated with the Penman-Monteith method (Allen et al., 1998). The following equation was then used in order to convert reference evapotranspiration into potential evapotranspiration of fynbos and *Acacia spp.* stands:

PET = Kc ETo

where Kc is commonly known as a crop coefficient because the methodology is mainly used to predict crop water requirements (Allen et al., 1998). As evapotranspiration was not measured in the study area, the value of Kc was assumed to be 1.5 for fynbos and 1.8 for *Acacia spp.* (see Deliverables 7 and 8 on enclosed CD).

Potential evaporation from the soil in the Cleared treatment was calculated using the method recommended by Allen et al. (1998). The Kc value for bare soil (Cleared treatment) was assumed to be equal to the coefficient of cultivated land with a crop at its initial stage of development. The average initial crop coefficient was then determined as a function of average ETo and the average interval between significant rains when wetting events are light to medium (3 to 10 mm per event) (see Deliverables 7 and 8 on enclosed CD).

The HYDRUS-2D model calculates actual evapotranspiration from potential evapotranspiration values and applies the method of Feddes to predict reduced transpiration due to water stress. Actual evaporation from the soil surface is calculated from soil water fluxes at the atmospheric boundary.

The third time variable boundary condition linked to the atmospheric boundary, namely N in NOx concentrations in the soil solution, was represented by values calculated with the polynomials in Figure 17. Therefore, the N concentrations in the top soil layer (at the atmospheric boundary) represented the source of N for rain water infiltrating into the soil.

4.1.3 Model simulations

The modelling procedure with HYDRUS-2D was carried out in two steps. Firstly, measured and simulated data of soil water content and N concentrations (expressed as concentrations of N in nitrates and nitrites in the soil solution) were compared. Secondly, cumulative water fluxes (evapotranspiration and recharge) and cumulative solute fluxes at the bottom nodes (N leaching) were simulated to be used as inputs in MODFLOW.

It should be underlined that the purpose of this exercise was not to test or validate the HYDRUS-2D model. Rather, the aim was to make sure that soil water contents and N concentrations are reasonably simulated in order to get confidence that the output data to be used in MODFLOW are realistic. In order to achieve this, data simulated with HYDRUS-2D were compared to measurements and sensitivity analyses were carried out in order to determine input values that resulted in the best fit between measurements and simulations. The most sensitive inputs were those related to the water balance, in particular rainfall, evapotranspiration and soil hydraulic properties, as well as those related to solute transport. Particular care was taken in the measurement and estimation of the most sensitive inputs.

Comparison between measured and simulated data

In order to get a realistic simulation of solute transport, it is imperative that soil water fluxes are predicted well by the model. This is because the dominant transport mode of solutes in the unsaturated zone is by convection through water movement. Figures 20, 21 and 22 show simulated volumetric soil water content data in the soil profiles of the Fynbos, Uncleared and Cleared treatments. The simulated data are shown in printout graphs of HYDRUS-2D. These were compared to measured data (Figures 12 to 14) as well as daily rainfall (Figure 15).

The comparison of volumetric soil water content data for the Fynbos treatment relates to Figure 12 (measurements) and Figure 20 (simulation). At the beginning of the simulation period (from 15/05/2007 to the end of June 2007), simulated data were higher than measurements, in particular in the top soil (5 cm depth). This could have been due to disturbance that occurred at installation of the sensors. Some time is required for the soil to settle and regenerate hydraulic connectivity after augering and re-packing the soil profile. The initial simulated soil water contents depended on equilibrium conditions in relation to the free water table set at the bottom of the profile (depth of groundwater). From July 2007 on, simulated soil water contents matched measured data generally well in terms of trends, values as well as depths. The soil water sensors responded very well to rainfall events (Figure 15) and the model matched these

responses. The absolute values of measured and simulated soil water contents were in the same range. Simulated soil water content at 150 cm (observation node N1 in Figure 20) was constant at saturation level equal to porosity (0.35) throughout the simulation period because this depth represented the bottom profile nodes with pressure head set at 0. The model also predicted very well the drying trend that occurred from September 2007 on (beginning of the summer season).

Similar considerations can be made for the Uncleared treatment (Figure 13 for measurements and Figure 21 for simulation). Measured data in the top soil (5 cm depth) were missing towards the latter part of the season due to malfunction of the sensors. The response to rainfall events occurring in November and December 2007 (Figure 15) is therefore not visible in the measurements' graph. Again, with the exception of the beginning of the season, the simulations followed measured trends well from July 2007 on, and the absolute values of predicted soil water content were in the range of those measured.

The comparison of volumetric soil water content data for the Fynbos treatment relates to Figure 14 (measurements) and Figure 22 (simulation). The treatment was cleared of alien vegetation on 18 June 2007 (day of simulation 35) and, from then on, the soil was subject to direct evaporation rather than evapotranspiration. Overall, the model underestimated soil evaporation and the simulated soil water content values were generally higher than measurements throughout the season. This was particularly evident in the latter part of the season, when measured soil water contents were below 5% in the top soil (5 cm depth), whilst the model's values were above 10%. This indicated that, given the evaporative demand conditions used as input, the model could not physically predict such large evaporative fluxes.

The general agreement between measured and simulated data gave confidence in the reliability of the Kc coefficients used. It should also be noted that simulated soil water contents below the depth of 80 cm increased almost to saturation levels during the rainy season, which is consistent with the increase in groundwater levels observed in the field (Figure 7). Besides the differences between measured and simulated soil water contents in the beginning of the season, possibly due to the settling of the soil around the sensors, other possible causes of discrepancies between measurements and simulations were attributed to the sensors' calibration (the manufacturer's calibration in the DataTrac software was used), incorrect assumptions on some soil hydraulic properties in HYDRUS-2D, as well as spatial variability. It should be noted that the initial condition that was set in the simulation, namely the initial pressure head of 0 at bottom nodes with equilibrium from the bottom nodes, was selected in order to avoid possible instabilities of the finite difference model. This, however, affected the soil water content predictions in the beginning of the season for all treatments. In addition, the model was run on a daily time step, whilst the measurements were done hourly. This caused the peaks of soil water content occurring during and immediately after rainfall to be higher in measured data compared to simulated data. In general, we can conclude that the model's prediction of soil water contents were satisfactory for a relatively long period of simulation.

Figures 23 to 25 show the comparison between simulated concentrations of N in NOx in the soil solution at three depths in the soil profile, namely 5, 40 and 80 cm. An additional observation point was set at 150 cm (bottom of the profile) in the simulation in order to record leachate concentration. The observation point at 150 cm (bottom of the profile) represents the concentration of leachate entering groundwater (Figures 23 to 25). Once the highly concentrated leachate from the soil has entered groundwater, it is subject to dilution depending on the thickness of the aquifer and the properties of the solute (e.g. dispersivity). The simulated data are shown in printout graphs of HYDRUS-2D. These were compared to measured N concentrations reported in Tables 11 to 13 and Figure 17. The concentrations are expressed in mg cm⁻³, the conversion factor to mg L⁻¹ is therefore 1000. It should be noted that the peaks in N

measured between August and September 2007 (Tables 11 to 13) were not included in Figure 17.

Figure 23 shows simulated data of N in NOx concentrations in the soil solution for the Fynbos treatment. Predicted values of N concentrations in the top soil (at 5 cm depth) matched very well measured values because the polynomial fitted through the measurements at 5 cm soil depth (Figure 17) represented the time-dependent solute concentration at the atmospheric boundary node in the model. Therefore, simulated N concentrations at 5 cm were higher at the beginning of the season, decreased during the rainy period (Figure 15) and increased again at the end of the season (November and December 2007) due to the decrease in soil water content and increase in soil temperature (Figure 16). Simulated N concentrations at 40 and 80 cm soil depth were similar to those measured in the beginning of the season. However, with the onset of the rainy period, simulated N concentrations increased first at 40 cm, followed by an increase at 80 cm around day of simulation 150 (September 2007). These increases in N concentrations deeper in the soil profile could correspond to the peaks in N concentrations measured from August to September 2007 (Tables 11 to 13). They were due to leaching of N from the top soil layer (atmospheric boundary representing the source of N) as well as due to drying out of the soil profile in the latter part of the season. The concentration of N at the bottom of the soil profile (150 cm) remained relatively stable throughout the period of simulation.

Similar considerations can be made on the comparison between measured and simulated N concentrations in the Uncleared treatment (Figures 17 and 24). Nitrogen concentrations were much higher in the Uncleared treatment compared to those measured and simulated in the Fynbos treatment (Figure 17). Measured and simulated N concentrations were similar at 5 cm soil depth throughout the season, and at 40 and 80 cm soil depth in the first part of the season. Thereafter, they increased in deeper layers due to leaching.

Figure 25 shows simulations for the Cleared treatment. The range of Y-axis was selected to note trends in N concentration in the low range, so peaks in concentrations were sometimes out of range. It is visible from the graph that the model's N concentrations at 5 cm depth followed some of the measured trends, although there was a period in the latter part of the season when measured data were not available due to soil water content data missing for the conversion in Table 14. Besides the peaks in N concentrations, measured and simulated values at 5 cm were similar. The model overestimated concentrations of N at 40 and 80 cm, which were high due to the absence of root water uptake and high soil moisture that caused more water to drain and larger convective transport of salts. As a result of the increased leaching, N concentrations at the bottom of the profile (150 cm depth) showed an increasing trend throughout the season. Nitrogen concentrations in the Cleared treatment were generally more unstable and more leaching was predicted due to wetter conditions in the soil profile compared to the Fynbos and Uncleared treatments (Figures 23 and 24).

Based on measured data, leaching of N was evident in the form of sudden pulses that were released after periods when specific conditions occurred, e.g. after dry spell with increased temperature that sped up mineralization. These conditions caused high peaks in measured N concentrations in the soil profile during the period between August and October 2007 (Tables 11 to 13). The sudden occurrence of peaks of N concentration in deeper soil layers and their disappearance thereafter implied that N transport might occur via strong preferential flow paths, possibly along plant roots. Disturbed soil samples were collected for laboratory analysis of N, so it wasn't possible to monitor N concentration continuously at the same positions during the season. The N concentrations simulated by the model did not generally show extreme peaks. However, the model predicted a relatively smooth increase in N concentrations in deeper layers during the rainy season with values far below the measured peak extreme concentrations. The model was not set to simulate preferential flow paths, as a much more detailed and localized data set would be required for this purpose.

Other possible sources of discrepancies between measurements and simulations may have been incorrect assumptions on some solute transport properties in HYDRUS-2D, as well as spatial variability. The initial N concentrations in the soil solution were those measured on 27/05/2007, which represented the first set of soil sampling after the starting date of simulation (15/05/2007).



Figure 20: Simulated volumetric soil water contents in the Fynbos treatment during 2007. The observation nodes are: N1 - 150 cm; N2 - 5 cm; N3 - 40 cm; N4 - 80 cm.



Figure 21: Simulated volumetric soil water contents in the Uncleared treatment during 2007. The observation nodes are: N1 - 150 cm; N2 - 5 cm; N3 - 40 cm; N4 - 80 cm.



Figure 22: Simulated volumetric soil water contents in the Cleared treatment during 2007. The observation nodes are: N1 - 150 cm; N2 - 5 cm; N3 - 40 cm; N4 - 80 cm.



Figure 23: Simulated NO_3^- concentrations in the soil solution in the Fynbos treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.



Figure 24: Simulated NO_3^- concentrations in the soil solution in the Uncleared treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.



Figure 25: Simulated NO_3^- concentrations in the soil solution in the Cleared treatment during 2007. The observation nodes are: N1 – 150 cm; N2 – 5 cm; N3 – 40 cm; N4 – 80 cm.

Simulated nitrogen leaching

Once the refinement of the model's inputs was completed and a reasonable simulation of soil water content and N concentrations was obtained, HYDRUS-2D was used to predict cumulative water fluxes (actual evapotranspiration and recharge) and cumulative solute fluxes at the bottom nodes (N leaching) for the three treatments. These output data were required as input in the spatial groundwater model.

Figure 26 shows the cumulative fluxes at the atmospheric boundary, potential evapotranspiration and actual evapotranspiration of fynbos. The graphs in Figure 26 are printouts of HYDRUS-2D outputs and the units are equivalent to cm of water. The cumulative flux at the atmospheric boundary represents rainfall and it is expressed as a negative number because water enters the system. The potential and actual evapotranspiration are expressed as positive numbers because they represent water leaving the system. Potential evapotranspiration, calculated from weather data and using a Kc of 1.5, was about 108 cm, whilst actual evapotranspiration calculated with Feddes' model for reduced plant water uptake was about 77 cm for the period between May and December 2007. Potential evapotranspiration was lower in the first part of the season (winter) compared to the second half of the season (summer). Actual evapotranspiration was relatively high both in winter and summer, indicating that the root system taps from the water table during the dry summer months when the soil is dry.

Figure 27 shows the cumulative water fluxes (representing recharge) and cumulative solute fluxes (representing leaching) at the bottom constant pressure head boundary in the Fynbos treatment. The units are equivalent to cm for cumulative water flux and mg per unit area (mg cm⁻²) for cumulative solute flux. The data practically represent the water and solutes moving into or from groundwater. The increase in cumulative fluxes indicates downward movement of water and solutes into the water table, whilst the decrease in cumulative fluxes indicates capillary rise and solute transport upwards. It is evident from the output graphs that recharge and leaching

occurred mainly during the rainy season in the period from May to September 2007. During this period, recharge was about 8.5 cm (about 19% of total rainfall), which is represented by the maximum cumulative water flux in the top output graph (Figure 27). Cumulative water flux decreased from October to December 2007, indicating that groundwater feeds the unsaturated zone and the root system through capillary action. The total estimated capillary rise during this period was 30.5 cm, almost half of actual evapotranspiration (77 cm). Leaching occurred during the periods of recharge from May to September 2007 (bottom output graph in Figure 27). The stepwise increase in cumulative solute flux indicates that leaching was occasional and occurred during or immediately after heavy rainfall events. Total leaching during this period was 0.35 mg cm⁻². Solute transport from groundwater upwards matched the period when capillary rise was dominant (October to December 2007).

Figure 28 represents the potential and actual cumulative evapotranspiration for the Uncleared treatment. The trends were similar to the Fynbos treatment (Figure 26). Evapotranspiration was higher than in fynbos because a Kc of 1.8 was used for *Acacia saligna* compared to a Kc of 1.5 for fynbos. High water uptake also occurred during the summer dry season with the deep root system tapping into the water table.

As a result of higher water use of alien invasive vegetation, lower recharge (about 6 cm or 13% of rainfall) was calculated compared to fynbos (Figure 29). Due to the higher concentrations of N in the soil solution, more solutes (0.61 mg cm⁻²) were predicted to be leached from the Uncleared treatment (Figure 29) compared to the Fynbos treatment (Figure 27). This also resulted in a more concentrated leachate compared to fynbos.

Figure 30 represents the cumulative fluxes at the atmospheric boundary, potential evapotranspiration and actual evapotranspiration in the Cleared treatment. The treatment had plants only for about a month (from 15/05/2007 to 18/06/2007, when the trees were cleared). From then on, root water uptake did not take place and only soil evaporation represented losses at the atmospheric boundary. The cumulative fluxes at the atmospheric boundary (top graph in Figure 30) therefore represent rainfall (decreasing cumulative flux as water entered the system) and soil evaporation (increasing cumulative flux as water left the system). By comparing and balancing the cumulative atmospheric fluxes in Figures 26 and 30, it was calculated that evaporation from bare soil was about 16 cm from 18/06/2007 until the end of the year. Potential evapotranspiration was about 8.5 cm and actual evapotranspiration was about 8.2 cm in the period from 15/05/2007 to 18/06/2007. No transpiration occurred after clearing.

Figure 31 shows the cumulative water fluxes (representing recharge) and cumulative solute fluxes (representing leaching) at the bottom constant pressure head boundary in the Cleared treatment. Due to the absence of root water uptake and plant transpiration, the soil profile at this site was wetter compared to the other two treatments throughout the season. As a result, more recharge occurred, totalling about 21 cm (46% of rainfall). In addition, recharge occurred almost throughout the year, including during and immediately after summer rainfall, and very little capillary rise was predicted. Leaching was also much higher compared to the other two treatments, totalling about 3.8 mg cm⁻² and occurring throughout the year. A more concentrated leachate from cleared bare land was generated compared to the other two treatments. This indicates that, immediately after clearing land of alien vegetation, more recharge, leachate and higher leachate concentrations are generated. However, this can last only until the source of nitrogen in the soil is depleted. Total leachate and leachate concentrations are therefore expected to decrease over time to background levels.



Figure 26: Simulated cumulative water fluxes at the atmospheric boundary (top graph), potential evapotranspiration (middle graph) and actual evapotranspiration (bottom graph) of the Fynbos treatment.



Figure 27: Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Fynbos treatment.



Figure 28: Simulated cumulative potential evapotranspiration (top graph) and actual evapotranspiration (bottom graph) in the Uncleared treatment.



Figure 29: Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Uncleared treatment.



Figure 30: Simulated cumulative water fluxes at the atmospheric boundary (top graph), potential evapotranspiration (middle graph) and actual evapotranspiration (bottom graph) in the Cleared treatment.


Figure 31: Simulated cumulative water fluxes (recharge, top graph) and solute fluxes (leaching, bottom graph) at the bottom constant pressure head boundary in the Cleared treatment.

Following the simulations of recharge and leaching with HYDRUS-2D, data required as inputs in Visual MODFLOW were generated and these are summarized in Table 14.

Table 14: Output values obtained with HYDRUS-2D for the period from 15/05/2007 to 31/12/2007 and used in Visual MODFLOW.

Variable	Treatment		
Vallable	Fynbos	Uncleared	Cleared
Potential evapotranspiration (mm)	1080	1300	85
Actual evapotranspiration (mm)	770	850	82
Soil evaporation (mm)	-	-	162
Recharge (mm)	85	60	210
Solutes leached (mg cm ⁻²)	0.35	0.61	3.80
Average recharge concentration (mg L ⁻¹)	41	102	181

4.2 Nitrogen transport and transformation processes in the saturated zone

Simulated recharge and nitrogen leaching from the unsaturated zone were used as input in Visual MODFLOW in order to predict the nitrogen spatial distribution occurring in the shallow sandy aquifer at Riverlands. This chapter includes a description of the Visual MODFLOW model (v. 2.8.2), a summary of inputs and simulations of spatial distribution of nitrogen concentration in groundwater.

4.2.1 Model description

Amongst the saturated flow and transport models available in the literature, Visual MODFLOW was considered suitable for application in this study (see Deliverable 5 on enclosed CD). Visual MODFLOW is a three-dimensional groundwater flow and contaminant transport model (Waterloo Hydrogeologic Inc., 1999). The integrated package combines MODFLOW, MODPATH, ZoneBudget, MT3D and PEST into a common graphical interface, whilst the CAD environment allows setting-up of complex spatial models and facilitates the visual control of input and output data. The MODFLOW version included in Visual MODFLOW v. 2.8.2 is the USGS MODFLOW 96 (U.S. Geological Survey), compiled for 32 bit applications in Windows 95/98/NT, the MODPATH and ZoneBudget are also USGS versions, whilst the contaminant transport numeric engines include several developments of the original MT3D v. 1.1 (DoD MT3D v. 1.5; MT3D 96; RT3D; DoD MT3DMS v. 3.00; MT3D 99). Minimum requirements to run Visual MODFLOW are a Pentium-based computer, recommended 64 MB RAM, a CD ROM drive, a hard drive with at least 100 Mb free and Windows 95/98/NT.

The MODFLOW model is used to simulate groundwater flow within a user-defined domain. MODPATH is used specifically to compute three-dimensional pathlines and the position of particles at specified points in time. ZoneBudget calculates sub-regional water budgets using results from steady-state or transient MODFLOW simulations. The contaminant transport is simulated with one of the numeric engines of MT3D. PEST is an independent model used to optimize MODFLOW parameters, in particular hydraulic conductivity, storage and recharge. The numeric engines are based on the theory of groundwater flow and mass transport (Freeze and Cherry, 1979; Domenico and Schwartz, 1990; Fetter, 1993; Zheng, 1993), finite-difference methods as well as explicit and implicit numerical methods.

In this study, MODFLOW and MT3DMS were used. MODFLOW (McDonald and Harbaugh, 1988) is a fully distributed model that calculates groundwater flow from aquifer characteristics. It solves the three-dimensional ground water flow equation using finite-difference approximations. The finite-difference procedure requires that the aquifer be divided into cells, where aquifer properties are assumed to be uniform within each cell. MODFLOW is designed to simulate aquifer systems in which saturated flow conditions exist, Darcy's Law applies and the density of groundwater is constant. MT3DMS is a finite-difference model code for groundwater contaminant and solute transport that can simulate advection, dispersion, dual-domain mass transfer and chemical reactions of dissolved constituents in groundwater (Zheng and Wang, 1999; Zheng et al., 2001). MT3DMS uses the out-head and cell-by-cell flow data computed by MODFLOW to establish the groundwater flow field.

4.2.2 Input data

The spatial model was set up using a background layer prepared in Surfer and imported in Visual MODFLOW as *.dxf file. The layer included a map of the experiment and treatments, topographical contours, borehole positioning and groundwater elevation isolines interpolated using groundwater levels measured on 28 February 2007 (Figure 5).

Ground surface data were imported from an input text file including columns with coordinates and elevations. All input text files used in Visual MODFLOW are in space-delimited format with data organized in columns. The bottom elevations were also imported from a space-delimited text file that included columns with coordinates and elevations of the bottom layer of the aquifer. The bottom layer of the aquifer was represented by the clay layer for which elevation data were obtained from borehole logs (see Deliverable 6 on enclosed CD). Observation wells and field data, initial heads measured on 28/02/2007, and observed groundwater concentrations of NO₃⁻ were also imported from separate text files. Concerning the hydraulic properties of the aquifer, saturated hydraulic conductivity was assumed to be 0.4785 m d⁻¹ for the entire area. This value was obtained from slug tests carried out at the boreholes (Table 3). Specific storage was assumed to be 0.0001 m⁻¹ and specific yield was 0.25. These data were obtained from the literature (Saayman et al., 2007), given the hydrogeological settings of the area. Effective and total porosity were 0.35 based on measured data (Table 9).

Initial N concentrations in groundwater (expressed as N in NOx in mg L⁻¹) were entered in the grid for areas representative of each treatment, based on the measured concentrations in borehole water sampled at the beginning of the season. The initial N concentrations for groups of boreholes within each treatment were averaged. The average values were 1.60 mg L⁻¹ for the Uncleared treatment, 1.78 mg L⁻¹ for the Cleared treatment and 0.75 mg L⁻¹ for the Fynbos treatment. The boreholes were RVLD 1, 2 and 13 for the Uncleared treatment, RVLD 3, 4, 10, 11 and 14 for the Cleared treatment, and RVLD 5, 6 and 9 for the Fynbos treatment (Figure 5). Default values were used for longitudinal dispersivity (10 m), horizontal to longitudinal dispersivity ratio (0.01) and molecular diffusion coefficient (0.001 m² d⁻¹). No sorption and kinetic reactions were simulated for N.

Concerning boundary conditions, a constant head boundary condition (111.5 m) and a constant N concentration in groundwater (1.60 mg L⁻¹) were assigned to the top left edge of the grid, based on the interpolated initial and output values of groundwater head in the vicinity of the block cell, as well as the initial N concentration measurements in the Uncleared treatment. The recharge, evapotranspiration and recharge concentration values calculated with the HYDRUS-2D model (Table 14) were entered in the grid for areas representative of each treatment. The extinction depth of evapotranspiration was 2 m.

4.2.3 Model simulations

Steady-state simulations were carried out with the Visual MODFLOW package. Groundwater flow was simulated with MODFLOW, whilst nitrate concentrations in groundwater (expressed as N in NOx in mg L⁻¹) were simulated with MT3D. In many ways, the type of problem dealt with in this study is of a transient nature, as it deals with pulses of solutes entering groundwater through recharge. However, a much more detailed and localized data set would be required for transient simulations compared to the spatial data set collected for this study. The main outputs that were analyzed were: i) spatial distribution of groundwater heads in order to describe groundwater flow, ii) net recharge and iii) N concentrations in groundwater. Figure 32 is an output map of MODFLOW that shows head equipotentials expressed in m of groundwater elevation for the unconfined aquifer. The heads varied between 108.5 m on the South-Eastern side to 111.5 m on the North-Western side. The groundwater flow direction therefore occurs from the North-West to the South-East.

Figure 33 represents the spatial distribution of net recharge (recharge minus evapotranspiration). Net recharge varied depending mainly on land cover. It was > 150 mm in the Cleared treatment plot, represented by the bottom left square in Figure 33. It is also visible that higher net recharge occurred in the vicinity of the South-Eastern corner of the Cleared treatment plot, in the direction of groundwater flow, compared to the surrounding area. In the areas with alien invasives and fynbos, no particular trend was visible and net recharge generally

varied between –250 and 50 mm depending mainly on water table depth, topography and water use by vegetation.

Figure 34 shows the spatial distribution of N concentrations in groundwater. The concentrations depended on vegetation, water balance and N sources. On land invaded by *Acacia* spp., the predicted concentrations ranged between 1.5 and 2.0 mg L⁻¹. Concentrations were generally just below 1.0 mg L⁻¹ in the fynbos and > 3.5 mg L⁻¹ in the Cleared treatment plot. Slightly higher concentrations were predicted in the vicinity of the South-Eastern corner of the Cleared treatment plot, in the direction of groundwater flow. It is interesting to note that abrupt changes in groundwater concentrations were predicted at the interfaces between treatments, in particular at the edge of the Cleared treatment plot and along the fence of the nature reserve (Figure 5). It should be noted that the configured grid of Visual MODFLOW did not match perfectly these interfaces in the background map.

The average saturated hydraulic conductivity obtained from slug tests was 0.4785 m d⁻¹ and this value was used in the MODFLOW simulations. The value is lower compared to those generally recommended in literature databases for sandy aguifers (Saayman et al., 2007). It was therefore decided to do a sensitivity analysis in order to test the effects of changing the input value of saturated hydraulic conductivity on the predictions of N concentration in groundwater. The neural network prediction in HYDRUS-2D calculated a saturated hydraulic conductivity of 11.46 m d⁻¹, given the soil properties at the experimental site. This value was then entered in MODFLOW and simulations re-run. The spatial pattern of N concentrations did not change considerably (Figure 35). In the calibration analysis between observations and predictions, a lower mean absolute error was calculated for groundwater head, namely 0.56 m compared to 0.60 m for saturated hydraulic conductivities obtained from slug tests. In Figure 35, it is visible that predicted N concentrations were just above 4 mg L⁻¹ in groundwater underlying the Cleared treatment plot, about 2.0 mg L⁻¹ on land invaded and about 1.0 mg L⁻¹ on fynbos land. These simulated values of N concentrations in groundwater approached the seasonal average values measured in boreholes within each treatment. The measured values were 4.40 mg L⁻¹ for the Cleared treatment, 2.72 mg L⁻¹ for the Uncleared treatment and 0.66 mg L⁻¹ for the Fynbos treatment.

The main outcome of the modelling exercise was that, by clearing alien invasives, a fast release of nitrogen is induced due to decreased evapotranspiration and increased recharge. However, in the long run, the increased N concentrations in groundwater underlying cleared land will occur only until all the leachable nitrogen has been depleted from the soil. A hypothetical simulation was therefore run using the same initial and recharge concentrations in the Cleared treatment plot as for the Fynbos treatment (0.75 mg L⁻¹ and 41 mg L⁻¹). The predicted N concentration in groundwater underlying cleared land was about 1.2 mg L⁻¹ (Figure 36), still higher than the value predicted on fynbos land, because of the lower evapotranspiration and higher recharge compared to fynbos, as well as the blending effect of the invaded land surrounding the Cleared treatment plot.

The time required to reach these conditions after clearing will depend on weather, in particular rainfall being the main leaching agent, soil moisture and temperature being the main factors for mineralization, as well as on the plant speciation in the secondary succession process of recolonization. Concentrations of N will also depend on conditions conducive to denitrification. Nitrate reduction in groundwater has been shown to follow first-order reaction kinetics. Pauwels et al. (1998) showed that autotrophic denitrification could be described with a first-order equation with a half-life ranging from 2.1 to 7.9 d. Molénat and Gascuel-Odoux (2002) used a half-life of 5 d to model autotrophic denitrification within a shale aquifer and small half-life of 0.5 d to describe fast heterotrophic denitrification observed within pyrite rich layers. Conan et al. (2003) used a half-life of 11 d for schists. Therefore, the values for half-life quoted in the literature differ significantly with different geologies. Pauwels et al. (1998) recommended the

need for denitrification rates to be evaluated for specific aquifers. Transformation processes of N in groundwater were not considered in this study, although modelling of denitrification is possible using literature data. However, this will have to be evaluated for the specific site.



113	
112	
111	
110	
109	
108	
107	
106	

Figure 32: Spatial distribution of head equipotentials (water table elevations) in m calculated with Visual MODFLOW.



250	
150	
50	
-50	
-150	
-250	
-350	
-450	

Figure 33: Spatial distribution of net recharge (recharge minus evapotranspration) in mm calculated with Visual MODFLOW.



4	
3.5	
3	
2.5	
2	
1.5	
1	
0.5	

Figure 34: Spatial distribution of N concentration in groundwater in mg L⁻¹ calculated with Visual MODFLOW.



Figure 35: Spatial distribution of N concentration in groundwater in mg L⁻¹ with saturated hydraulic conductivity equal to $0.000133 \text{ m s}^{-1}$ (11.46 m d⁻¹) calculated with Visual MODFLOW.



4	
3.5	
3	
2.5	
2	
1.5	
1	
0.5	

Figure 36: Spatial distribution of N concentration in groundwater in mg L^{-1} with initial N concentration in groundwater equal to 0.75 mg L^{-1} and recharge concentration equal to 41 mg L^{-1} in the Cleared treatment (same as for Fynbos treatment).

5. CONCLUSIONS

5.1 Outcomes of the research

The hypothesis of this study was that clearing invasive alien vegetation might disturb the alien vegetation-microorganism-soil N cycling system by producing a large episodic input of fresh litter rich in N and by eliminating a large N sink. In addition, changes to the local microclimate and the soil chemistry and physics may result in increased net N mineralization beyond the N requirements of the remaining biota. Both field measurements of groundwater quality and modelled spatial distribution of N concentration in groundwater at the experimental site confirmed this hypothesis.

Therefore, the main outcome of the research was that, by clearing alien invasives, a fast release of nitrogen is induced due to decreased evapotranspiration and increased recharge. However, in the long run and in the absence of N fixation, the increased N concentrations in groundwater underlying cleared land will occur only until all the leachable nitrogen has been depleted from the soil. A decrease in N concentration in groundwater can be expected thereafter. Clearing land from alien invasive legumes may therefore have a beneficial effect on reduced groundwater contamination from nitrate, besides the reduction in water use in catchments. The trend of decrease in N concentration will depend on weather conditions, in particular rainfall being the main leaching agent, soil moisture and temperature being the main factors for mineralization, as well as the plant speciation in the secondary succession process of re-colonization.

Specific outcomes of the research can be summarized as follows:

- The hydraulic conductivity of the aquifer was calculated to be between 0.173 and 0.784 m d⁻¹ using the results of slug tests. The range falls close to the range of minimum hydraulic conductivities for fine to medium sand.
- Groundwater levels changed in response to mainly vertical recharge events.
- Electrical conductivity in groundwater was generally below 200 mS m⁻¹ at all borehole sites. Higher EC values, alkalinity and hardness were measured in the presence of a laterite layer.
- Oxidized forms of N (NO₃⁻ and NO₂⁻) were dominant in groundwater. Total nitrogen (nitrate plus nitrite) in groundwater of the Cleared and Uncleared treatments were not significantly different (4.40 and 2.72 mg L⁻¹ on average respectively), dependent on rainfall and leaching, and significantly higher than those measured in the Fynbos treatment (0.66 mg L⁻¹ on average). Due to lack of nitrogen fixation and turnover on land cleared from alien legumes, one could expect a reduction of nitrogen leaching over time, but this needs to be investigated further.
- The texture of the soils is sandy (>98% sand), which results in relatively high bulk densities, low porosities and a quick release of water in the wet range of soil moisture. This was particularly evident in the soil of the Fynbos treatment, which has a larger fraction of medium sand compared to the other two treatments having fine sand as dominant fraction.
- Root density measurements indicated that both *Acacia* and fynbos may display phreatophytic behaviour, but more data are required in order to confirm this.
- Soil water sensors installed in the field responded to rainfall. Rapid drainage of excess water was recorded after rainfall events, in particular in the Fynbos treatment. Generally, soil water content tended to increase over time from the onset of the rainy season until mid-September 2007, it decreased thereafter.

- Soil temperature at shallow depths followed diurnal variations in air temperature. Soil temperature readings from deeper sensors were more stable and higher compared to shallow sensors in winter, and lower in summer. Generally, soil temperature tended to decrease over time from May to the beginning of August 2007, it increased thereafter.
- Considerable interception of water by the *Acacia* canopy was measured (18% of total rainfall).
- Higher concentrations of oxidized N in soils were generally measured in the Uncleared and Cleared treatments compared to the Fynbos treatment due to N fixation associated with *Acacia saligna*. Higher N concentrations were generally measured in the top soil compared to deeper soil layers in all three treatments.
- The pattern of oxidized N concentrations in the soil solution appeared to be sinusoidal depending on the season (higher concentrations during the dry summer due to mineralization of organic matter and lower concentrations during the rainy winter due to dilution and leaching). Peaks of high N concentrations were measured occasionally from August to October 2007, possibly due to dry spells with high temperatures that sped up the mineralization processes. Inorganic nitrogen was then leached by rains after these dry spells, possibly through preferential flow paths along plant roots.
- The modelling exercise and the comparison between measurements and simulations gave confidence in the predictive capabilities of HYDRUS-2D and Visual MODFLOW. The modelling procedure adopted in this study could be applied to other catchments, provided accurate input data are available, in particular those related to the conceptual groundwater model, groundwater levels and quality, soil physical properties, solute properties, weather and evapotranspiration.

5.2 Recommendations for further research

It will be beneficial to confirm the outcomes of this research through long-term measurements and, in particular, to determine how long it takes for all excess nitrogen to be leached from the soil in the absence of N fixation. A continuation of field measurements is also recommended to fully describe the seasonal patterns of nitrogen mineralization and leaching.

The modelling exercise carried out in this study made use of a large number of data collected in the field as inputs to models. Although particular attention was given to use accurate inputs, some data were not collected because of the high costs and resources required with a limited budget, and therefore they were not available for modelling. In particular, measurements of evapotranspiration and root density distribution of *Acacia saligna* and fynbos proved to be of utmost importance. Evapotranspiration had to be simulated using assumptions based on the scarce data available in the literature. Comparisons between measured and simulated soil water contents indicated that evapotranspiration was estimated reasonably well. It is, however, recommended that evapotranspiration of *Acacia saligna* and fynbos be measured in future research as this has not been carried out in this area.

During one of the inception visits to Riverlands Nature Reserve, Cape Nature Conservation officials indicated that different practices are being tried in order to clear land of alien invasives, e.g. burning, pesticide application etc. It would be very beneficial to investigate the impacts of all these practices on the effectiveness of clearance, resilience of invasives and the environment (groundwater and surface waters).

It is likely to be appropriate to expand the scope of this research to include catchments across the country and to develop appropriate methods for managing risks to water resource quality posed by clearing invasive alien vegetation.

6. REFERENCES

- ABER JD, BOTKIN DB and MELILLO JM (1978) Predicting the effects of different harvest regimes on forest floor dynamics in northern hardwoods, *Can. J. Forest Res.* **8** 306-315.
- ALLEN RG, PEREIRA LS, RAES D and SMITH M (1998) Crop Evapotranspiration: Guidelines for Computing Crop Water Requirements. United Nations Food and Agriculture Organization, Irrigation and Drainage Paper 56. Rome, Italy, 300 pp.
- BEAUJOUAN V, DURAND P and RUIZ L (2001) Modelling the effect of the spatial distribution of agricultural practices on nitrogen fluxes in rural catchments. *Ecological Modelling* **137** 93–105.
- BIRP (1999) Birds in Reserves Project. Site Summary for Riverlands Nature Reserve. Avian Demography Unit, University of Cape Town (adu@adu.uct.ac.za).
- BOUWER H (1978) Groundwater Hydrology. McGraw-Hill, New York.
- BOUWER H and RICE RC (1976) A slug test method for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. *Water Resources Research* **12(3)** 423-428.
- BROWALDH M (1997) Change in soil mineral nitrogen and respiration following harvesting form an agrisilvicultural system in Sweden. *Agroforestry System* **35** 131-138.
- COLVIN C and GENTHE B (1999) Increased risk of methaemoglobinaemia as a result of bottle feeding by HIV positive mothers in South Africa. Report No. ENV-S-R 9951, CSIR, Stellenbosch.
- CONAN C, BOURAOUI F, TURPIN N, DE MARSILY G and BIDOGLIO G (2003) Modeling flow and nitrate fate at catchment scale in Brittany (France). *J. Environ. Qual.* **32** 2026–2032.
- CONRAD JE, COLVIN C, SILILO O, GORGENS A, WEAVER J and REINHARDT C (1999) Assessment of the Impact of Agricultural Practices on the Quality of Groundwater Resources in South Africa. Report No. 641/1/99, Water Research Commission, Pretoria, South Africa.
- CULLIS J (2004) First Order Estimate of the Contribution of Agriculture to Non-Point Source Pollution in South Africa. Report to the Water Research Commission on the project No. K5/1516 "Modelling non-point source pollution in agriculture from field to catchment scale: A scoping study", Pretoria, South Africa.
- CWCFPA (2005) Business Plan. Cape West Coast Fire Protection Association (CWCFPA), June 2005.
- DOMENICO PA and SCHWARTZ FW (1990) Physical and Chemical Hydrogeology. John Wiley and Sons Inc., New York. 824 pp.
- DOMINSKI AS (1971) N transformations in a northern-hardwood podzol on cutover and forested sites. PhD thesis, Yale University, Diss. Abstr. 32: 6775-B. 156p.
- DWAF (1997) The Working for Water Programme: Annual Report 1996/97. Department of Water Affairs and Forestry, Pretoria.
- EHRENFELD JG (2003) Effects of exotic plant invasions on soil nutrient cycling processes. *Ecosystems* **6** 503-523.
- FAILLAT JP and RAMBAUD A (1999) Deforestation and leaching of nitrogen as nitrates into underground water in intertropical zones: The example of Cote d'Ivoire. *Environmental Geology* **17** 133-140.
- FETTER CW (1993) Contaminant Hydrogeology. MacMillan Publishing Co., New York. 458 pp.
- FIRESTONE MK (1982) Biological denitrification. In FJ Stevenson (ed.) Nitrogen in Agricultural Soils, Am. Soc. of Agron., Madison, Wisconsin, 289-326.
- FREEZE RA and CHERRY JA (1979) Groundwater. Prentice-Hall Inc. Englewood Cliffs, New Jersey. 604 pp.
- FUKUZAWA K, SHIBATA H, TAKAGI K, NOMURA M, KURIMA N, FUKAZAWA T, SATOH F and SASA K (2006) Effects of clear-cutting on nitrogen leaching and fine root dynamics

in a cool temperate forested watershed in Northern Japan. *Forest Ecology and management* **225** 257-261.

- GOSZ JR (1981) Nitrogen cycling in coniferous ecosystems. In FE Clark and TR Rosswall (eds.) Terrestrial N Cycles. Processes, Ecosystem Strategies and Management Impacts. Ecological Bulletins, Stockholm, 405-426.
- HAVLIN JL, BEATON JD, TISDALE SL and NELSON WL (1999) Soil Fertility and Fertilizers: An Introduction to Nutrient Management. Prentice Hall, New Jersey.
- HAYNES RJ (1986) Mineral nitrogen in the plant-soil system. Physiological Ecology, a Series of Monographs, Texts, and Treatises. Academic Press, New York.
- HOBBIE SE (1992) Effects of plant species on nutrient cycling. Tree 7(10).
- HOFFMANN JR (2005) Non-point Source Pollution in the Hennops River Valley. Report No. 518/1/95, Water Research Commission, Pretoria, South Africa.
- HVORSLEV MJ (1951) Time Lag and Soil Permeability in Ground-Water Observations. Bulletin no. 26, Waterways Experiment Station, Corps of Engineers, U.S. Army, Vicksburg, Mississippi.
- JUSSY JH, RANGER J, BIENAIME S and DAMBRINE E (2004) Effects of a clear-cut on the in situ nitrogen mineralisation and the nitrogen cycle in a 67-year-old Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) plantation. *Ann. For. Sci.* **61(5)** 397-408.
- LE MAITRE DC, RICHARDSON DM and CHAPMAN RA (2004) Alien plant invasions in South Africa: driving forces and the human dimension. *South African Journal of Science* **100** 103-112.
- LE MAITRE DC, VERSFELD DB and CHAPMAN RA (2000) The impact of invading alien plants on surface water resources in South Africa: A preliminary assessment. *Water SA* **26(3)** 397-408.
- MA L and SHAFFER MJ (2001) A review of carbon and nitrogen processes in nine U.S. soil nitrogen dynamics models. In MJ Shaffer, L Ma and S Hansen (eds.) Modeling Carbon and Nitrogen Dynamics for Soil Management. Lewis Publishers, Boca Raton, FL, 55 102.
- MANNING J and GOLDBLATT P (1996) West Coast. South African Wild Flower Guide 7. Botanical Society of South Africa, Kirstenbosch.
- MCDONALD MG and HARBAUGH AW (1988) A Modular Three-Dimensional Finite Difference Ground-Water Model. U.S. Geological Survey Techniques of Water Resource Investigations, Book 6, 586 pp.
- MELILLO JM (1981) Nitrogen cycling in deciduous forests. In FE Clark and TR Rosswall (eds.) Terrestrial N Cycles. Processes, Ecosystem Strategies and Management Impacts. Ecological Bulletins, Stockholm, 427-442.
- MOLENAT J and GASCUEL-ODOUX C (2002) Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality. *Hydrol. Process.* **16** 479-492.
- PAUWELS H, KLOPPMANN W, FOUCHER JC, MARTELAT A and FRITSCHE V (1998) Field tracer test for denitrification in a pyrite-bearing schist aquifer. *Applied Geochemistry* **13** 767–778.
- PEGRAM GC and GORGENS AHM (2001) A Guide to Non-Point Source Assessment. Report No. TT 142/01, Water Research Commission, Pretoria, South Africa.
- POSTMA D, BOESEN C, KRISTIANSEN H and LARSEN F (1991) Nitrate reduction in an unconfined sandy aquifer: water chestry, reduction processes, and geochemical modelling. *Water Resour. Res.* **27** 2027-2045.
- REBELO AG, BOUCHER C, HELME N, MUCINA L and RUTHERFORD MC (2006) Fynbos biome. In L Mucina and MC Rutherford (eds.) The Vegetation of South Africa, Lesotho and Swaziland. Strelitzia 19. South African National Biodiversity Institute, Pretoria, 53-219.
- RICE EL and PANCHOLY SK (1972) Inhibition of nitrification by climax ecosystems. *Am. J. Bot.* **59** 1033-1040.

- ROSSWALL T (1976) The internal N cycle between micro-organisms, vegetation and soil. In BH Svensson and R Soderlund (eds.) N, Phosphorous and Sulphur - Global Cycles. Ecological Bulletins, Stockholm, 157-167.
- SAAYMAN IC, BEEKMAN HE, ADAMS S, CAMPBELL RB, CONRAD J, FEY MV, JOVANOVIC N, THOMAS A and USHER BH (2007) Assessment of Aquifer Vulnerability in South Africa. Report No. TT 1432/1/07, Water Research Commission, Pretoria, South Africa.
- SALA A, SMITH SD and DEVITT DA (1996) Water use by *Tamarix ramosissima* and associated phreatophytes in a mojave desert floodplain. *Ecol. Appl.* **6** 888-898.
- SIGMA BETA (2004) Knowledge Review of Modelling Non-Point Source Pollution in Agriculture from Field to Catchment Scale. Report No. K5/1516 "Modelling non-point source pollution in agriculture from field to catchment scale: A scoping study", Water Research Commission, Pretoria, South Africa.
- SIMONIC M (1999) The Assessment of Ambient Groundwater Quality, at a National Scale in the Republic of South Africa. Report No. K5/841, Water Research Commission, Pretoria, South Africa.
- SIMUNEK J, SEJNA M and VAN GENUCHTEN MTh (1999) The HYDRUS-2D software package for simulating two-dimensional movement of water, heat, and multiple solutes in variably-saturated media, Version 2.0. U.S. Salinity Laboratory, USDA, ARS, Riverside, California.
- SIMUNEK J, VOGEL T and VAN GENUCHTEN MTh (1994) The SWMS_2D code for simulating water flow and solute transport in two-dimensional variably saturated media, Version 1.21. Research Report No. 132, U.S. Salinity Laboratory, USDA, ARS, Riverside, California, pp. 197.
- SMITH RL, HOWES BL and DUFF JH (1991) Denitrification in sand in nitrate contaminated groundwater: Occurence in steep vertical gradients. *Geochim. Cosmochim. Acta* **55** 1815-1825.
- SOIL CLASSIFICATION WORKING GROUP (1991) Soil Classification. A Taxonomic System for South Africa. Dept. of Agricultural Development, Pretoria, South Africa.
- STEVENSON FJ (1982) Nitrogen in Agricultural Soils. Am. Soc. Agron., Madison, Wisconsin.
- STOCK WD and LEWIS OAM (1984) Uptake and assimilation of nitrate and ammonium by an evergreen Fynbos shrub species *Protea Repens* L. (Proteaceae). *New Phytol.* **97** 261-268.
- STONE E (1973) The impact of timber harvest on soil and water.- In: President's Advisory Panel on Timber and Environment Report, US Government Printing Office, Washington DC, 427-467.
- SWANK WT, VOSE JM and ELLIOTT KJ (2001) Long term hydrologic water quality responses following commercial clear-cutting of mixed hard woods on Southern Appalachian catchment. *For. Ecol. Manage.* **43** 163-178.
- TODD RL, SWANK WT, DOUGLASS JE, KERR PC, BROCKWAY DL and MONK D (1975) The relationship between nitrate concentrations in Southern Appalachian mountain streams and terrestrial nitrifiers. *Agro-Ecosystems* **2** 127-132.
- TREDOUX G (1993) A Preliminary Investigation of the Nitrate Content of Groundwater and Limitation of the Nitrate Input. Report No. 368/1/93, Water Research Commission, Pretoria, South Africa.
- VAN GINKEL C (2002) Trophic Status Assessment Executive summary. Institute for Water Quality Studies, Department of Water Affairs and Forestry, Pretoria, South Africa.
- VITOUSEK PM (1981) Clear-cutting and the N cycle. In FE Clark and TR Rosswall (eds.) Terrestrial N Cycles. Processes, Ecosystem Strategies and Management Impacts. Ecological Bulletins, Stockholm, 631-642.
- VITOUSEK PM and MELILO JM (1979) Nitrate losses from disturbed forests: Patterns and Mechanisms. *Forest Sci.* **25** 605-619.
- VITOUSEK PM and REINERS WA (1976) Ecosystem development and the biological of streamwater chemistry. In JO Niriagu (ed.) Environmental Biogeochemistry, Ann Arbor Science, 665-680.

- VITOUSEK PM and REINERS WA (1975) Ecosystem succession and nutrient retention: A hypothesis. *Bioscience* **25** 376-381.
- WATERLOO HYDROGEOLOGIC Inc. (1999) User's manual for Visual MODFLOW. Waterloo Hydrogeologic Inc., Waterloo, Ontario, Canada.
- YELENIK SG, STOCK WD and RICHARDSON DM (2004) Ecosystem level impacts of invasive Acacia saligna in the South African fynbos. Restoration Ecology **12(1)** 44-51.
- ZHENG C and WANG PP (1999) MT3DMS: A modular three-dimensional multi-species model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater systems: Documentation and user's guide, SERDP-99-1, U.S. Army Engineer Research and Development Centre, Vicksburg, MS.
- ZHENG C (1993) Extension of the method of characteristics for simulation of solute transport in three dimensions. *Ground Water* **31(3)** 456-465.
- ZHENG C, HILL MC, HSIEH PA (2001) MODFLOW-2000, the U.S. Geological Survey modular ground-water model User guide to the LMT6 package, the linkage to MT3DMS for multispecies mass transport modelling, U.S Geological Survey Open-File Rep. 01-82, 43 pp.