

Modelling the relationship between flow and water quality in South African rivers.

This thesis is submitted in fulfillment of the requirements for the degree of
Doctor of Philosophy at Rhodes University.

By
Andrew Robert Slaughter
May 2011

Supervised by
D.A. Hughes and W.J. Muller

Abstract

The National Water Act (Act 36 of 1998) provides for an ecological Reserve as the quantity (flow) and quality of water needed to protect aquatic ecosystems. While there are methods available to quantify the ecological Reserve in terms of flow, methods of linking flow to water quality are lacking. Therefore, the research presented in this thesis investigated various modelling techniques to estimate the effect of flow on water quality. The aims of the research presented in this thesis were:

Aim 1: Can the relationship between flow and water quality be accurately represented by simple statistical models?

Aim 2: Can relatively simple models accurately represent the relationship between flow and water quality?

Aim 3: Can the effect of diffuse sources be omitted from a water quality model and still obtain realistic simulations, and if so under what conditions?

Aim 4: Can models that solely use historical monitoring data, accurately represent the relationships between flow and water quality?

In Chapter 3, simple Q-C regressions of flow and water quality were investigated using Department of Water Affairs (DWA) historical monitoring data. It was found that while flow versus salinity regressions gave good regression fits in many cases, the Q-C regression approach is limited. A mechanistic/statistical model that attempted to estimate the point and diffuse signatures of nutrients in response to flow was developed in Chapter 4 using DWA historical monitoring data. The model was verified as accurate in certain case studies using observed point loading information. In Chapter 5, statistical models that link land cover information to diffuse nutrient signatures in response to flow using DWA historical data were developed. While the model estimations are uncertain due to a lack of data, they do provide an estimation of the diffuse signature within catchments where there is flow and land cover information available. Chapter 6 investigates the extension of an existing mass-balance salinity model to estimate the effect of saline irrigation return flow on in-stream salinity. The model gave accurate salinity estimates for a low order stream with little or no irrigation within its catchment, and for a permanently flowing river within a catchment used extensively for irrigation. Chapter 7

investigated a modelling method to estimate the reaction coefficients involved in nitrification using only DWA historical monitoring data. Here, the model used flow information to estimate the residence time of nutrients within the studied river reaches. While the model obtained good estimations of nitrification for the data it was applied to, very few DWA data sets were suitable for the model. Chapter 8 investigated the ability of the in-stream model QUAL2K to estimate nutrient concentrations downstream of point and diffuse inputs of nutrients. It was found that the QUAL2K model can give accurate results in cases where point sources dominate the total nutrient inputs into a river. However, the QUAL2K simulations are too uncertain in cases where there are large diffuse source inputs of nutrients as the load of the diffuse inputs is difficult to measure in the field. This research highlights the problem of data scarcity in terms of temporal resolution as well as the range of constituents measured within DWA historical monitoring data for water quality. This thesis in addition argues that the approach of applying a number of models is preferable to applying one model to investigate the research aims, as particular models would be suited to particular circumstances, and the development of new models allowed the research aims of this thesis to be explored more thoroughly. It is also argued that simpler models that simulate a few key processes that explain the variation in observed data, are more suitable for implementing Integrated Water Resource Management (IWRM) than large comprehensive water quality models. From this research, it is clear that simple statistical models are not adequate for modelling the relationship between flow and water quality, however, relatively simple mechanistic models that simulate a limited number of processes and water quality variables, can provide accurate representations of this relationship. Under conditions where diffuse sources are not a major factor within a catchment, models that omit diffuse sources can obtain realistic simulations of the relationship between flow and water quality. Most of the models investigated in this thesis demonstrate that accurate simulations of the relationships between flow and water quality can be obtained using solely historical monitoring data.

Table of Contents

Abstract	I
Table of Contents	III
Glossary	VI
List of Tables	IX
List of Figures	XI
Acknowledgements	XVI
Declaration	XVII
Chapter 1: General Introduction	1
1.1. The current water quantity and quality situation in South Africa	1
1.2. Integrated Water Resource Management (IWRM)	4
1.3. The ecological Reserve	7
1.4. Data constraints on representing the relationship between flow and water quality	8
1.5. Flow – water quality model requirements to be useful in the context of IWRM	9
1.6. Aims	12
Chapter 2: Literature Review	14
2.1. Water quality constituents that may be changed by flow	14
2.1.1. Salinity	14
2.1.2 Turbidity	15
2.1.3. Nutrients	16
2.1.4 BOD	22
2.2 Impoundments and IBTs	23
2.3 The link between diffuse sources and high flow, and point sources and low flow	24
2.4 The difference between load and concentration	26
2.5 Factors influencing in-stream water quality	27
2.6 Modelling the relationship between flow and water quality	28
2.6.1 Model introduction	28
2.6.2 Brief history of water quality modelling	30
2.6.3 Possible future directions for water quality modelling	31
2.6.4 The modelling process	33
2.6.4.1 Modelling of a stream or river	33
2.6.4.2 Good data for modelling	34
2.6.4.3 Modelling conservative versus non-conservative water quality constituents	35
2.6.4.4 Temporal and spatial scales	36
2.6.4.5 Simple models versus complex models	36
2.6.4.6 Model calibration and validation	38
2.6.4.7 Steady state models versus variable flow models	41
2.6.4.8 Uncertainty	41
2.6.5 Examples of models	44
2.6.5.1 Water quality models by temporal and spatial scale	44
2.6.5.2 Export coefficients	46
2.6.5.3 Statistical water quality models	47
2.6.5.4 Mass – balance models	48

2.6.5.5 Parameter calibration models versus physically based models	49
2.6.6 Shortcomings of current models	50
2.7 Concluding remarks	51
Chapter 3: Statistical modelling of the effect of flow on water quality	53
3.1 Introduction.....	53
3.2. Data and methods.....	54
3.2.1 Data	54
3.2.2 Methods.....	55
3.3. Results.....	56
3.4 Discussion	59
Chapter 4: A simple mechanistic model to relate flow to water quality	64
4.1 Introduction.....	64
4.2 Data and methods.....	67
4.2.1 Data	67
4.2.2 The model used	68
4.3 Results.....	75
4.3.1 A case study of a point source dominated monitoring point.....	75
4.3.2 A case study of a diffuse source dominated monitoring point	78
4.3.3 Results of model applied to all data.....	80
4.4 Discussion	83
4.5 Conclusion	86
Chapter 5: A simple model to relate land cover and flow to water quality	87
5.1 Introduction.....	87
5.2 Methods.....	88
5.2.1 Data	88
5.2.2 Model development	91
5.3 Results.....	95
5.4 Discussion	114
Chapter 6: Extending a mechanistic mass-balance model linking flow to salinity to account for the effect of saline agricultural return flow	125
6.1 Introduction.....	125
6.2 Model description and studied areas.....	127
6.2.1 Model description	127
6.2.2 Study Areas	133
6.2.2.1 The Balfour River	133
6.2.2.2 The Breede River Catchment.....	135
6.3 Results.....	138
6.3.1 Results of model applied to the Balfour River.....	138
6.3.2 Results of model applied to the Breede River	139
6.4 Discussion	144
Chapter 7: A simple nutrient model to predict nitrification reaction coefficients using historical monitoring data	151
7.1 Introduction.....	151
7.2 Model description and data.....	154
7.2.1 Model description	154
7.2.2 Model data	161

7.3 Results.....	167
7.3.1 Model applied to the Buffalo River	167
7.3.3 Model applied to the Crocodile River.....	170
7.3.2 Model applied to the Orange River.....	171
7.4 Discussion.....	182
Chapter 8: Application of QUAL2K to the Buffalo River and Bloukrans River.....	186
8.1 Introduction.....	186
8.2 Sites, Data and Model	188
8.2.1 Sites.....	188
8.2.1.1 The Buffalo River	188
8.2.1.2 The Bloukrans River	193
8.2.2. Data	195
8.2.3 QUAL2K modelling procedure	196
8.3 Results.....	202
8.3.1 The Buffalo River system	202
8.3.1.1 Field Data.....	202
8.3.1.1 Model Results	203
8.3.2 The Bloukrans River system.....	207
8.3.2.1. Field Data.....	207
8.3.2.2. Model Results	209
8.4 Discussion	216
8.4.1 Discussion of the Buffalo model results	216
8.4.2 Discussion of the Bloukrans model results.....	219
8.4.3 Implications for modelling point sources versus diffuse sources with QUAL2K	220
8.4.4. Potential use of QUAL2K in water quality and flow management.....	221
Chapter 9: Conclusions and Recommendations	223
9.1. Outcomes of the models investigated	223
9.2. Aims addressed in the research.....	232
9.3. The effect of data scarcity on model development and confirmation.....	234
9.4. Shortcomings and advantages of the investigated models in representing the relationship between flow and water quality	236
9.5. Recommendations for model use in the context of IWRM in South Africa.....	240
9.6. The argument for investigating multiple models in this research.....	245
9.7. Possible further research directions	247
Appendix A	250
Appendix B	298
References.....	322

Glossary

- ADAPT:** Agricultural Drainage and Pesticide Transport model.
- Antecedent rainfall:** Preceding rainfall conditions. May have an effect on present rainfall – runoff responses within a catchment.
- Anthropogenic:** Caused by humans.
- Aquatic ecosystem:** An ecosystem located in a body of water.
- Assimilation:** The conversion of nutrients into living tissue.
- Base flow:** Streamflow which results from precipitation that infiltrates into the soil and eventually moves through the soil to the stream channel.
- BASINS:** Better Assessment Science Integrating Point and Non-point Sources.
- Bioavailability:** The extent to which chemical contaminants are available for assimilation by organisms.
- BOD:** Biochemical oxygen demand.
- Calibrate:** Process of adjusting model parameters to obtain an optimal fit between model simulated and observed data.
- Catchment:** The area drained by a river.
- Class I models:** Beck (1987) definition of a complex model consisting of a collection of hypotheses.
- Class II models:** Beck (1987) definition of a model of intermediate complexity with a limited number of processes simulated.
- Class III models:** Beck (1987) definition of a simple model that is a basic cause effect relationship such as a statistical regression.
- Confirm:** Term suggested by Oreskes *et al.* (1994) to be used in place of ‘validate’.
- Conservative water quality variable:** A water quality variable that does not change chemical form throughout its residence in a water body.
- Determinism:** Values of dynamic variables of a system and of the forces acting on the system at a given time, completely determine the values of the variables at any later time
- DISPLA:** Dynamic Interactive Simulation of Phosphorus Loss Areas.
- DO:** Dissolved oxygen.
- DWA:** South African Department of Water Affairs.
- EC:** Electrical Conductivity.
- Effluent:** Liquid waste or sewage discharged into a river.
- Ephemeral rivers:** Rivers that do not flow continuously.
- Eutrophication:** Excessive richness of nutrients in a body of water.
- Export coefficients:** In the units $\text{Kg.m}^{-2}.\text{yr}^{-1}$ and used to estimate the load of pollutants exported from specific land use types.
- Extrapolation:** Model prediction outside of the range of observed results. Similar to scenario analysis.
- Faecal coliforms:** Bacteria found in the intestinal tracts of mammals. Their presence in water is an indicator of pollution and possible contamination by sewage.
- GIS:** Geographical Information System.
- GLUE:** Generalized Likelihood Uncertainty Estimation.
- GWR:** Geographically Weighted Regression.
- Halotolerant biota:** Biota adapted to living in water of high salinity.

- Holistic:** Characterized by comprehension of the parts of something as intimately interconnected and explicable only by reference to the whole
- HSPF:** Hydrological Simulation Program in Fortran.
- IBT:** Inter-basin transfer.
- Impoundment:** A body of water formed by impounding.
- INCA:** Integrated Nitrogen CAatchment model.
- Indeterminism:** The theory that the most basic constituents of matter at times behave indeterministically or randomly.
- Integrative:** Combining and coordinating diverse elements into a whole.
- Interpolation:** Model prediction within the range of observed results.
- IWRM:** Integrated Water Resource Management.
- Land cover:** Physical material at the surface of the earth.
- Land use:** Human modification of natural environment or wilderness into built environment such as fields, pastures, and settlements.
- Macrophyte:** A macrophyte is an aquatic plant that grows in or near water and is either emergent, submergent, or floating.
- Manning Equation:** An equation used to compute the velocity of uniform flow in an open channel.
- Mechanistic model:** A model that attempts to simulate processes within a system.
- Model framework:** A collection of models that simulate different aspects of a water resource e.g. (flow and water quality), and a set of guidelines on how to integrate the components.
- Model parameters:** Variables within a model that control the rate of processes. Parameters values can be changed to get a good model simulation to observed data.
- Non-conservative water quality variable:** A water quality variable that may change chemical form during its residence in a water body.
- Nutrients:** Chemical species that are assimilated by flora within natural water systems.
- OLS:** Ordinary Least Squares regression.
- Parameter equifinality:** When several sets of parameters in a model calibration can lead to the same modelling results.
- PCA:** Principle Component Analysis.
- Perennial rivers:** Rivers that flow continuously.
- Periphyton:** Sessile organisms, such as algae and small crustaceans, that live attached to surfaces projecting from the bottom of a freshwater aquatic environment.
- Phytoplankton:** The collection of small or microscopic organisms, including algae and protozoans that float or drift in great numbers near the surface within a water body.
- Point & non-point sources of pollutants:** A Point source is easily identifiable and discharges from a specific and confined space such as a pipe. Diffuse sources are due to rainfall runoff from the surface of a catchment, may be spatially and temporally intermittent and occur over a large and diffuse area.
- Q-C Regressions:** Simple linear regression of flow versus concentration of a water quality variable.
- Quaternary catchment:** Smallest hydrological unit in a national hierarchical drainage subdivision system that was developed by the DWA.
- Reaction coefficients:** Parameters relating to the reaction rates of certain chemical species as they change form from one species to another.
- Regional sensitivity analysis (RSA):** A process that uses previously defined regions of

acceptable model predictions to estimate plausible parameter values.

Riparian: Of, relating to, or situated on the banks of a river.

Risk: A combined measure of the degree of detriment to society or the aquatic ecosystem caused by a defined event (or combinations of events), and the probability of that event occurring.

River Flow: Movement of water within a river in a longitudinal direction from higher lying areas to lower lying areas.

Salinity: Concentration of inorganic salts within water

Salt: An ionic compound.

Scenario Analysis: The exploration of hypothetical situations for managing a water resource using a model.

Sensitivity analysis: The study of how the variation (uncertainty) in the output of a mathematical model can be apportioned, qualitatively or quantitatively, to different sources of variation in the input of a model

SOD: Sediment oxygen demand.

Spatial variability: Variability across space or area.

SQL: Standard Query Language, used to select datasets from a database according to certain criteria.

Stakeholder: A person with an interest or concern in something.

Stochastic: Having a random probability distribution or pattern that may be analyzed statistically but may not be predicted precisely.

Sustainability: Preserving biological systems so as to remain diverse and productive over time

SWAT: Soil Water Assessment Tool.

TDS: Total Dissolved Solids.

Temporal variability: Variability over time.

Tributary: A river or stream flowing into a larger river or lake.

Turbidity: A measure of the clarity of water as suspended particles within water decrease clarity and increase turbidity.

Validate: Process of confirming a calibrated model by running the model on an independent data set of observed data.

WASP5: Water quality Analysis Simulation Program version 5.

Water quality: The physical, chemical and biological characteristics of water.

Water quality model: A tool that is used to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data.

WQS: Water Quality Sulphate model.

WQT: Water Quality TDS model.

WRPM: Water Resource Planning Model.

WWTW: Waste water treatment works.

List of Tables

Table 3.1: Summary of simple regression results for EC, phosphate and nitrate + nitrite	56
Table 4.1: Summary of DWA monitoring data for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}) for two sewerage treatment works (WWTWs) on the Buffalo River	76
Table 4.2: Flow and nutrient measures taken in grab samples from effluent from two sewerage treatment works (WWTWs) along the Buffalo River	76
Table 5.1: Categories used from the Department of Water Affairs (DWA) Groundwater Resource Directed Measures database to develop a simple model to relate land cover to flow and water quality in rivers	90
Table 5.2: Water management regions based on natural water chemistry as determined by Day et al. (1998)	91
Table 5.3: Land cover categories determined by PCA to have a correlation with either the A or B parameters from a diffuse signature model for phosphates. All categories have a positive correlation unless indicated by a '-' symbol.....	96
Table 5.4: Land cover categories determined by PCA to have a correlation with either the A or B parameters from a diffuse signature model for nitrites plus nitrates. All categories have a positive correlation unless indicated by a '-' symbol.....	97
Table 5.5: Results of land cover model for phosphates, including land cover categories that correlate with diffuse model parameters, the final model, and an indication of model goodness of fit.....	98
Table 5.6: Results of land cover model for nitrates + nitrites, including land cover categories that correlate with diffuse model parameters, the final models, and an indication of model goodness of fit.....	100
Table 5.7: Point and diffuse signature model parameters and water quality regions for monitoring sites used to confirm the land cover model.....	103
Table 5.8: χ^2 values indicating model fit between the land cover model prediction of the diffuse signature and the diffuse signature predicted by the model from Chapter 4 for Phosphate data.	115
Table 5.9: χ^2 values indicating model fit between the land cover model prediction of the diffuse signature and the diffuse signature predicted by the model from Chapter 4 for nitrite plus nitrate data.	115
Table 6.1: Salinity signatures used in a mass-balance water quality model.....	138
Table 6.2: Monthly averaged Flow and TDS signatures entering and leaving the Breede River between the DWA monitoring points H4H017 and H5004 as well as the monthly averaged salt load introduced by irrigation return flow as estimated by a mass-balance model between the years 1980 – 1990.....	148
Table 7.1. Attributes of DWA monitoring point data used in a simple nutrient model	162
Table 7.2: Parameters characterizing point and diffuse inputs in the studied regions as estimated by the Mechanistic/Statistical Nutrient Model.	181
Table 7.3. Summary of values for calibrated parameters used in the nutrient model to simulate ammonification and nitrification processes.	182
Table 8.1: Sites chosen on the middle Buffalo River for water quality modelling	192
Table 8.2: Sites chosen on the Bloukrans River for water quality modelling	194
Table 8.3: Values of water quality parameters measured in the Buffalo River. All water quality	

values measured are in mg.L^{-1} while flow is measured in $\text{m}^3.\text{sec}^{-1}$. Standard deviation is listed in brackets after average values where several replicates were measured.....	204
Table 8.4: Rate constants used in QUAL2K to model water quality in the Buffalo River and the Bloukrans River. Default values listed are taken from Bowie et al. (1985). QUAL2K uses many more rate constants, but the default values in the program were used if not indicated here.	210
Table 8.5: Values of water quality parameters measured in the Bloukrans River. All water quality values measured are in mg.L^{-1} while flow is measured in $\text{m}^3.\text{sec}^{-1}$. Variance is listed in brackets after average values where several replicates were measured.....	211
Table 8.6: Possible diffuse sources influencing the Bloukrans River as determined by calibrating the QUAL2K model to observed data	212
Appendix A Table 1: Department of Water Affairs (DWA) flow and water quality monitoring sites	250
Appendix A Table 2: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data.....	268
Appendix A Table 3.: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data	273
Appendix A Table 4: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated	278
Appendix A Table 5: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated.....	288

List of Figures

Figure 1.1: Strings of filamentous algae (<i>Batrachospermum</i>) attached to the stream bed of the Bloukrans River in the Eastern Cape, South Africa, in December 2009.	2
Figure 1.2: Floating invasive water hyacinth (<i>Eichhornia</i>) on the Buffalo River just before Laing Dam in the Eastern Cape, South Africa in late 2009, caused by a combination of nutrient enrichment and alien invasives.	3
Figure 1.3: The main steps in the IWRM cycle. Taken from van der Keur et al. (2008).	5
Figure 2.1: Diagram showing the nitrogen cycle in water. Taken from Chapra (1997).	17
Figure 3.1: Regression of daily flow versus EC for three DWA monitoring stations occurring in different geological areas. E2H002: $9.98 \times 10^{-0.094}$, $R^2 = 0.32$; J4H004: $29.94x^{-0.14}$, $R^2 = 0.41$; Q1H001: $268.76x^{-0.80}$, $R^2=0.50$	57
Figure 3.2: Daily flow versus phosphate for the DWA monitoring station R2H010 on the Buffalo River, within ten km of two major point sources of phosphate.	58
Figure 3.3: Daily flow versus nitrate + nitrite for the DWA monitoring station R2H010 on the Buffalo River, within ten km of two major point sources of phosphate.	59
Figure 4.1: Example calibration process for estimating the point source signature in the historical data for DWA monitoring point R2H010.	70
Figure 4.2: Flow ($\text{m}^3.\text{sec}^{-1}$) versus the absolute residuals (observed – simulated water quality) generated by a simple conceptual model that predicts the point source signature in the relationship between flow and nutrient concentration. a. monitoring point R2H010 for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}); b. monitoring point B6H001 for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}); c. A2H012 for $\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N}$ (mg.L^{-1}); d. X1H001 for $\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N}$ (mg.L^{-1}).	72
Figure 4.3: Values of Y (Equation 4.10) in relation to flow and observed phosphate concentration. Graph 4.3a shows the point source dominated DWA monitoring point R2H010 and graph 4.3b shows the diffuse source influenced X3H006.	74
Figure 4.4: Graph a shows flow ($\text{m}^3.\text{sec}^{-1}$) versus $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}) observed data, as well as model simulated data for the DWA monitoring point R2H010. Graph 4.4b shows flow ($\text{m}^3.\text{sec}^{-1}$) versus $\text{NO}_3^- \text{-N} + \text{NO}_2^- \text{-N}$ (mg.L^{-1}) observed data, as well as model simulated data for the DWA monitoring point R2H010.	77
Figure 4.5: Diagram demonstrating the steps in a simple mechanistic model to separate the point source and diffuse source signatures in relation to flow in historical nutrient water quality modelling. This example is for the DWA monitoring point X3H006.	79
Figure 4.6: Examples of a simple mechanistic model applied to phosphate historical monitoring data of various DWA monitoring sites. a – A7H001; b – B3H021; c – R2H027; d – W5H026; e – X3H004; f – X3H008.	81
Figure 4.7: Examples of a simple mechanistic model applied to nitrate + nitrite historical monitoring data of various DWA monitoring sites. a – D3H015; b – S7H001; c – T1H001; d – V2H006; e – W5H026; f – X3H008.	82
Figure 5.1: Water quality management regions according to Day et al. (1998). Diagram taken from Day et al. (1998). Question marks indicate unclassified subcatchments.	89
Figure 5.2: PCA correlation biplot for PCA Axis 1 and PCA axis 2 for PCA applied to phosphate data for region 3. (Explanation of the abbreviations can be found in Table 5.1).	93
Figure 5.3: Land cover estimations of the diffuse source signature in historical monitoring	

data for phosphate. Four models were run on each confirmation data set: a- all regions; b- all regions riparian, c-region; d-region riparian.....	104
Figure 5.4: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b- all regions riparian, c-region; d-region riparian.....	109
Figure 5.5: Location map of cultivated land in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006).....	117
Figure 5.6: Location map of mines in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006).....	117
Figure 5.7: Location map of forest plantation in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006).....	118
Figure 6.1: Diagram representing a conceptual cross section of catchment and the movement of flow components through the catchment. The salinity signatures of the components of flow shown in the diagram are modelled by the mass-balance water quality model.	130
Figure 6.2: A conceptual diagram showing the partitioning of the catchment into two zones which represent irrigated area within a catchment. The salinity water quality model treats the two zones as separate units, with the top soil zone conducting interflow, and the bottom ground water zone conducting ground water flow. Water flows from the soil zone to the groundwater zone as groundwater recharge.....	131
Figure 6.3: Diagram showing the location of the Balfour River catchment within South Africa, and the dominant land cover types within the catchment. Water quality data were obtained from the weir Q9H019, indicated on the map.....	134
Figure 6.4: Diagram showing the location of the Breede River catchment within South Africa, and the dominant land cover types within the catchment as well as the position of the water quality monitoring gauges.....	137
Figure 6.5: Flow duration curve for the Balfour River, showing observed flow, and modelled flow using scenarios of no irrigation, 0.5 km ² irrigation and 1 km ² irrigation.	139
Figure 6.6: Duration curve for the Balfour River, showing observed and modelled TDS using scenarios of no irrigation, 0.5 km ² irrigation and 1 km ² irrigation.	141
Figure 6.7: Flow duration curve for the Breede River for the upstream site H4H017 showing observed and modelled flow.	142
Figure 6.8: Flow duration curve for the Breede River for the downstream site H5H005 showing observed and modelled flow.....	142
Figure 6.9: Graph showing observed TDS over time at the site H4H017 and the model monthly mean TDS simulations. Graph a – 1980 to 1985. Graph b – 1986 to 1990.....	143
Figure 6.10: Graph showing observed TDS over time at the sites H5H002 and H5H004 and the model monthly mean TDS simulations. Graph a – 1980 to 1985. Graph b – 1986 to 1990.....	146
Figure 6.11: Observed and model estimated seasonal distribution of TDS for the studied section of the Breede River. a – Upstream TDS; b- Downstream TDS.....	147
Figure 7.1: The Manning Equation is based on the assumption that a river channel cross sectional shape can be represented by a trapezoidal shape. B ₀ represents the bottom width, d represents the depth and s represents the side slope (Chapra, 1997).	156
Figure 7.2: a - Position of the Buffalo River catchment within South Africa. b - The catchment of the Buffalo River which lies within the Eastern Cape. c - The land cover categories occurring in the catchment of the Buffalo River in the vicinity of the DWA monitoring	

points R2R001 and R2H027.	164
Figure 7.3: a. Relevant land cover categories. b. Position of the Crocodile River catchment within South Africa. c. Land cover of the immediate catchment surrounding the monitoring points X2H017 and X2H016 on the Crocodile River.	165
Figure 7.4: a. Relevant land cover categories. b. Position of the modelled segment of the Orange River within South Africa. c. Land cover of the immediate catchment surrounding the monitoring points D8H008 and D8H004 on the Orange River.	166
Figure 7.5: Results of the Point - Diffuse Model applied to DWA historical data for the investigated section of the Buffalo River. a and d – R2R001; b and e – R2H027; c and f – model estimated point and diffuse signatures for the reach between R2R001 and R2H027.	168
Figure 7.6: Results of the calibration process for the Buffalo River. Flow on the x- axis represents the recorded flow at R2H027. a- observed and model estimated results for ammonium; b- observed and model estimated results for nitrite plus nitrate.	169
Figure 7.7: Results of the Point - Diffuse Model applied to DWA data for the investigated section of the Crocodile River. a, d and g – X2H017; b, e and h – X2H016; c, f and i – model estimated point and diffuse signatures for the reach between X2H017 and X2H016.	172
Figure 7.8: Results of the calibration process for the Crocodile River for Organic Nitrogen. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for observed flow up to $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$; b- model estimated results for observed flow greater than $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$	173
Figure 7.9: Results of the calibration process for the Crocodile River for ammonium. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for ammonium for observed flow up to $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$; b- model estimated results for ammonium for observed flow greater than $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$	173
Figure 7.10: Results of the calibration process for the Crocodile River for nitrite plus nitrate. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for nitrite plus nitrate for observed flow up to $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$; b- model estimated results for nitrite plus nitrate for observed flow greater than $0.4 \text{ m}^3 \cdot \text{sec}^{-1}$	174
Figure 7.11: Results of the confirmation process for the Crocodile River. Flow on the x- axis represents the recorded flow at X2H016. a- observed and model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.	175
Figure 7.12: Results of the Point - Diffuse Model applied to DWA data for the investigated section of the Orange River. a, d and g – D8H004; b, e and h – D8H008; c, f and i – model estimated point and diffuse signatures for the reach between D8H004 and D8H008.	177
Figure 7.13: Results of the calibration process for the Orange River. Flow on the x- axis represents the recorded flow at D8H008. a- model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.	178
Figure 7.14: Results of the confirmation process for the Orange River. Flow on the x- axis represents the recorded flow at D8H008. a- model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.	179

Figure 7.15: Examples taken from the Crocodile River calibration model showing how ammonification and nitrification leads to a decrease in model estimated organic nitrogen and ammonium respectively with residence time from the upstream site.	180
Figure 8.1: Map showing South Africa, with the Bloukrans River catchment outlined near Port Elizabeth, and the Buffalo River catchment outlined near East London.	188
Figure 8.2: Buffalo River catchment, showing sites investigated as well as predominant land cover.	191
Figure 8.3: Bloukrans River catchment showing sites investigated as well as predominant land cover.	197
Figure 8.4: QUAL2K model flow estimations as compared to observed flow measures in the Buffalo River for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of flow were taken.	206
Figure 8.5: QUAL2K model estimations as compared to observed water quality measures in the Buffalo River for a range of water quality constituents and for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of water quality were taken. The dotted lines indicate measures of maximum and minimum simulated data.	208
Figure 8.6: QUAL2K model flow estimations as compared to observed flow measures in the Bloukrans River for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of flow were taken.	214
Figure 8.7: QUAL2K model estimations as compared to observed water quality measures in the Bloukrans River for a range of water quality constituents and for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of water quality were taken. The dotted lines indicate measures of maximum and minimum simulated data.	215
Figure 9.1. An example of how the Mechanistic/Statistical Nutrient model and the land cover models developed in Chapters 4 and 5 can be used in scenario analysis for management.	243
Appendix B Figure 1: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.	298
Appendix B Figure 2: Linear regressions of flow versus nitrite + nitrate for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.	309
Appendix B Figure 3: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: a – all regions; b- all regions riparian zone.	310
Appendix B Figure 4: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: c – region 1; d- region 1 riparian zone.	311
Appendix B Figure 5: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: e – region 2b; f- region 2b riparian zone.	312
Appendix B Figure 6: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: g – region 3; h- region 3 riparian zone.	313
Appendix B Figure 7: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: i – region 4; j- region 4 riparian zone.	314

Appendix B Figure 8: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: k- region 5; l- region 5 riparian zone.	315
Appendix B Figure 9: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: a – all regions; b- all regions riparian zone.....	316
Appendix B Figure 10: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: c- region 1; d- region 1 riparian zone.	317
Appendix B Figure 11: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: e – region 2b; f- region 2b riparian zone.	318
Appendix B Figure 12: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: g- region 3; h- region 3 riparian zone.	319
Appendix B Figure 13: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: i – region 4; j- region 4 riparian zone.	320
Appendix B Figure 14: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: k- region 5; l- region 5 riparian zone.	321

Acknowledgements

I would like to acknowledge my supervisors, Nikite and Denis, for providing excellent supervision for this thesis. Sukhmani Mantel also acted as an unofficial supervisor. I must thank Roman Tandlich for showing me how to measure nutrient concentrations in water samples, on which much of this research depended. Nelson Odume, Bonga Zuma and Paul Mensah all helped on the field trips that I had to undertake for this research.

Declaration

The following thesis has not been submitted to a university other than Rhodes University, Grahamstown, South Africa. The work presented here is that of the author.

Chapter 1: General Introduction

1.1. The current water quantity and quality situation in South Africa

Demand for water has put freshwater resources in South Africa under increasing pressure. The natural flow regimes of rivers have been altered as all major rivers in South Africa are being regulated to some degree (Walmsley *et al.*, 1999). The majority of available fresh water in South Africa has already been allocated (Walmsley *et al.*, 1999), and return flow from point and non-point sources are becoming an increasingly large proportion of the low flow regimes of rivers (Herold and le Roux, 2004).

In addition, anthropogenic factors have influenced the quality of freshwater resources. There is a strong trend of increasing salinity in South African water resources, the causes including flow reduction in rivers, evaporative losses in surface waters, irrigation return flow, runoff from dry-land agriculture, saline industrial effluents, urban development contributions of point and non-point sources and atmospheric deposition (Anonymous, 2009; Kefford *et al.*, 2006; Kirchner *et al.*, 1997). Salinization of freshwater resources has a direct economic cost as water with a salinity of higher than 1000 mg.L⁻¹ becomes unsuitable for agriculture, human consumption and most industrial purposes, unless treated (Williams, 2001). Anthropogenically caused salinization in addition has negative effects on aquatic biota. The indigenous fauna and flora of southern Africa are typically adapted to temporal and spatial variability in salinity (Walmsley *et al.*, 1999). Anthropogenic influences often break down this natural variability and can lead to salinity levels in many impacted rivers being on average higher than natural levels with less temporal variability (Kefford *et al.*, 2002). Higher average salinities within impacted rivers in modern times have probably excluded the possibility of refuges for aquatic communities during high salinity periods, which in turn have decreased the level of re-colonization of rivers once salinities decrease (Kefford *et al.*, 2002). It is clear that salinization of freshwater resources needs to be managed and controlled to alleviate problems associated with salinity.

In addition, of concern are high levels of nutrients found in many South African rivers because of domestic and industrial effluent releases, which led to high levels of eutrophication (Walmsley *et al.*, 1999). Eutrophication, caused by an increase in urbanization and agriculture, has led to a range of environmental, social and economic problems (Withers and Jarvie, 2008). Environmental problems caused by eutrophication include an increase in periphyton growth (Figure 1.1) in shallow fast running streams and a reduced abundance of macrophytes, while slower moving streams have been affected by surface algal scum, low oxygen conditions and low light penetration (Withers and Jarvie, 2008), and in slower moving streams and impoundments, a high abundance of floating macrophytes (van Wyke and van Wilgen, 2002) (Figure 1.2). Besides eutrophication, nutrients can have direct toxic effects. For instance, nitrate pollution can cause human health problems (Chapra, 1997), while ammonia can in addition be toxic to fish (Chapra, 1997).



Figure 1.1: Strings of filamentous algae (*Batrachospermum*) attached to the stream bed of the Bloukrans River in the Eastern Cape, South Africa, in December 2009.

Effluents from point and diffuse sources, in addition introduce other environmentally damaging water quality variables to South African rivers, such as organic compounds that cause a decrease in dissolved oxygen as the decomposition process breaks down these compounds (Walmsley *et al.*, 1999). In addition, associated with point and diffuse source effluents are the introduction of faecal coliforms (Walmsley *et al.*, 1999), which can impact human and livestock health downstream. And of increasing concern within southern Africa, is the introduction of sulphate, suspended solids and metals to rivers due to acid mine drainage, which cause an acidification of water resources (Walmsley *et al.*, 1999). Pesticide application to crops often lead to contamination of water resources due to runoff from rainfall events, and Schulz (2001) has shown that pesticides can persist in water resources for a period of multiple months after the initial exposure.



Figure 1.2: Floating invasive water hyacinth (*Eichhornia*) on the Buffalo River just before Laing Dam in the Eastern Cape, South Africa in late 2009, caused by a combination of nutrient enrichment and alien invasives.

Water quality has become such a drastic problem in South Africa, that at the 14th South

African National Hydrology Symposium (Pietermaritzburg, South Africa, 21 - 23 September 2009), a representative of the Department of Water Affairs (DWA) commented that, in his opinion, a water crisis in South Africa is more likely to manifest itself as problems with water quality before a water quantity problem.

1.2. Integrated Water Resource Management (IWRM)

Aquatic ecosystems deserve protection, for reasons beyond just their intrinsic value and the protection of plant and animal species associated with aquatic habitats. This is because aquatic ecosystems provide various ecological goods and services. Aquatic ecosystems act as natural water purifying systems, and they provide resources such as fish, recreational possibilities and many other benefits (ANZECC, 1992; Costanza, 1987; Daily, 1999; DWA, 1996; Jewitt, 2002; Palmer *et al.*, 2002). Therefore, aquatic ecosystems should be developed and managed in a sustainable way so that the resilience and integrity of aquatic ecosystems are maintained within agreed limits. Recently, the argument has been made that the interaction between water resources such as surface and groundwater, and water vapour represented by the flow of water to the atmosphere, is of vital importance to understand as these are considered to control important terrestrial and aquatic ecosystem services (Jewitt, 2002). In this regard, the role of land use within a catchment is of critical importance (Jewitt, 2002). This is an example of the complexities and interactions within natural systems that need to be considered if resources are to be utilized in a sustainable way. Considering the need for integration of various complex natural processes, as well as consideration of water requirements of industry and society when managing water resources for sustainability, resulted in the development of the paradigm of Integrated Water Resources Management or IWRM.

IWRM as a paradigm, was developed in response to the need to find a reasonable compromise among various competing water users (Garcia, 2008), and aims to be integrative and holistic, considering the needs of various stakeholders, including the ecosystem (Anderson *et al.*, 2008). The need for a paradigm such as IWRM has increased in recent decades, as degradation of water resources worsen, and concerns over impacts

of climate change on water availability increase (Garcia, 2008). There are many definitions of IWRM, but the most accepted one internationally is that of the Global Water Partnership (GWP, 2003), which defines IWRM as: “a process which promotes the co-coordinated development and management of water, land and related resources, in order to maximize the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems”. Figure 1.3 shows the main steps in the IWRM cycle (van der Keur *et al.*, 2008).

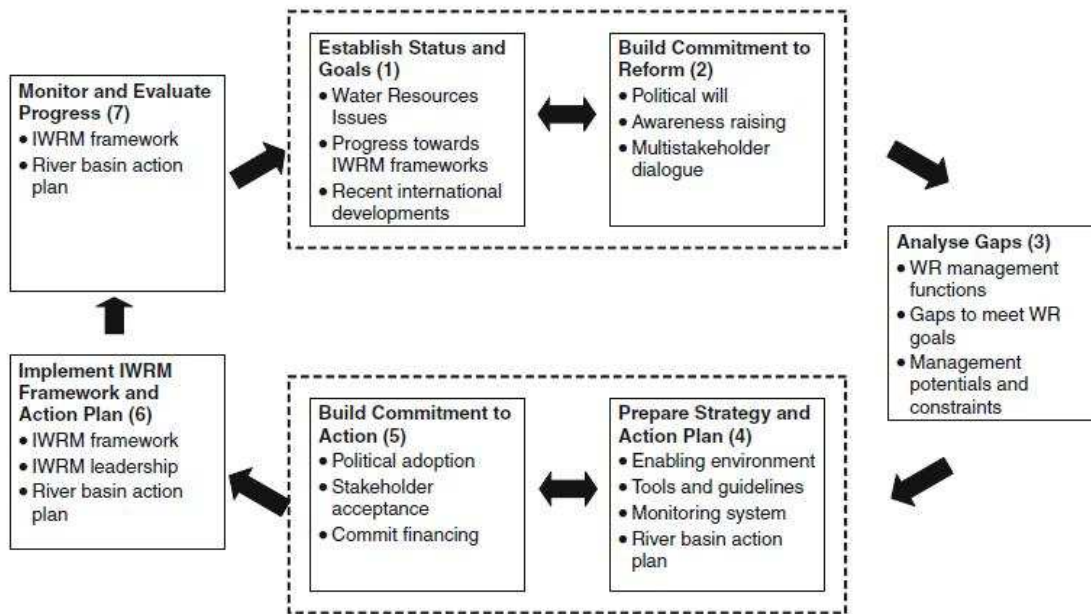


Figure 1.3: The main steps in the IWRM cycle. Taken from van der Keur *et al.* (2008).

Aquatic ecosystems stand to potentially benefit from IWRM, as the paradigm allows the environment a voice in the allocation debate, as well as highlighting the importance of maintaining aquatic ecosystems to other users (Leenderste *et al.*, 2008). The push for the adoption of IWRM principles from an ecosystem approach is especially strong from the environmental sector, as IWRM in this context places emphasis on maintaining the underlying ecosystem as the shared aim that can join other stakeholders when deciding management actions (Leenderste *et al.*, 2008). In the South African context, the National Water Act (Act 36 of 1998) was created in recognition that a fundamental reform of the

law was required to ensure that South Africa's scarce and unevenly distributed water resources are managed in a sustainable way for the benefit of all users (Wimberley and Coleman, 2005). The Act adheres to the principles of IWRM in that it seeks to address integration, redistribution, allocation equity, sustainable use, resource protection and participation in management by all relevant stakeholders (Pollard and du Toit, 2008). In South Africa, the enabling environment for IWRM is provided by Resource Directed Measures (RDM) within the National Water Act (Leenderste *et al.*, 2008). RDM comprises the classification of water resources, the Reserve, and the setting of resource quality objectives (RQOs) (Leenderste *et al.*, 2008). Pollution is managed through source directed controls on the principle of 'polluter pays', so as to ensure RQOs can be met (Leenderste *et al.*, 2008). The Reserve consists of the human needs Reserve and the ecological Reserve (Leenderste *et al.*, 2008). Catchment Management Agencies (CMAs) which work on a river basin level have been proposed in South Africa to implement IWRM (Leenderste *et al.*, 2008) and some are in operation.

While many countries such as South Africa have in the recent past moved towards adopting policies that recognize IWRM, recently, the IWRM paradigm has received increasing criticism, with some authors questioning why IWRM has failed to deliver results (Garcia, 2008; Jonker, 2007; McDonnell, 2008). Some, for example Merrey (2008), have even called for IWRM to be abandoned for more suitable paradigms. Merrey (2008) for example proposes a bottom up approach of focusing on finding solutions for specific problems identified within a basin within an integrated framework, rather than starting with broad principles and applying these to specific situations. According to the Global Water Partnership (2000), the successful implementation of IWRM depends on putting in place the appropriate policies and legislation, appropriate institutional frameworks through which policies can be implemented, and finally implementing appropriate management tools to enforce policies and legislation. IWRM is easier to implement at the constitutional and associated strategic or policy levels, but there are major obstacles to implementing IWRM at the operational level. There are various contributing factors to this problem, with the factor that is most applicable to this thesis being the lack of data and hence knowledge, either measured or simulated, to

represent various processes that one would have to consider when implementing IWRM policies at the operational level. Biswas (2008) has listed approximately 41 sets of issues that cannot be integrated at our present level of knowledge, both in South Africa and globally. These include processes such as surface water and groundwater interactions, irrigation and drainage, and many others. Biswas (2008) warned that unless our knowledge on these processes increases, so as to translate integrated processes into operational reality, IWRM as a paradigm will fade in a few years such as similar paradigms that came before it. One of the processes for which there are few operational simulation methods, is the relationship between flow and water quality (Biswas, 2008; Garcia, 2008). The relationship between flow and water quality is especially important in relation to the National Water Act (Act 36 of 1998). This is because the Act includes the provision for an ecological Reserve, or the quantity and quality of water required to maintain aquatic ecosystems.

1.3. The ecological Reserve

The ecological Reserve stipulates two components of water resources needed to maintain aquatic ecosystems, namely flow (quantity) and quality. It is therefore important for methods to be available that would quantify these two components. Methods have been developed to determine the flow (quantity) requirements in rivers needed to maintain aquatic ecosystems both nationally and internationally. International examples include the Instream Flow Incremental Methodology (IFIM) developed in the United States (Stalnaker *et al.*, 1994) and the ‘Holistic Method’ developed in Australia (Arthington, 1992). In South Africa, the Building Block Methodology or BBM was developed to determine the quantity component of the ecological Reserve (King and Louw, 1998; King *et al.*, 2000; O’Keeffe, 2000). This is typically a 5 stage process where the first stage is the generation of data, either from existing flow gauges or from rainfall – runoff modelling. The second stage is a data interpretation stage involving a workshop where flow data is separated into duration curves, base flow, high and low flow. The third stage involves determining the ecological flow for maintenance and drought conditions. The fourth stage involves scenario modelling while the last stage involves implementing the

recommendations.

In contrast to the relative maturity of ecological flow Reserve assessment methods, the water quality consequences of flow within a river remain a relatively undeveloped area of research. Usually, only descriptive predictions of flow consequences on water quality are made (Malan and Day, 2002a), or regression or statistical models relating flow to water quality are used (Wimberley and Coleman, 2005). Malan and Day (2002a) made an initial attempt at confronting this problem, but much more research is required before it can be claimed that methods have reached any level of maturity. Unless the issue of water quality is addressed when determining the flow regime required to maintain riverine ecosystems, optimal ecosystem health will not be attained (King and Louw, 1998). Therefore, quantitative predictive methods of linking river flow to water quality are needed (Malan and Day, 2002a).

1.4. Data constraints on representing the relationship between flow and water quality

McDonnel (2008) has highlighted the prerequisite of basic data to support IWRM. While many countries have reasonably good flow data for main river reaches, there are often a paucity of water quality data (McDonnel, 2008). This is mirrored by the situation in South Africa. While the Department of Water Affairs (DWA) has reasonably good daily flow data for various rivers, water quality data is sparse in comparison, with temporal gaps of multiple years between measures in some extreme cases. While the Department of Water Affairs (DWA) maintains a hydrological database that provides much of the data that would be needed for salinity modelling, the database only provides some of the data that would be required for nutrient modelling (Wimberley and Coleman, 2005). However, these are the only easily available data with which to work, and it is important that any research into the relationship between flow and water quality be focused on using these data in an optimal way. Therefore, models that are either developed from scratch, or adopted, must be able to obtain reliable results using the available data.

1.5. Flow – water quality model requirements to be useful in the context of IWRM

As has been mentioned previously, the current lack of knowledge in regards to the interactions between flow and water quality, are a barrier to successfully implementing IWRM policies. Water resource managers, who have the task of implementing policies that are in line with IWRM, will have to make decisions in the face of high system complexity and uncertainty (Liu *et al.*, 2008). In regards to the interrelationships between flow and water quality, the integration of reliable scientific information will facilitate water managers to make these decisions with more confidence.

While there are a range of modelling approaches that can be investigated, this thesis has investigated multiple models that are appropriate for the data that are easily available, as well as a complex model that required dedicated data collection. In the context of implementing IWRM in South Africa, where managers may not have the training or resources to utilize complex models, simpler and easier to understand models may be more appropriate than complex models. In addition, the availability of simple models that only simulate a few key processes, or restrict the water quality variables simulated to one or two variables, may be more appropriate than complex models in specific cases. For example, where there are certain critical processes and water quality variables of concern within a catchment. The option of a suite of relatively simple models would allow managers to concentrate on the appropriate model or models, thereby cutting out the extra data requirements, complexity, time and money that would be spent on more complex models that simulate non-critical processes and water quality variables in addition to the critical ones. There is much debate in the literature regarding the question of whether complex models are more useful than simple models for water resource management, for example Beck (1987), McIntyre *et al.* (2003), Reckhow (1994), and Young *et al.* (1996). This issue is pursued further in Chapter 2, but it can be mentioned here that generally water quality managers avoid large mechanistic models and tend to prefer relatively simple models (Reckhow, 1994). In addition, as highlighted by Beck (1987), it can be mentioned here that very simple models are not appropriate for water resource

management. Very simple models, such as simple statistical relationships, will base cause-effect relationships on past behavior of a system. Unless some mechanistic understanding is incorporated, these models will predict incorrect future behavior if there are changing conditions, and even more seriously, will assign high confidence to these predictions. For an example, see the models investigated in Chapter 3. However, at the other extreme, very complicated models, while capable of predicting correct future behavior, will have very little confidence assigned to their predictions as they are too complex to be proven accurate. Another argument against the use of complex models is the increasing need to incorporate uncertainty into model predictions. This is linked to risk assessment in management of water resources. Risk can be defined as ‘a combined measure of the degree of detriment to society or the aquatic ecosystem caused by a defined event (or combinations of events), and the probability of that event occurring’ (McIntyre, 2003). McIntyre (2003) states that uncertainty in model output should be viewed as a form of risk, and that risk assessment can be used to determine management actions that achieve an acceptably low failure probability. The incorporation of uncertainty into models is useful for management of water resources, as managers need to know the risk of implementing certain management actions, and the uncertainty of model simulations of reality needs to be explicitly shown, so as to highlight the areas where further research is required (Reckhow, 1994). As model complexity increases, the ability to evaluate uncertainty in these models will decrease due to the large number of uncertain model components (McIntyre *et al.*, 2003). Therefore, relatively simple models that give approximate solutions may be more appropriate than extremely complex models, as it is possible to supply an indication of uncertainty around predictions (McIntyre *et al.*, 2003). Therefore, it is clear that very simple models as well as very complex models may be inappropriate for use in making management decisions. This research has therefore aimed to investigate models that are relatively simple, and fall somewhere in between the very simple models and the very complex models in terms of complexity.

This thesis progresses from investigating simpler models such as statistical models and simple mechanistic models to the more complex QUAL2K (Pelletier *et al.*, 2006) model. The investigation of QUAL2K demonstrates the data that would be required to run a relatively complex model, and whether this sort of model could be appropriate for

implementing IWRM policies in South Africa. While the scope of this thesis did not allow for the investigation of complex catchment scale model frameworks such as BASINS (Better Assessment Science Integrating Point and Non-point Sources) (Wimberly and Coleman, 2005), QUAL2E is incorporated as the water quality model in the BASINS framework (Tong and Chen, 2002). Since QUAL2K is the modernized version of QUAL2E (Wimberly and Coleman, 2005), the investigation of QUAL2K in this thesis can give an idea of how appropriate a framework such as BASINS would be in the context of implementing IWRM in South Africa.

Research into the relationship between flow and water quality, and the development of models to simulate the relationship, will help reduce the uncertainty of decision makers with regards complexities and processes within freshwater systems. This type of uncertainty is called epistemic uncertainty, or uncertainty due to imperfect knowledge of a system (van der Keur *et al.*, 2008), and in the context of this thesis, imperfect knowledge of the relationship between flow and water quality. Epistemic uncertainty occurs due to limitations in observed data, limitations of models and limited understanding of processes (van der Keur *et al.*, 2008). Therefore, reducing this form of uncertainty with regards to the relationship between flow and water quality can be obtained by collecting more observed data, research into understanding how flow affects water quality, and refining models to be more representative of the processes where flow affects water quality. Within the process of implementing IWRM policies (Figure 1.3), research into modelling the relationship between flow and water quality, should reduce the uncertainty within step 4 (see Figure 1.3), as tools to represent the relationship between flow and water quality would be improved.

It can be seen that models that predict the relationship between flow and water quality, bring improved understanding of just one of many relationships within freshwater systems that must be considered within the IWRM paradigm. However, this is an important relationship, and current knowledge levels are insufficient. Therefore, this research can be an important step in increasing the success of implementing the IWRM paradigm within southern African watersheds.

1.6. Aims

Within the scope of the research topic of this thesis, there are various factors to consider, which will have an important influence on the aims of the research. These factors are listed below:

1. More complex models do not necessarily have more utility. The complexity of the model appropriate for a particular system depends on the complexity of the system, the most important processes acting on that system, the resources available (data, money, time and expertise) and the aims of the modelling exercise. Therefore, it is important to start with simpler models and progressively investigate and develop more complex models.
2. It is important to consider the effect of catchment use/land cover on water quality because of the effect of diffuse sources.
3. Point sources have a major effect on river water quality, especially rivers dominated by low flow and flowing through areas of dense industrial activity and urban settlement. It is therefore important to investigate an in-stream model that can simulate the effect of point sources on water quality.
4. Data availability for modelling in South Africa is a problem, especially in terms of water quality data. Therefore, it is important to investigate models that can utilize data that are available as effectively as possible.

Therefore, the aims identified in this thesis are:

Aim 1: Can the relationship between flow and water quality be accurately represented by simple statistical models?

Aim 2: Can relatively simple models accurately represent the relationship between flow and water quality?

Aim 3: Can the effect of diffuse sources be omitted from a water quality model and still obtain realistic simulations, and if so under what conditions?

Aim 4: Can models that solely use historical monitoring data, accurately represent the relationships between flow and water quality?

The structure of the chapters is therefore:

1. Chapter 2 is a literature review of the relationships between flow and water quality and issues around modelling these relationships.
2. Chapter 3 addresses Aim 1 and partly Aim 4, and investigates statistical methods of relating water quality to flow. The models investigated in this chapter will be termed ‘Q-C Regressions’ throughout the thesis.
3. Chapter 4 partly addresses Aim 2 and Aim 4 and investigates a simple mechanistic/statistical method of relating water quality to flow. This model will be termed the ‘Mechanistic/Statistical Nutrient Model’ throughout this thesis.
4. Chapter 5 partly addresses Aim 2 and Aim 3 and investigates a statistical method of relating land cover to flow and water quality. This model will be termed the ‘Land Cover Model’ throughout this thesis.
5. Chapter 6 partly addresses Aim 2 and outlines the extension of a mass – balance salinity model that models salinity in ephemeral and perennial rivers, considering the effect of irrigation return flow. This model will be termed the ‘Mass Balance Salinity Model’ throughout this thesis.
6. Chapter 7 partly addresses Aim 2 and Aim 4, and outlines a simple nutrient model developed specifically to use the sparse DWA flow and water quality data that are available in the most effective way possible. This model will be termed the ‘Simple Nutrient Model’ throughout this thesis.
7. Chapter 8 partly addresses Aim 3, and investigates the use of QUAL2K on two rivers in the Eastern Cape, South Africa.
8. Chapter 9 provides conclusions and recommendations learnt from the previous chapters.

Chapter 2: Literature Review

2.1. Water quality constituents that may be changed by flow

Water quality constituents are generally classified as either conservative or non-conservative. Conservative constituents remain relatively unchanged in chemical composition throughout their movement along a river channel, while non-conservative constituents typically undergo chemical changes over time (Malan and Day, 2002a). Examples of conservative water quality constituents are the inorganic salts that contribute to salinity such as chlorides (Malan and Day, 2002a,b). Nitrogen and phosphorus chemical species are examples of non-conservative chemical constituents as they change form over time (Malan and Day, 2002a,b).

Flow velocity has a direct effect on both conservative and non-conservative water quality constituents. Freshwater flow dilutes water quality constituents and controls the velocity at which pollutants move downstream, and in addition affects reaction coefficients (Hydroscience, Inc., 1971). In addition, flow controls the residence time of water within a river reach, and therefore, the time available for nutrients to be assimilated by biota, undergo chemical changes, or settle to the sediment.

The relationships of water quality constituents to flow differ according to the water quality constituent, and the relationship may be site specific, where factors such as climatic region, land use and underlying geochemistry play a role (Malan and Day, 2002a). Some generalizations can be made with some water quality constituents, but the high variability in response makes quantifying a general relationship difficult and prone to error (Malan and Day, 2002a).

2.1.1. Salinity

Inorganic salts collectively influence the salinity of natural surface waters. In South Africa, these salts include sodium chloride, calcium carbonate and salts containing

sulphates and magnesium (Day, 1993; Day and King, 1995). Salinity values as electrical conductivity (EC) are generally well represented within the Department of Water Affairs (DWA) data (Wimberley and Coleman, 2005).

In South Africa, salinity shows a general trend of increasing in low flow and decreasing in high flow as salts become diluted (Malan and Day, 2002a,b). This trend may however be obscured by anthropological effects, such as the first rain washoff event on irrigated land that has become salinized. Malan and Day (2002a) did some initial research on discharge – concentration or Q-C patterns in South Africa. In this study, Department of Water Affairs (DWA) mean monthly flow data and median monthly water quality data for particular monitoring sites were statistically analyzed for relationships using simple regression. The researchers in addition tried to identify patterns in relationships according to ecoregions (Kleynhans and Hill, 1999) and drainage regions. They found that conservative variables including electrical conductivity and various salts, decreased either logarithmically or linearly with flow. Simpson (1991) studied 6 catchments in South Africa with wide ranging diffuse source influences, and found that EC followed a consistent trend of decreasing with increasing flow, except for 1 catchment which contained a livestock feedlot, where EC increased with increasing flow. Wang and Yin (1997) found that conductivity was negatively correlated with flow in a study of the relationship between land use and water quality of stations along the Miami River in the US. McDiffet *et al.* (1989) found that in a small stream in the US, fed by a farm dam, that the concentrations of Ca^{+2} and Mg^{+2} were negatively correlated with flow rate. The authors concluded that Ca^{+2} and Mg^{+2} behave in such a way in their study because they are derived from groundwater.

2.1.2 Turbidity

The turbidity of natural surface water relates to the amount of suspended particles within the water column, and high turbidities in rivers usually occur after heavy rainfall that washes sediments into rivers. Turbidity generally increases with increasing flow, but high levels of turbidity may level off as silt from the surrounding catchment becomes depleted

(Malan and Day, 2002a,b). However, this relationship is variable and depends on land use, hydrology and geomorphology of a particular region (DWA, 1996). Anthropogenic caused problems such as overgrazing, agriculture, removal of riparian vegetation and forestry cause an increase in erosion and therefore, increased loads of suspended solids in rivers (DWA, 1996). All rivers in South Africa, except for those found in the foothills of the Drakensburg and the southern parts of the Western Cape, become more turbid with increasing flow (DWA, 1996). Point sources may in addition contribute to turbidity in rivers (DWA, 1996). Simpson (1991), in a study of land use effects on water quality within 6 South African catchments influenced by various diffuse sources, found that turbidity increased with increasing flow, although the rate of increase was variable between the catchments. Hunter and Walton (2008), in a study of the Johnstone River catchment of the Great Barrier Reef, found that suspended sediment concentrations were low under base flow conditions, but increased sharply with runoff events. However, this relationship was variable and depended on land cover.

Turbidity values are not well represented within the DWA data, and data that are available are recorded as Nephelometric Turbidity Units (NTUs).

2.1.3. Nutrients

Phosphorus and nitrogen chemical species that occur in aquatic environments are broadly termed nutrients, as they are utilized by flora such as algae, phytoplankton and macrophytes. The main natural sources of nutrients are from erosion, the atmosphere and riparian vegetation (Withers and Jarvie, 2008). Anthropogenic sources of nutrients include agricultural runoff, waste water treatment plants, and road runoff.

Phosphorus can occur in water as particulate or dissolved fractions. In addition, phosphorus can be bound to organic matter, or occur as inorganic phosphate, which is the most bio-available form to flora. Total Phosphorus (TP) is a measure of all available phosphorus in water, including the particular organic and inorganic forms, and the soluble organic and inorganic forms. Soluble Reactive Phosphorus (SRP) is more biologically

available and is a mixture of dissolved inorganic and organic species. Nitrogen in addition exists in particulate and dissolved forms within water. The dissolved inorganic forms of nitrate, nitrite and ammonium are the most bioavailable (Khalili and Weyhenmeyer, 2009). Nitrate (NO_3^-) concentrations usually exceed ammonium (NH_4^+) and nitrite (NO_2^-) concentrations in streams (Khalili and Weyhenmeyer, 2009). Nitrogen species undergo a cycle in natural waters (Chapra, 1997) (see Figure 2.1). Chapra (1997) summarizes the process well: nitrogen existing as organic nitrogen can undergo a process called ammonification, being converted to ammonium. Ammonium can undergo nitrification to form nitrite. Nitrite can in turn be nitrified to nitrate. The process of nitrification consumes oxygen. However, both nitrate and nitrite under anoxic conditions undergo denitrification, which releases oxygen.

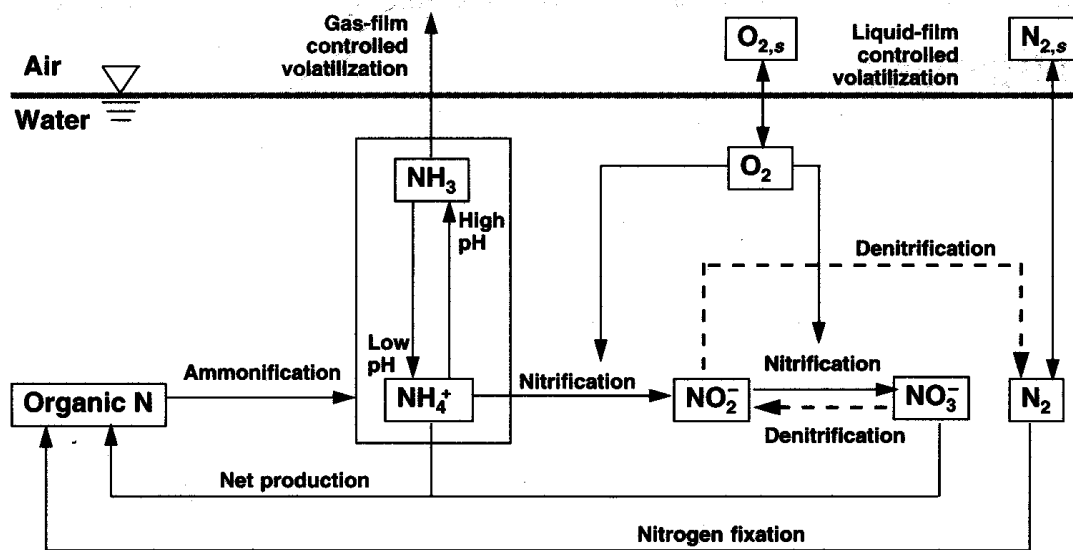


Figure 2.1: Diagram showing the nitrogen cycle in water. Taken from Chapra (1997).

Since phosphorus is a nutrient that is assimilated by flora within water systems, in-stream phosphorus concentrations can be influenced by biotic factors (Lottig and Stanley, 2007). These biotic factors include assimilation by primary producers and decomposers as well

as mineralization of organic phosphorus (Lottig and Stanley, 2007). Gosselain *et al.* (1998), in a study of the Belgian section of the River Meuse, found that grazers influence control over the population of phytoplankton, and consequently over phosphorus concentrations, during low flows when residence times of water are high. Ruggiero *et al.* (2006) in a study of nutrient retention of a 3rd order stream in Italy, found that nutrient retention is negatively correlated with discharge. This supports the idea that lower discharge increases residence time and allows longer interaction of chemicals in the water column with the streambed, allowing increased abiotic and biotic processes at the interface between the streambed and water column. The increased residence time allows greater nutrient assimilation by algae, heterotrophic microbes, macrophytes, bryophytes and riparian plants (Ruggiero *et al.*, 2006). This is supported with findings by Behrendt and Opitz (2000), who found that phosphorus retention was higher for smaller catchments with low runoff and low flow in a study of 100 different river basins in central Europe. In contrast, abiotic processes tend to control phosphorus during high flow, such as the phosphorus equilibrium between suspended sediment and soluble phosphorus, and shorter residence times allowing less biological uptake (Froelich, 1988). Larger rivers tend to transport more sediment, with associated particulate phosphorus which gets deposited onto river beds (James and Larson, 2008). A significant percentage of this deposited phosphorus can become biologically available over time through equilibrium processes and bacterial transformations. This effectively keeps phosphorus concentrations in the water column high in some rivers, even during low flow. Factors influencing this process include redox status, pH, cation concentrations, variation in sediment composition and particle size (Froelich, 1988).

Sediments can act as important sinks for phosphorus, which bind readily to sediment particles, and it is generally accepted that the concentration of soluble reactive phosphorus is regulated by exchange between the sediment and the water column (Stutter and Lumsdon, 2008). Stutter and Lumsdon (2008) investigated the hypothesis that sediments can act as a phosphorus sink during moderate to high flows, but phosphorus sources during base flows. In a study of impacted and un-impacted tributaries in a river system in north-east Scotland, Stutter and Lumsdon (2008) found that sediments

remained a phosphorus sink in impacted tributaries during changing flow conditions, while sediments in un-impacted tributaries switched from being phosphorus sinks during high flows to phosphorus sources during base flows. The authors hypothesize that the phosphorus equilibrium in impacted tributaries stayed in the direction of phosphorus moving from the water column to sediments, because of internal biochemical cycling. This study in addition found large stores of phosphorus in sediments in impacted tributaries. This supports the hypothesis that sediments in impacted tributaries may act as phosphorus sources for an extended period after sources of phosphorus loading are reduced or removed. However, Van Nieuwenhuysse (2007) found that after a gradual reduction of phosphorus in the Rhine River by a factor of almost 3, concentrations of chlorophyll-a declined by a factor of 4. The same study found that an abrupt reduction of phosphorus in the San Joaquin Delta in Sacramento by a factor of 1.5, led to an equally abrupt decrease in chlorophyll-a by a factor of almost 3. Both systems were previously receiving phosphorus concentrations in the range of 10 – 100 mg.m⁻³. This led the authors to conclude that the control of phosphorus may be an effective tool for managing eutrophication in rivers.

In South Africa, total phosphorus shows a general trend of increasing with flow, as a large proportion of phosphorus is bound to sediments (Malan and Day, 2002a,b). This however, does depend on the amount of phosphorus in the catchment soil profile, and elevated amounts of phosphorus can enter rivers where the surrounding land use introduced phosphorus to the soil, such as the case with agriculture (Malan and Day, 2002a). Grobler and Silberbauer (1985) in a study of phosphate loading in the Vaal and Limpopo River basins in South Africa, found that phosphate loads in relation to runoff in the Vaal was higher than in the Limpopo because of the sedimentary geology that dominates in the Vaal basin. This supports the assertion that phosphorus is often bound to particulate matter leading to phosphorus loading into rivers usually occurring during strong rain events that cause erosion and sediment movement into rivers. Simpson (1991) quantified the effects of land use on runoff water quality in 6 catchments within South Africa. These catchments had land use practices associated with diffuse sources of pollutants ranging from farming to forestry, natural to subsistence farming. When studying the relationship

between particulate phosphorus and flow, Simpson (1991) found that particulate P increased with increasing flow, although the rate of increase was different between the catchments. Jordan *et al.* (1997a) found that phosphorus concentrations correlated strongly with particulate matter concentrations in the water quality data, indicating that phosphorus loading occurred predominantly as particulate forms during runoff associated with rainfall events. Washoff from urban areas can in addition cause an influx of phosphorus into rivers during high flow, as these areas have sources of phosphorus on the soil surface and in groundwater (Hughes and van Ginkel, 1994). Britton, Day and Henshall-Howard (1993) investigated the effect of storm events on water quality in a South African mountain catchment and found that the relationship between PO_4^{3-} concentrations and flow varied seasonally. McDiffet *et al.* (1989) investigated the relationship between nutrient concentration and discharge during storm events in a small stream in the US. In this stream, fed from a nutrient rich farm dam, phosphate showed an initial trend of increasing concentration early in a storm event, with dilution starting later in the event.

Using data from the River Swale, River Frome and River Avon in the United Kingdom, Bowes *et al.* (2008) recognized distinct statistical relationships between flow and phosphate loading, according to whether loading occurs through point or diffuse sources. In rivers receiving a majority of point source inputs of phosphorus, concentrations will be highest at low flow and will decrease with higher natural flow as the phosphorus laden waste water is diluted. However, rivers that receive diffuse sources of phosphorus will exhibit an increase in phosphorus concentration with an increase in natural flow caused by rainfall runoff. The conclusions drawn up by Bowes *et al.* (2008) are supported by Jarvie *et al.* (2005) and Withers and Jarvie (2008). Wood *et al.* (2005), in an evaluation of diffuse and point phosphorus sources on the Taw River basin in England, found that there were large increases in phosphorus in some rivers during low flow, indicating point sources, while there were increases in phosphorus with high discharge in some areas associated with diffuse sources, although the regression relationships were weak ($R^2 < 0.35$). Interestingly, according to the results obtained by Wood *et al.* (2005), phosphorus export may be linked to specific soil types and land use, and less to the volume of

discharge from waste water treatment plants.

Nitrate is highly soluble in water, and nitrate concentrations in rivers may increase during storm events (Malan and Day, 2002a,b). This however, in addition depends on the land use within river catchments (Malan and Day, 2002a). As is the case for phosphorus, Hughes and van Ginkel (1994) showed that urban areas are sources of nitrogen on the soil surface and in groundwater, which may lead to elevated levels of nitrogen in rivers during washoff events and associated high flows. Britton, Day and Henshall-Howard (1993) investigated the effect of storm events on water quality in a South African mountain catchment and found that the relationship of NO_2^- and NO_3^- with flow varied seasonally while NH_4^+ was not influenced by season. NO_3^- was significantly positively related to flow during summer storms. Simpson, in the study of land use effects on water quality within 6 South African catchments influenced by diffuse sources, found that nitrate concentrations increased with increasing flow. As was the case with phosphate, McDiffet *et al.* (1989) found that in a stream fed from a nutrient rich farm dam, nitrogen showed an initial trend of increasing concentration early in a storm event, with dilution starting later in the event.

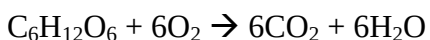
Groundwater usually transports NO_3^- in well drained soils as NO_3^- is highly soluble. This is supported by Jordan *et al.* (1997b) in a study of watersheds in the Chesapeake Bay drainage region. This study found that there was a strong correlation between proportions of cropland and a baseflow index (a measure of the importance of base flow relative to total flow, including periodic high flow events) to NO_3^- concentrations, and that the rate of increase in NO_3^- is greater for watersheds that are dominated by baseflow. The baseflow index did not have the same correlation however with ammonium and phosphorus. In a study of nutrient concentration patterns of flow in an agriculturally dominated catchment in the north-east United States, Pionke *et al.* (1999) found that NO_3^- concentrations were the highest in elevated baseflow (flow following a storm). In an assessment of nutrient fluxes along the River Avon, United Kingdom, Jarvie *et al.* (2005) found that NO_3^- concentrations increased with flow, showing the importance of diffuse source inputs to the river. The river Avon is groundwater dominated, and the authors of

this study hypothesized that nitrate is introduced primarily from the mobilization of near-surface soil waters during rainfall, which seep into groundwater sources. Hunter and Walton (2008), in a study of the Johnstone River catchment of the Great Barrier Reef found that dissolved NO_3^- concentrations increased with higher flows and remained high for a considerable time, indicating that nitrogen was probably being introduced through ground water.

There is limited representation of nutrients within the DWA data. Inorganic phosphate as orthophosphate (PO_4^{3-}) is relatively well represented. The inorganic forms of nitrogen are relatively well represented, with NO_3^- being the most frequently represented, while there are occasionally measured values of NO_2^- and NH_4^+ available. There are some values of organic nitrogen, as Kjeldahl nitrogen, in the data sets for a few gauging stations.

2.1.4 BOD

Organic compounds in water undergo decomposition, which utilizes oxygen (Chapra, 1997). The process can be written out as a chemical reaction if organic matter is assumed to be a simple sugar like glucose (Chapra, 1997):



One could model the decomposition of organic matter in water by measuring the decomposition rate of glucose in the laboratory. However, this approach would be problematic as organic matter is not composed of simple sugars, and varies greatly in composition both between different sources and over time. Because it is very difficult to determine the composition of organic matter in water, the analysts who developed the method of measuring oxygen consumption due to decomposition of organic matter, ignored the composition of water samples, and a method was developed where samples were simply introduced to a batch reactor and the amount of oxygen consumed was measured (Chapra, 1997). The quantity was termed Biochemical Oxygen Demand or BOD (Chapra, 1997). Two measures of BOD are usually measured. A shorter reacting

time measure called the BOD₅ over 5 days, and an ultimate BOD value over 21 days, or the BOD₂₁, where it is assumed that all organic matter in the sample has decomposed.

Although there are not many published studies that provide knowledge regarding the effect of flow on BOD, intuitively, one would expect higher flows to decrease residence times of water within a river reach, thereby limiting the effect of decomposition processes on decreasing dissolved oxygen concentrations. Chung *et al.* (2008) investigated the effect of reservoir flushing on the Geum River in Korea and found that there was a sharp increase in BOD and a slight decrease in DO, possibly due to re-suspension of organic matter.

The DWA does not routinely measure BOD, although measures of dissolved oxygen (DO) are fairly well represented.

2.2 Impoundments and IBTs

This research focuses on modelling the effect of flow on water quality within rivers. However, it should be mentioned that impoundments and inter-basin transfer schemes (IBTs) impact water quality in ways that are fundamentally different to the dynamics that control flow and water quality interactions in rivers, and as such, are beyond the scope of this thesis.

There is not much research on the effect of flow on water quality within impoundments, although there has been some work on the effect of impoundments on water quality in general. In a comparison of the effect of impoundments on water quality on the Buffalo River in the Eastern Cape, and the Palmiet River in the Western Cape, O'Keefe *et al.* (1990) found that impoundments changed the temperature of water flowing downstream, with the temperature increasing after impoundments in the upper reaches, and decreasing after impoundments in the lower reaches. O'Keefe *et al.* (1990) in addition found that changes in TSS, salinity, alkalinity and nitrates occurred downstream of impoundments. However, there were few consistent changes in the variables affected across all

impoundments and the authors declined to claim generalizations but did stress that the position of the dam on the river, the release mechanism and influent pollution are important. Palmer and O'Keeffe (1989) found that the effects of impoundments on the Buffalo River were restricted to no more than 15 km downstream. Nitrogen and phosphate species decreased in concentration due to dilution.

Inter-basin transfers (IBTs) change the flow regime of both recipient and donor systems. In South Africa, the transfer scheme from the Orange to the Fish River resulted in a lower salinity in the Fish River (Snaddon, Davies and Wishart, 1999). The transfer of water from Riviersonderend River to the Eerste Rivier in the Western Cape, resulted in changes to pH, conductivity, TSS, TDS, Na^+ , Mg^{+2} , K^+ and Ca^{+2} , SO_4^{-2} and Cl^- in the recipient river (Snaddon, Davies and Wishart, 1999).

2.3 The link between diffuse sources and high flow, and point sources and low flow

A point source of pollution is a source that is easily identifiable and is a source that discharges from a specific and confined space, such as a pipe for example (Pegram and Gorgens, 2001). Diffuse sources (non-point sources) on the other hand, are due to rainfall runoff from the surface of a catchment and may be intermittent and result in input of pollutants to surface waters over a large and diffuse area (Pegram and Gorgens, 2001).

Generally, pollutants from diffuse sources, such as agriculture, livestock farming and human settlements, become washed into rivers in significant amounts only during rainfall events (Pegram and Gorgens, 2001). Grobler and Silberbauer (1985) found that variation in phosphorus export within and between studied catchments not influenced by point sources in South Africa, were a function of runoff. Variation in export of phosphorus within catchments that contained mostly point sources of phosphorus was not a function of runoff. In addition, Grobler and Silberbauer (1985) found that a certain threshold of runoff is required before export of phosphorus can occur. Simpson and Stone (1988), in a study of urban runoff pollution, found that the magnitudes of export coefficients of

pollutants in the catchment studied were a function of rainfall, with higher rainfall resulting in higher pollutant load exports. Simpson (1991) in a study that attempted to quantify the effects of land use on runoff water quality within certain catchments in Kwazulu-Natal, found that concentrations of suspended solids, particulate phosphorus and nitrate, increased with increasing flow.

It can be argued that model development for simulating the effect of nutrient input to South African rivers, should at this stage focus on point sources, with a long term goal of incorporating the effect of diffuse sources as data become available. Firstly, rainfall events are infrequent in a large proportion of South Africa and therefore, pollutant loadings from diffuse sources are an infrequent event. Secondly, pollutant loads from diffuse sources are likely to occur during high flows and would therefore be diluted. Thirdly, high flow would in addition decrease the residence time of nutrients in rivers, effectively flushing the nutrients downstream before they can be assimilated by flora. High flow and the associated load from diffuse sources would in addition very likely coincide with high turbidity levels, thereby lessening the effects of eutrophication as primary production would be limited by low light penetration. Some of these arguments however can become invalid in the case where impoundments have been built along rivers. Impoundments would trap pollutant loads from diffuse sources, unless flow was high enough to flush dams.

In contrast, it can be argued that point sources of pollutants are very important to control, especially in the South African context, for various reasons. Firstly, point sources are relatively constant compared to diffuse sources, and release pollutants that affect the low flow of rivers, which is the predominant flow within South African rivers. Secondly, low flow coincides with the growing season of algae and phytoplankton in winter rainfall areas such as the Western Cape. Thirdly, low flow would in addition most likely be of a low turbidity, and would allow high algae and phytoplankton growth in the presence of nutrients due to increased penetration of light.

Depending on whether point sources can be effectively monitored and whether

monitoring data for point sources are reasonably accurate, it may be simpler to model the effect of point sources of pollutants on water quality than to attempt to model the effect of diffuse sources on water quality. It can be argued that simpler models that initially only model point sources may be a useful compromise where less monitoring data are required, and models are likely to be more accurate. As data become available, models can be made more complex to consider the effect of diffuse sources on water quality.

An initial emphasis on modelling the effect of point source pollutants on water quality would facilitate the goals of Integrated Water Resource Management (IWRM) for catchments that are dominated by low flow conditions. Simpler models that disregard the effect of diffuse sources would require less data to calibrate. It is in addition possible for simpler models to be constructed in a way so as to give an indication of uncertainty around predictions, allowing managers an estimation of risk when making management decisions (McIntyre *et al.*, 2003). Simpler models that initially disregard diffuse source inputs could facilitate management in a much shorter time, as they are easy to construct and require less data.

2.4 The difference between load and concentration

Concentration is a measure of the amount of a particular water quality variable of interest that is relative to the volume of water the variable is present in. Very often, ecologists are interested in the biological effect of a particular water quality variable, and this will depend on the concentration of a particular pollutant. The concentration of a water quality variable will dictate how much of that variable is biologically available. However, sometimes an absolute value of a particular water quality variable within water systems measured in mass (kgs or tons for example) is useful. This measure is especially useful to water quality modellers as models route water and the associated pollutants down a river reach. Using load values for water quality variables, allows modellers to apply the principles of mass-balance within their models. When considering the various processes within rivers that effect flow and water quality, such as abstractions, inflow from tributaries and evaporation, it is simpler to work in loads. Loads can be converted back to

concentrations by taking into account the mass of pollutant, and the volume of water at any point.

2.5 Factors influencing in-stream water quality

In stream water quality is influenced by the geology of the catchment. Day *et al.* (1998) divided South Africa into regions based on natural water quality of rivers. Here, regions were based on the extent of TDS and ions such as Na, Cl, Ca, Mg and HCO_3 found in natural waters, which were related to the geology of the catchment. Rivers in southern Africa flowing through regions dominated by marine sediments, often have higher salinity than for example, rivers flowing through regions dominated by Table Mountain Sandstone (TMS) type geology. Diffuse sources of nutrients are usually associated with land use practices in the surrounding catchment. Grobler and Silberbauer (1985), Simpson and Stone (1988) and Simpson (1991) are three examples of studies in South Africa that have attempted to characterize pollutant loads for specific land use practices. Natural undisturbed areas contribute to a background concentration of certain water quality variables (Pegram and Gorgens, 2001), and wetlands have been known to be sinks for certain pollutants and therefore have an ameliorating affect on water quality. Anthropogenic land use causes excessive loads of pollutants to be washed into rivers during rainfall runoff events. The most damaging land use practice in terms of the magnitude of pollutant load washed into rivers appears to be urban and industrial land (Simpson and Stone, 1988). Agriculture and forestry also are associated with elevated amounts of nutrient loads washed into rivers (Pegram and Gorgens, 2001; Simpson, 1991). Climate and hydrology also have an important effect on in-stream water quality. Rainfall within a region can have ameliorating and detrimental affects on water quality. Increased runoff within a catchment where land use practices are conducive to pollution, cause increased loads of pollutants to be washed into rivers. The variability of rainfall is also important. A long dry spell allows pollutants to build up within a catchment, with the next major rainfall event being associated with excessive amounts of pollution load being washed into rivers. Simpson and Stone (1988) found that within an urban catchment, rainfall runoff events following a dry year were associated with excessively elevated

loads of pollutants. This is called a ‘first flush’ event, when rainfall runoff events follow a prolonged dry period. However, increased rainfall causes greater flow within rivers, and this can have a diluting effect on pollutants, and can wash pollutants down river, decreasing their residence time within the river. Temperature can influence in-stream water quality, by controlling evaporation, and algal growth rates.

Point sources releasing effluent obviously affect in – stream water quality. Point sources are usually more of an influence on water quality during base flow periods, as there is very little diluting potential from the natural flow.

2.6 Modelling the relationship between flow and water quality

2.6.1 Model introduction

A water quality model is a tool that is used to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data (Rouch *et al.*, 1998). Water quality models find their use in management of water resources (Beck, 1987), e.g. in:

1. The rehabilitation of damaged aquatic ecosystems.
2. Management of aquatic environments while undergoing development.
3. Maintenance of aquatic environments while subjected to a variety of conditions.

While it is true that real measured data are in most cases a lot more certain than data estimated from a model, it must be remembered that some sort of model in all cases is used to evaluate data (Glaser and Bridges, 2007), and models can provide some understanding of how the underlying processes work (Glaser and Bridges, 2007). It is not practical to physically observe how a river reacts for all different pollutant loading scenarios, and models provide a way of investigating the consequences of different potential management options (Glaser and Bridges, 2007). Models provide the link between observed environmental problems in rivers, data observed from the field and laboratory, and current scientific understanding (Thomann, 1998). Modellers and models

do not make management decisions, but provide a tool that can assist in the process (Thomann, 1998). Thomann (1998) lists various reasons why models have gained increasing importance and complexity in recent years, including the fact that management of rivers require answers to increasingly more complex problems such as understanding the influence of diffuse sources. In addition, the economic consequences of regulation and making the right decisions have increased. The accuracy of the science behind models has come under scrutiny and has to be defended as enforcement of pollution limits requires scientific veracity.

Broadly speaking, models consist of science, i.e. model structure, algorithms, parameters etc, and data i.e. numerical values that are site specific (Chapra, 2003). Data used in models include (Chapra, 2003):

1. Monitoring data which are measured on a routine basis for reasons other than modelling. These data are usually measured for compliance reasons and may not be adequate for modelling. A South African example would be the data collected by DWA (Department of Water Affairs) which often has large temporal gaps between water quality measures.
2. Data from previous modelling efforts.
3. Data collected specifically for the present modelling effort.

Reckhow (1983) outlines the general process of constructing a water quality model:

1. Conceptualization of functions and relationships of the system to be modelled.
2. The specification of the mathematical relationships or model selection and development. Here additional data may need to be collected.
3. The estimation of model parameters or model calibration.
4. The validation of the model by a series of confirmation tests by applying the model to situations different from the one it was calibrated for.
5. Integration of the model into a decision support system (DSS) to facilitate its use in decision making.

It is generally recognized that water quality models have become increasingly more

complex over the last few decades (Chapra, 1997, 2003). Presently, models exist in varying forms of complexity, from simple Streeter – Phelps models to models such as QUAL2E or QUAL2K which describe nutrient cycling and oxygen, to ecosystem models (Rouch *et al.*, 1998). There are some general model types that will be expanded on further in this chapter.

2.6.2 Brief history of water quality modelling

Water quality models existed as early as the 1920s, when Streeter and Phelps (1925) provided a model that simulated DO in streams. Between 1925 to 1980, all models incorporated sources of pollutants as external inputs into the model, i.e. the effects of pollutants were not actively influencing processes within the models, but effects such as oxygen consumption were input to the model as external inputs (Thomann, 1998). In addition, all through this period, sediment oxygen demand, primary production and respiration were externally input to the models. O'Connor and Dobbins (1958) incorporated the theoretical basis for the reaeration coefficient. In later years, as legislation controlled the effect of point sources, the effect of diffuse sources became more important. The need to simulate processes occurring within the sediments in addition became increasingly important. Using external inputs for these processes were no longer sufficient as these processes obviously interacted with each other and point and diffuse sources. Controlling eutrophication became a priority, and model simulation complexity increased in the number of variables simulated. Model frameworks began to incorporate interactions between nutrients, phytoplankton and zooplankton such as that of Di Toro *et al.* (1971). The period between 1980 to 1995 was characterized by a rapid expansion in the size of water quality models and an increase in the number of state variables simulated. Sediment processes were internalized for toxics and nutrients (eg O'Connor *et al.*, 1983, Thomann and Di Toro, 1983; O'Connor, 1988, Di Toro *et al.*, 1990, Di Toro and Fitzpatrick, 1993). Watershed models were in addition linked to water quality models in this period so that non-point sources could be linked to originating inputs e.g. Donigan *et al.* (1991). As with all models, the importance of uncertainty is mirrored in recent and contemporary water quality modelling research. Beck (1987) was

the first to consider uncertainty analysis in water quality modelling. Spear and Hornberger (1980) introduced the concept of sensitivity analysis in water quality modelling and Reckow (1990) was the first to use Bayesian analysis in water quality modelling. Since then, developments have greatly increased the complexity and accuracy of water quality models. Cole and Buckak (1995) greatly improved hydrodynamics in nutrient modelling. Traditionally, measuring organic carbon in surface waters was difficult, and Connolly and Coffin (2005) were the first to explicitly model organic carbon fate within surface waters.

2.6.3 Possible future directions for water quality modelling

Future developments in water quality modelling will no doubt be driven by the need for an integrative modelling approach to support Integrated Water Resources Management (IWRM). Decision making in the context of IWRM requires scientific understanding of the processes occurring in water resources (Liu *et al.*, 2008). While water quality models have in the past moved towards being as comprehensive as possible, by simulating as many variables and processes as possible, Liu *et al.* (2008) stress that integrative models are not necessarily the same as comprehensive models. Integrative models should identify and accurately simulate the key processes that account for the greatest variability in system behavior. From a management context, various authors have criticized very complex models, and have advocated models that are fairly limited in complexity but concentrate on key processes e.g. Beck (1987), McIntyre *et al.* (2003), Reckhow (1994) and Young *et al.* (1996). One is likely to see an emphasis on relatively simple integrative models in the future, which explicitly give estimates of uncertainty around predictions.

Glabally, there is a lack of scientific understanding around certain processes, such as surface and groundwater interactions, irrigation and drainage, and many others (Biswas, 2008), which limit the implementation of IWRM policies within catchments. Therefore, future research is likely to concentrate on developing models to increase understanding of these processes, just as this thesis has attempted to increase scientific knowledge and to develop management tools in regards to the relationship between flow and water quality.

Within South Africa, Wimberly and Coleman (2005) have identified the need for ecological models or ecological model frameworks that can interface between water quantity, quality and biota. Similarly, Thomann (1998) recognized the international need for models that focus on entire ecosystems, or living resource models. Sivapalan *et al.* (2003) has emphasized the need for methods of predicting water quality within ungauged catchments, and it is likely that there will be many future developments in that regard.

Although there have been great strides in water quality modelling, research gaps still exist. Very few models of surface water quality consider rooted and attached plants, even though they may be the primary way in which eutrophication is manifested in surface waters, and they can impact a system's light environment and nutrient budget (Reckhow and Chapra, 1999). There is in addition a gap in knowledge within water quality models in that water quality model simulation of phytoplankton deals with this constituent as a single broad classification, and does not break phytoplankton down into its three functional groups i.e. diatoms, green algae and cyanobacteria (Reckhow and Chapra, 1999). Each group has different consequences for water quality, and a useful function for a water quality model would be the ability to predict at what point increased loadings lead to a shift from one form of phytoplankton to another (Reckhow and Chapra, 1999). Another knowledge gap in surface water quality modelling is that in representing microbial kinetics (Reckhow and Chapra, 1999). Most models simulate microbial kinetics as a first order decomposition reaction when in fact microbial populations are driven by the substrate as well as microbial concentrations and would therefore, more accurately be simulated by second order reactions (Reckhow and Chapra, 1999). In water quality models, microorganism types and population dynamics must in addition be considered, as the micro-organisms affect processes such as nitrification and heterotrophic activity (Stéphanie *et al.*, 1998; Shanahan *et al.*, 1998). There are gaps in knowledge in this respect, especially in terms of simulating sessile bacteria population dynamics, as is the case with QUAL2E (Shanahan *et al.*, 1998).

2.6.4 The modelling process

2.6.4.1 Modelling of a stream or river

There are some general characteristics of streams or rivers as opposed to other water bodies that must be considered when modelling. Firstly, the simplest representation of streams or rivers is a 1 dimensional representation where dispersion of modelled material is assumed to be negligible compared to flow, and dispersion is therefore, ignored (Hydrosience, Inc., 1971). Here, flow is assumed to be the major mass transport mechanism. Secondly, point and diffuse sources of pollutants will affect downstream water quality as opposed to upstream. Therefore, there is a definite strong directional component as compared to a reservoir or lake, and when modelling the fate of pollutants in a river, it is important to characterize spatial and temporal distributions of point and diffuse sources of pollutants (Hydrosience, Inc., 1971).

Modelling of water quality in impoundments and lakes is very different to modelling water quality in rivers. Within rivers, one needs to consider movement of water and water quality variables in a longitudinal direction. However, within lakes and impoundments, there is potentially movement in a longitudinal, horizontal and vertical direction. An added complication within impoundments is that during summer, an impoundment becomes stratified into layers defined by temperature, oxygen and salinity, with warmer, less saline and more oxygenated layers near the surface, and colder, more saline and less oxygenated water nearer the bottom. While there are models that have been designed specifically to simulate water quality in lakes, such as the Impoundment Management and Planning Assessment Model (IMPAQ) and CE-QUAL-W2 (Cole and Buchak, 1995), the focus of this study is on the relationship between flow and water quality in rivers, and reservoir/lake models will not be investigated in any great detail.

As is common practice in modelling all types of systems, the deciding factors for model selection when modelling a river or stream, must be the problem requirements and available resources (Chapra, 2003). Since modelling is a process, the best way to

maximize the trade offs between model reliability and cost is to start by developing simpler models and add complexity as modelling problems require and costs allow.

2.6.4.2 Good data for modelling

Good water quality data should be of a sufficient resolution to capture temporal variations (Wimberley and Coleman, 2005). Wimberley and Coleman (2005) recommended the frequency of data for modelling to ideally be weekly for un-impacted catchments and daily for impacted catchments. Wimberley and Coleman (2005) in addition recommended that water quality sampling should be of fine enough spatial resolution to capture spatial variation in water quality, such as would be affected by diffuse and point sources. Where possible, direct water quality measures of point sources should be performed to aid with modelling. Most available monitoring data falls far short of these recommendations. For instance in South Africa, while DWA routinely monitors daily flows, water quality data monitoring frequency is at most twice weekly and in some cases has gaps of up to multiple years between measurements. Obviously, model development and accuracy benefits when there are a lot of observed data available. Of course, for the variable of interest, if there are continuous data of a sufficiently fine spatial and temporal resolution, then there is no need to model a system as the observed data would be available. In the majority of cases, the temporal and spatial resolution of data are sparse, and models perform a vital role in estimating processes within the system using the observed data, thereby predicting outcomes for where no observed data are available. Models require observed data to calibrate the parameters that control the rate of processes within the model. Observed data independent of the calibration data are in addition required to verify that the model parameters are correct. It could be argued that the best way to monitor systems in a way that would benefit model development and accuracy, would be periods of high frequency observations during particular specific conditions such as high or low flow. In this way, models could be calibrated with high resolution observed data to estimate processes during specific conditions.

Modelling the relationship between flow and water quality using low resolution water

quality such as is typical of the DWA data, can lead to the omission of important transient events from the modelling exercise such as those associated with short but intense storm events. This is highlighted in a study by Jordan *et al.* (2007), who used a continuous bank side analyzer over 6 months to measure phosphorus in a river in northern Ireland. The study recognized three distinct phosphorus trends: A long term trend of increasing phosphorus concentrations with suppressed baseflows, initial increases in phosphorus during storm events and a drop in phosphorus concentrations with subsequent storms as diffuse sources are exhausted, and lastly high concentrations of phosphorus that are unrelated to changes in flow that are probably related to single pollution events. While DWA data would probably capture the trend of increasing phosphorus concentrations with low flow conditions, there are less data that capture storm events and probably no data capturing single pollution events.

2.6.4.3 Modelling conservative versus non-conservative water quality constituents

Modelling conservative water quality constituents such as salinity is comparatively simple compared to modelling non-conservative constituents such as nutrients, as nutrients may be subject to chemical change over time, and may be assimilated by biota, whereas conservative constituents are usually primarily affected by dilution (Malan and Day, 2002a). While conservative constituents can typically be modelled using a mass-balance model, the concentration of a particular non-conservative substance downstream can be modelled in a non-dispersive system using a differential equation, where one requires the initial concentration, the reaction rate, the river flow and distance downstream from the initial point (Hydroscience, Inc., 1971). However, for some non-conservative chemical species found in rivers, such as the nitrogen chemical species, chemical speciation may cause one equation to feed into another (Hydroscience, Inc., 1971). When modelling nutrient fate in rivers, nutrient models must in addition consider water temperature, as it controls reaction coefficients (Hydroscience, Inc., 1971).

Traditionally and before the dawn of modern computers, nutrient fate was estimated by models using first order analysis with error terms represented by the variance (Reckhow

and Chapra, 1999). First order kinetics assume that the rate of the reaction is proportional to the concentration of the substance (Hydroscience, Inc., 1971). This kind of analysis has the disadvantage of not being exact when modelling processes that work in a non-linear way, however, first order kinetics do approximate many reactions in freshwater systems (Hydroscience, Inc., 1971).

2.6.4.4 Temporal and spatial scales

The temporal scale of the water quality constituent to be estimated is important. Conservative constituents may change over a longer time period that may be as much as a few years, while eutrophication status of a system may change in a matter of weeks, while algal blooms may occur in days (Hydroscience, Inc., 1971). Spatial scales are obviously in addition important to consider when modelling a system, as point or diffuse sources of pollutants for example, may affect very distinct sections of a river.

2.6.4.5 Simple models versus complex models

The ability of a model to accurately simulate flow and water quality does not necessarily depend on the complexity of a model (Chapra, 2003). There are various trade offs involved when choosing a water quality model, with complex models not necessarily being superior to simple models. These trade offs being amongst other things, complexity, reliability, cost and time (Chapra, 2003). Complex models in general would have higher data requirements that are rarely satisfied with the data available. In an ideal world, where cost is not a factor, more complex models will be more reliable to a certain point. In reality, Chapra (2003) recognizes two extremes in terms of model complexity:

1. Very simple models that are so unrealistic that they are unreliable
2. Models that are so complex so as to be over parameterized and that become unreliable because of parameter uncertainty.

While a complex model may obtain a good fit to observed data, over parameterization could make a model less generic and would require the model to be re-calibrated for each application. Lindenschmidt (2006) used the WASP5 (Water quality Analysis Simulation

Program version 5) to simulate oxygen, nutrient cycles, and production in the Saale River in Germany, so as to investigate the effect of complexity on model sensitivity and accuracy. By progressively including more processes in the modelling exercise, the investigators came to the conclusion that the model with the greatest predictive power was the most complex one, where DO, BOD and phytoplankton – nutrient dynamics were represented. However, removing the DO-BOD cycle only slightly decreased the model's predictive power. This study demonstrated that the most complex models are not always the most useful, as in this exercise, removing a large part of the model complexity and data requirements, did not in any large way decrease the model's predictive power.

Beck (1987) brings attention to the Popper (1968) definition of science, as being a hypothesis that can be falsified. Using the concept that models are a collection of hypotheses, Beck (1987) tends to move away from the idea that models are either empirical (statistical) or mechanistic, and rather classifies models as being in Class I, Class II or Class III. Here, a Class III model is a basic modelled cause – effect relationship or a single hypothesis, such as a regression curve for example. Class I models are complex archives of hypotheses that attempt to simulate as many of the cause effect relationships in natural processes as possible. Class II models are somewhere in between, and consist of a collection of hypotheses, but are restricted in the number of processes simulated. Beck (1987) brings attention to the fact that it is impossible to falsify Class I models:

1. Because of uncertainty in observed data.
2. Current limitations in methods for identifying suitable model structure.
3. Difficulty in determining which hypothesis has failed when the entire model gives erroneous predictions.
4. The complex non-linear processes simulated in Class I models are impossible to verify with experiments or observed data as they are too complicated.

While Class III models are too simple to be useful, and Class I models are too complex to verify as accurate, Class II models are an appropriate compromise, as the limited number of hypotheses they incorporate are capable of being proved accurate.

As was mentioned in Chapter 1, simple models that simulate a few key processes may be more appropriate than complex models in the context of implementing IWRM. Simpler models may not necessarily lose predictive power, and would require less data to calibrate, while being simpler to implement. Generally, in practice, water quality managers avoid large mechanistic models in favour of relatively simple models (Reckhow, 1994). It is in addition impossible or very difficult to assign uncertainty to predictions given by very complex models (Beck, 1987), while uncertainty is readily incorporated into relatively simple models. Managers are required to understand the risk involved in making management decisions within IWRM, and models that give an indication of uncertainty around model predictions are therefore essential (McIntyre, 2003).

2.6.4.6 Model calibration and validation

Typically, parameter calibration models require at least two independent data sets, one set to ‘calibrate’ the model, and another data set to ‘validate’ the model. The first model run should be performed with default parameters and any measured process rates, using the first independent data set, or the ‘calibration’ data set. Model parameters should at this point be adjusted to obtain a good fit between the model output and the first data set (Chapra, 2003). The values of the reaction coefficients chosen should be compared to the range found in the literature, so as to ensure valid rates are being used. The model is considered calibrated by performing the required statistical test or graphical comparison when comparing simulated data to observed data (Chapra, 2003). Once the model is deemed calibrated, the model can be re-run using the independent validation data set. If the model predictions are sufficiently similar to the observed validation data, then the model can be regarded as validated. The most useful data sets for calibration and validation of models may be at extreme or unusual conditions, such as very low flow, where pollutant inputs would have very definite effects, or extreme high flow, where rain wash off into the river would introduce the effect of diffuse pollution sources (Shanahan *et al.*, 1998). The evaluation and calibration of a model should be approached from various angles to be scientifically rigorous (Glaser and Bridges, 2007). This includes an

assessment of the quality of the underlying theory of the model and the quality and quantity of field and laboratory data used to estimate key parameters (Glaser and Bridges, 2007).

According to Reckhow (1983), validation of the model is often neglected. Models need to be validated by independent observations (Reckhow, 1983; Glaser and Bridges, 2007). A consideration of whether data sets are independent is very important as predictions and observations in water quality are often time series and autocorrelation may be present in either (Reckhow, 1983). Validating a model does not necessarily prove that a model is accurate in its representation of processes, but merely proves that the model predictions are sufficiently credible for decision making (Chapra, 2003). If, when validating a model with an independent data set to that of the calibration data set, the parameters have to change dramatically so that they are not within the confidence limits of the calibration data set, then there is a problem with the model formulation (Glaser and Bridges, 2007). Chapra (2003) recommends validation of a model on three different levels:

1. Validation of a model where the validation data were collected under conditions that are similar to the conditions that calibration data were collected under, i.e. flow, diffuse and point loadings in the validation data are very similar to that found in the data used in the calibration of the model.
2. Validation of a model where the validation data involves wetter conditions or more natural flow than the data used to calibrate the model.
3. Validation of the model where the validation data contains significantly different loadings from point and diffuse sources than the data use to calibrate the model.

It is therefore recommended that models be validated by multiple independent data sets collected during markedly different conditions. In addition to the recommendations given above by Chapra (2003), Glaser and Bridges (2007) stressed that it is important that the validation data be of the same space and time scale as the output of the model.

Many researchers have picked up problems with typical parameter calibration models. Thomann (1998) for instance, questions the logic of neatly dividing data sets into

calibration and validation data sets, as new insights are continually uncovered with increasing data. Oreskes *et al.* (1994) claimed that validation of models of natural systems is impossible as these systems are open so one cannot claim that a simulation is absolutely the truth. Observation data are always uncertain and prone to error, therefore, continuing observational data provide more information, and the validation process is never complete. Oreskes *et al.* (1994) suggests that the word ‘confirmed’ be used instead of ‘validated’, as model confirmation implies an increasing possibility of being true. According to Chapra (2003), the only real validation of a model is by confirmation by independent observations. Chapra (2003) in addition encourages the use of the term ‘confirm’ rather than ‘validate’, arguing that we can never be absolutely sure of the correctness of a model, and at best can assign a high probability to a model’s accuracy. The process of confirming a model is performed to ensure that model predictions are sufficiently accurate for decision making, and not to determine whether a model is ‘true’ (Chapra, 2003). Due to the above considerations, the research presented in the rest of this thesis will refer to model ‘confirmation’ rather than ‘validation’ or ‘verification’.

Shanahan *et al.* (1998) points to another potential problem with parameter calibration models. Model parameters that are fixed based on calibration data sets may not be appropriate for other data sets if the model lacks the ability to change parameters to reflect the changes in the river. An example given by Shanahan *et al.* (1998) is that of the situation where untreated sewage is changed to treated sewage, where most models would not be able to simulate the resulting changes in light penetration, sediment oxygen demand due to the depletion of sludge banks, or the transition of a river from anaerobic to aerobic conditions and the cessation of denitrification that occurs under anaerobic conditions (Shanahan *et al.*, 1998).

Beck (1981) stresses that only relatively small models can be calibrated against field data, and that for larger models, ambiguities can be partially circumvented by using information other than field data such as independent laboratory experiments or parameter values obtained from modelling similar systems.

2.6.4.7 Steady state models versus variable flow models

Very often, models use a steady state, gradually variable representation of flow based on the Manning Equation (Rouch *et al.*, 1998). There have been comparatively few models that have attempted to model variable flow, mainly because the mathematics behind modelling fluid dynamics are extremely complicated. An example of a study that modelled variable flow is the model used by Chung *et al.* (2008) who investigated the effect of reservoir flushing on the Geum River in Korea. Here the model used was KORIV1-WIN (Chung, 2004) which can simulate the hydraulics of unsteady river flows. Gorgens and de Clercq (2006) applied the 1-dimensional hydrodynamic river flow model DUFLOW to the Berg River. DUFLOW is a dynamic model which takes the variability of variables in time and space into account. In the case of the Berg River, this model was used to allow the modelling of reservoir releases as flow downstream.

The models investigated in this thesis assume steady state flow, as models that simulate variable flow are relatively rare, difficult to understand and implement, and would probably require data that are not readily available. The nutrient model investigated in Chapter 7 for example, uses the Manning Equation, while the Pitman Model used in Chapter 6 assumes steady state flow. QUAL2K investigated in Chapter 8, was in addition set up to utilize the Manning Equation.

2.6.4.8 Uncertainty

Uncertainty in water quality modelling was generally ignored in the 1960s and 1970s (Beck, 1987). However, there is currently a shift to indeterminism from determinism in water quality modelling, which is partly a reflection of an increasing maturing of the science of water quality modelling (Beck, 1987). History has favored the development of deterministic models, as it is possible to design careful experiments within engineering research that have little ‘noise’. However, experiments within environmental science normally give results with a lot of ‘noise’, and there is a growing perception that models

that incorporate uncertainty are more reflective of natural processes (Young *et al.*, 1996). An example can be made with the scientific maturity that hydrological modelling has achieved as compared to water quality modelling. Hydrology has advanced to the stage where there is critical review of assumptions made about stochastic processes affecting model structure, while water quality modelling has in the recent past focused on developing bigger and more complex models that attempt to simulate a growing number of natural processes (Beck, 1987). In recent times, there has been increasing importance placed on the estimation of uncertainty in water quality model predictions (Chapra, 2003). The estimation of error in model results is a difficult task and must consider uncertainty due to error in observed data, parameter error, model error, covariance, parameter equifinality and predictions of future behavior (Beck, 1987; Chapra, 2003; McIntyre *et al.*, 2003). While models should ideally be designed to incorporate uncertainty from the bottom up, Reckhow (2003) has suggested that in the short term, practical, if incomplete uncertainty analysis can be performed on existing models. In the long term, existing models should be restructured to incorporate uncertainty, while new models should consider uncertainty from the beginning. One way to estimate uncertainty in model predictions is to run Monte Carlo simulations. A Monte Carlo simulation generates a distribution of model results that characterize the uncertainty in model predictions and is generated through multiple model runs using random sampling of the original data set (Reckhow and Chapra, 1999; Glaser and Bridges, 2007). One other estimation of model uncertainty is the difference between model prediction data and observed data (Reckhow and Chapra, 1999). In this case, confirmation of the model must be rigorous, especially with models with many parameters that can be tuned to fit the observed data (Reckhow and Chapra, 1999). Here, confirmation in a rigorous way would involve confirming the model with observed data that were collected under markedly different conditions from the data that were used to calibrate the model (Reckhow and Chapra, 1999). If the model still generates accurate predictions under these conditions, then in all likelihood, the parameter values chosen during calibration, accurately drive the simulation of real life processes. The correct estimation of parameter values for mechanistic models with many parameters can be difficult, and regional sensitivity analysis is a process that can improve this situation and decrease model uncertainty

(Reckhow and Chapra, 1999). In addition, tabulations of suggested model parameters have been published (Bowie *et al.*, 1985). Spear and Hornberger (1980) however proposed regional sensitivity analysis (RSA) as a process that uses previously defined regions of acceptable model predictions to estimate plausible parameter values (Reckhow and Chapra, 1999). This is achieved through a series of steps (Reckhow and Chapra, 1999):

1. The possible range of model predictions is divided into regions of plausible and un-plausible.
2. Monte Carlo simulations then randomly sample from parameter distributions and a model run is performed with each selection, with model results being classified as plausible or un – plausible.
3. The parameters that gave plausible results are then considered to accurately map the parameter range that should serve as the basis for further parameter estimates.

Generalized Likelihood Uncertainty Estimation (GLUE) (Bevan and Binley (1992) is an extension of RSA in that every feasible model is weighted with a likelihood. GLUE provides a framework where all sources of uncertainty can be incorporated into parameter and prediction uncertainty (McIntyre *et al.*, 2003).

Within the context of IWRM, it is vital that models give some indication of uncertainty around predictions. It is important that managers have some indication of the risk involved in making management decisions, and estimations of uncertainty around model predictions can provide managers with an estimate of risk (McIntyre, 2003).

Where possible, models developed or investigated in this thesis have included estimations of uncertainty around predictions. The estimations of uncertainty, where they are included, are relatively simple estimations. However, uncertainty estimation was not the main aim of this research, and is beyond the scope of this thesis.

2.6.5 Examples of models

2.6.5.1 Water quality models by temporal and spatial scale

Existing water quality models use a range of temporal scales, from a monthly time step to less than a daily time step. QUAL2E/QUAL2K is an example of a model that operates at a time step of less than a day, as the model simulates diurnal water quality kinetics (Wimberley and Coleman, 2005). Models that operate at a short time step are usually applied to manage components of water resource systems such as river reaches and dams (Wimberley and Coleman, 2005), and typically require a lot of data for calibration and confirmation. Once these types of models are calibrated, however, they are useful in investigating management scenarios such as changing flow or load scenarios (Wimberley and Coleman, 2005).

Water quality models work on spatial scales ranging from in-stream models that require external inputs of point and diffuse pollutants, to models that operate at a watershed level, and explicitly model the effect of land use within a river catchment. QUAL2E/QUAL2K is an example of an in-stream model. This is a local scale impact assessment model that can assess the effect of local impacts on a river such as discharges (Wimberley and Coleman, 2005). QUAL2K is a modern version of QUAL2E and simulates a diurnal heat budget and diurnal water quality kinetics (Wimberley and Coleman, 2005). Another local scale model is HSPF (Wimberley and Coleman, 2005). BASINS (Better Assessment Science Integrating Point and Non-point Sources) is an example of a modelling framework that integrates environmental data, tools and models to manage watersheds (Wimberley and Coleman, 2005). Within South Africa, various models and modelling frameworks have been applied at a scale that is at least at quaternary level and consider the impacts of land use, impoundments, inter-basin transfers (IBTs), abstractions and discharges (Wimberley and Coleman, 2005). A quaternary catchment is the smallest hydrological unit in a national hierarchical drainage subdivision system that was developed by the DWA (Midgley *et al.*, 1994). Catchment scale models and modelling frameworks include the Water Resource Planning Model (WRPM), the Water quality

TDS/ Water quality Sulphate (WQT/WQS) models, the IPAQ model which simulates salinity, nutrients, primary production and e-coli, FLOSAL which simulates daily or monthly salinity, the Hydrological Simulation Program in Fortran or HSPF which models both conservative and non conservative water quality constituents and WQ2000 which is a salinity model (Wimberley and Coleman, 2005). Rousseau *et al.* (2000) developed an integrated daily time step water quality modelling system for river basin management called GIBSI, which includes a database, simulation models for hydrology, soil erosion, agriculture, point and non-point sources, reservoirs and a GIS. The framework uses a relational database in MS Access. The hydrological model is HYDROTEL (Fortin *et al.*, 1995). Sediment transport algorithms are taken from USLE (Wishmeier and Smith, 1978), nutrient transport algorithms are taken from SWAT (Arnold and Williams, 1995) and EPIC (Williams, 1995) while the water quality model is built around QUAL2E. The framework allows the user to manage point sources, agricultural non-point sources and reservoirs. GIBSI can simulate flow as well as the water quality associated with flow.

Internationally, there are various models or model frameworks that work on a catchment scale. Kato (2005) developed a monthly time step water quality tank model for a small catchment of the Yamada River in Japan. The model used a database detailing land use types, fertilizer application, population and livestock. Wimberly and Coleman (2005) attempted to model climate change impacts on water quality and quantity on the Kennet River in the United Kingdom. This project used the hydrological model CATCHMOD and the water quality model INCA. CATCHMOD consists of four zone models, namely baseflow from an aquifer, runoff from clay, runoff from riparian areas and flow from urban areas. The INCA (Integrated Nitrogen CAatchment) model was developed to integrate catchment and river processes in terms of nitrogen input, and models nitrogen vertically, by simulating nitrogen inputs from the atmosphere through to soil and river, and horizontally, by incorporating spatial variation across a catchment (Whitehead *et al.*, 1998). Wade *et al.* (2002) outlines some modifications made to the INCA model so as to make the model more applicable to smaller catchments. Jarvie *et al.* (2002) used INCA to model nitrogen in the Tweed River in Scotland, and found that INCA could simulate long term trends in nitrogen at a seasonal or longer period, but was less accurate in simulating

the effect of short events, such as individual storms, on nitrogen concentrations. The model also limits water quality simulation to nitrate and ammonium, and therefore, the model's water quality simulation capacity is limited. The GIS interface within INCA also recognizes only 6 land use classes (Whitehead *et al.*, 1998) that are not entirely applicable to southern Africa. For example, no provision is made within INCA to distinguish irrigated land, which is known to be a source of diffuse pollutants. SWAT or Soil Water Assessment Tool (Arnold *et al.*, 1998) is another well known international catchment level model. SWAT is a physically based model that simulates catchment and instream processes at a high level of spatial detail (Santhi *et al.*, 2006). The SWAT model is useful for evaluating different scenarios of point and diffuse sources on water quality in large ungauged basins. Avila *et al.* (1996) used the MAGIC model to assess the effects of climate change on flow and water quality in a Mediterranean catchment. MAGIC is a long term, catchment scale lumped parameter model. The model has two sub-models, with one representing processes of cation exchange in the soil zone and the other groundwater contributions to baseflow. Gowda *et al.* (2007) used the ADAPT (Agricultural Drainage and Pesticide Transport) model to assess management strategies to reduce nitrogen loading in two agricultural watersheds in the upper Mississippi basin in the USA. ADAPT is a daily time step management simulation model developed by integrating GLEAMS (Leonard *et al.*, 1987) with subsurface drainage algorithms from DRAINMOD (Skaggs, 1982). GLEAMS is a root zone water quality model (Gowda *et al.*, 2007). While these models simulate nitrogen input into the river, they do not simulate the in-stream fate of nutrients and the study found that ADAPT simulated flow generally well, while nitrate simulations were in close agreement with observed values taken from grab samples.

2.6.5.2 Export coefficients

Export coefficients are used specifically to estimate the load of pollutants exported from specific land use types. However, it is generally recognized that there is a large variability in calculated export coefficients values within and between land use types. Within South Africa, there have been various studies that have attempted to quantify the load of

pollutants exported from specific land use types. Grobler and Silberbauer (1985) studied the combined effect of geology, phosphate sources and runoff on phosphate export. They found that there were large variations in annual phosphorus export within and between the observed catchments, which they related to annual variation in rainfall runoff and differences in land use. Simpson and Stone (1988) characterized the runoff water quality and determined annual export coefficients for an urban catchment in Durban, South Africa. They concluded that there is markedly higher exports of pollutants from urban areas as compared to other land use types, and also that higher rainfall was linked to greater export of pollutants. Simpson (1991) attempted to determine export of pollutants from several small catchments in Kwazulu-Natal in South Africa. This study concluded that pollutant export varied appreciably between years within and between catchments, which they linked to annual variations in runoff, and recommended that long term monitoring of catchments is necessary in order to calculate long term mean export coefficients. Pegram and Gorgens (2001) give a summary of export coefficients calculated for catchments in South Africa and categorized according to predominant land use. Importantly, they showed that there is generally more variation in loading within a land use category, than between categories.

It is extremely evident that the export coefficient approach is a gross generalization and extreme average of the relationship between land use and diffuse pollutant loads, and therefore the approach is very limited. It is also clear that variation in annual rainfall runoff affects diffuse pollutant loads, which the export coefficient approach does not take account of.

2.6.5.3 Statistical water quality models

Statistical models fall into the category of empirical models which are equations based strictly on a statistical summary of the data (Reckhow and Chapra, 1999). The work of Malan and Day (2002a) is outlined earlier in this chapter, where they constructed flow-concentration (Q-C) relationships on a monthly time scale to investigate regional patterns between flow and water quality within South Africa. Bowes *et al.* (2008) constructed

statistical regression models that recognized distinct statistical relationships between flow and phosphate loading, according to whether the source is point or diffuse.

Statistical models can in addition be used to link land use/cover to water quality. In the past this has usually been done using Ordinary Least Squares regression (OLS) (Tu and Xia, 2008). This however, can lead to spatial autocorrelation, and spatial non-stationarity (Tu and Xia, 2008). Tu and Xia (2008) proposed the use of Geographically Weighted Regression (GWR) as a statistical method that may overcome these problems.

2.6.5.4 Mass – balance models

In a mass balance model, transport of material is either represented as convectional flux or dispersion flux, and the changes within a chosen volume of the modelled system must be in balance (Hendricks, 1979).

Berka *et al.* (2001) linked water quality with land use in a watershed in British Columbia using a mass balance model. The authors show how a mass balance model can be used in combination with GIS to predict water quality at the watershed scale. A GIS database of the study area was developed that included topography, soil, land use, animal stocking density and crop data. Nutrient mass balance calculations were done using the model developed by Brisbin (1995).

Hughes (2008) simulated the salinity of an ephemeral river in South Africa using a mass – balance model, where salinity was balanced from the various inputs and outputs such as surface water and ground water input, and the movement of salt to and from the surrounding channel and the water column and pools.

Meals *et al.* (2008) coupled a long term distributed phosphate mass balance model with spatially variable land use and agronomic data. The model is called the Dynamic Interactive Simulation of Phosphorus Loss Areas (DISPLA) model. DISPLA is composed of smaller mass balance models, each simulating phosphorus accounting for a

homogeneous land unit on an annual time scale. DISPLA uses an adapted phosphorus index, and in addition the concept of variable runoff to determine the phosphorus transport potential by surface runoff. The model is used in a spatial modelling environment (SME). The model was tested on the Little Otter Creek watershed in Canada, a mixture of agricultural, forest and urban land, for different scenarios of present day conditions, nutrient management, erosion control and land use change. DISPLA proved useful in providing a view to long term trends of the input, output, storage and flux of phosphate in soils, vegetation, livestock and water.

2.6.5.5 Parameter calibration models versus physically based models

Parameter calibration models require parameter values to be set to control simulated processes such as re-aeration, nutrient uptake by phytoplankton etc. Typically, parameter models require independent calibration data sets, where parameters are adjusted until simulated model results are close to observed data. An example is the QUAL2K model which requires a variety of parameters to be set, ranging from re-aeration coefficients, to settling velocities of various variables to decomposition rates for BOD and nitrification rates. Another example is the Eutrof1 water quality module which was used by Gorgens and de Clercq (2006) along with a hydrodynamic model called DUFLOW to model temperature, TDS and phosphate in the Berg River, South Africa.

In contrast, physically based water quality models aim to simulate how in-stream processes work, and discrepancies between model simulations and observed data are resolved through a better understanding of the processes and not through adjusting parameters. An example is the water quality model RIVE, which is the water quality module of PROSE, which was used to model water quality of the Seine River in France (Eiger *et al.*, 2007). The RIVE model, in contrast with most water quality models, requires a complete description of the kinetics of the processes, obtained from experimental observation, and does not involve parameter fitting through calibration (St'ephane *et al.*, 1998).

2.6.6 Shortcomings of current models

Beck (1981) emphasizes the distinction between hard and soft environmental systems, with regards to issues revolving around evaluating model reliability. Hard theory behind some models is relatively easy to prove correct, while soft theory is difficult to prove correct and often subjective. Water quality models are typically hard to prove correct, and Beck (1981) points out the danger of disguising ‘opinion’ as ‘objective evidence’ when it comes to water quality models. Water quality models are soft, in that observed data is scarce and subject to high levels of error and uncertainty. Usually, there are limited data in the literature dealing with how these systems are supposed to work.

Many models make the assumption of complete mixing on the lateral and vertical scale, and assume a one dimensional structure, i.e. transport along the longitudinal scale. However, according to Mahamah (1998), the assumption may be violated to a high degree in shallow rivers with long residence times with differences between simulated and observed results being as much as 20%. Most water quality models in addition assume steady state reaction kinetics (Mahamah, 1998). According to Mahamah (1998) citing Gibbons (1981) and Mahamah (1984), while there are many interacting complex reactions, the reactions taken as a whole approximate first order reactions, and therefore, this assumption is not particularly invalid.

Water quality models that simulate DO are typically very sensitive to the re-aeration coefficient (Shanahan *et al.*, 1998). The re-aeration coefficient is a function of temperature, depth and velocity. However, in typical model applications, the coefficient is determined by calibration to a specific data set and the re-aeration coefficient is imposed on subsequent data sets, even though temperature, depth and velocity may have changed (Shanahan *et al.*, 1998).

Parameter calibration models such as QUAL2E and many others have been criticized in that several sets of parameters in a model calibration can lead to the same modelling

results (Shanahan *et al.*, 1998). This has been termed equifinality by Bevan and Freer (2001) in hydrological modelling. This means that parameter models may in some cases not represent processes accurately, even if simulated results are similar to some observed data sets, and parameter calibration models may not simulate observed data well if applied to data that are very different from the data used to calibrate the model.

Statistical water quality models, such as the Q-C regressions of Malan and Day (2002a), may be simple, easy to understand and less data intensive. However, they are of little use for investigating management scenarios, as statistical models generally fail if the conditions characterizing the data that were used to formulate the model change (Beck, 1987; Glaser and Bridges, 2007).

As was mentioned earlier in this chapter, traditional methods of statistically relating land use/land cover to water quality through linear regression, overlook two very important factors that may cause the results to be inaccurate. One is called spatial non-stationarity, and occurs when parameters of a particular model are fixed over space. The other is spatial autocorrelation where water quality at a particular point on a river reach may be affected by land use/cover within close proximity, as well as land use/cover further away.

2.7 Concluding remarks

It is clear that management within the paradigm of IWRM, requires more scientific knowledge regarding the relationships between flow and water quality, if IWRM policies are to be implemented successfully within South Africa. In addition, management tools in the form of relatively simple models that incorporate an estimation of uncertainty are required. Since relatively simple models are needed that focus on key processes or variables of concern, a range of models that simulate specific key processes or variables of interest are needed. Uncertainty estimations around model predictions have been recognized as a key component of models if they are to be useful within the context of IWRM, however, uncertainty has not been the main thrust of this research. The incorporation of uncertainty estimation into water quality models would require

exhaustive research which is probably a thesis in itself. For water quality models to be useful for management within South Africa, they must be designed so as to give accurate simulations using the available data. An examination of the DWA historical monitoring data has shown that salinity as electrical conductivity (EC) is fairly well represented in the DWA data. Nutrient data in the form of the inorganic forms of phosphorus and nitrogen are in addition relatively well represented in the DWA data compared to other water quality constituents. Turbidity is however not well represented within the DWA data. Therefore, models that could possibly be developed to give useful simulations should focus on salinity or nutrients.

Chapter 3: Statistical modelling of the effect of flow on water quality

3.1 Introduction

Malan and Day (2002a) constructed flow-concentration (Q-C) regression relationships on a monthly time scale to investigate regional patterns between flow and water quality within South Africa. This kind of simple regression analysis, which attempts to model a single cause-effect relationship, could be regarded as a Class III model according to the Beck (1987) definition. Beck argued for models to be either classed as Class III, which are simple, probably statistical, single cause – effect relationships, Class I models which are complex archives of cause effect relationships, or Class II models which are a compromise between the two other classes, in other words, models comprising a limited number of cause – effect relationships. Just as Beck (1987) and others (McIntyre *et al.*, 2003; Reckhow, 1994; Young *et al.*, 1996) have discouraged the use of complex models, the use of Class III models has in addition been discouraged as they are viewed as being too simple to give realistic simulations of reality (Beck, 1987; Chapra, 2003). Using existing flow and water quality data to develop a statistical relationship does not explain how the relationship works, and therefore, the relationship is restricted to interpolation within observed data (Beck, 1987). One cannot therefore, use these statistical models for ‘what if’ scenarios, where hypothetical situations are explored. In addition, without linking the water quality and flow relationship to land use, the statistical models developed using historical data may become inappropriate as land use changes in the future. Statistical methods of linking water quality to flow are in addition very constrained by availability of data (Malan and Day, 2002a). This chapter aims to address Aim 1, in that the research presented here attempts to determine whether simple regression relationships can sufficiently accurately model the relationship between flow and water quality. Since the models presented use solely historical monitoring data, this chapter also to some degree attempts to address Aim 4.

As long as the limitations of simple regression models are recognized, the use of statistical models can be useful. Simple regression models have the advantage of being relatively simple to understand compared to most mechanistic models and therefore, could be advantageous in a management context as they would require less time and training to use. In the context of this thesis, the interrogation of simple cause effect relationships between flow and water quality through regression, allowed some conceptual understanding to develop, and contributed to the development of more mechanistic models outlined in later chapters (Chapter 4 and 5).

The research presented here is restricted to describing statistical predictive methods linking flow to water quality. So called Flow–Concentration (Q-C) modelling (Malan and Day, 2002a) is explored as a simple predictive method.

3.2. Data and methods

3.2.1 Data

All flow and water quality data investigated were obtained from the Department of Water Affairs (DWA) (Appendix A Table 1). All data are available via the DWA Resource Quality Service website here: <http://WWTW.dwa.gov.za/iwqs/report.asp>.

Daily flow data were available for monitoring points. However, the temporal periodicity of water quality data from DWA monitoring points ranged from as much as two observations per week to gaps of up to multiple years between observations.

Data were analyzed according to monitoring points i.e. data from different monitoring points were kept separate. Daily flow data were read from a text file into a relational database, from which data could be extracted according to specific conditions using Standard Query Language (SQL). The available water quality data were read from an excel file into the relational database in a similar fashion. The DWA data contains

information for a limited number of water quality constituents that are represented fairly consistently. Therefore, water quality constituents were restricted to electrical conductivity in mS.m^{-1} (EC), nitrogen as nitrates (NO_3^- -N) plus nitrites (NO_2^- -N) in mg.L^{-1} , and phosphorus as ortho-phosphate (PO_4^{3-} -P) in mg.L^{-1} . Data from the DWA flow and water quality monitoring sites listed in the Appendix A Table 1 were used in the regression analyses.

3.2.2 Methods

Flow and water quality data were extracted from the database and used in simple regressions to form predictive models. An initial investigation of two temporal scales was performed using only data from the DWA primary drainage regions Q and R. Monthly average flow values were regressed against monthly average water quality values. Secondly, daily flow values were regressed against corresponding available water quality values for the same date. This initial investigation indicated that generally, regressing daily flow values against available daily water quality values provided better R^2 values. Therefore, all subsequent regressions on remaining data from across all regions of South Africa, were done at the daily scale. The initial investigation in addition showed that there was no real relationship between flow and the chosen water quality constituents for sites measuring outflows from reservoirs, therefore, reservoir sites were excluded from the analysis and are not included in the Appendix A Table 1.

Regressions were performed in Microsoft Office 2003 Excel. Various models were fitted to the data to obtain the best fit, including linear, logarithmic and power models. As was done by Malan and Day (2002a), for regressions obtaining an R^2 better than 0.5, data were divided into two sets: those collected in even years, and those collected in odd years. Data from even years were regarded as calibration data, and 95% prediction intervals were calculated for the regressions fitted to these data. Data transformations were performed if necessary. The regression models were regarded as confirmed if 75% of the data points from odd years fitted within the 95% prediction intervals from even years.

3.3. Results

Table 3.1 is a summary of R^2 values obtained and the regression equations used for EC, phosphate and nitrate + nitrite.

Table 3.1: Summary of simple regression results for EC, phosphate and nitrate + nitrite					
Water Quality Constituent	R^2				Regression equations used
	Average	Min	Max	% > 0.5	
EC	0.32	0	0.82	21	$y = (A \cdot x) + B$; $y = A \cdot x^{(B-1)}$
Phosphate	0.06	0	0.42	0	$y = A \cdot x^{(B-1)}$
Nitrite + nitrite	0.11	0	0.58	1	$y = A \cdot x^{(B-1)}$

Table 3.1 shows that on average, regression models applied to flow versus EC, achieved an R^2 of 0.32. Of all the sites investigated, 21% had regression fits of EC to flow of 0.5 or greater. This is better than the regression fits obtained for flow versus phosphate (average $R^2 = 0.06$) and flow versus nitrate + nitrite (average $R^2 = 0.11$). Most of the regression models for EC took the form of the power model type regression: $y = A \cdot x^B$. This regression model was in addition used predominantly for the flow versus phosphate and flow versus nitrate + nitrite regressions, however, generally the R^2 values were so poor for the nutrient regressions that one cannot realistically claim that any simple regression equation was suitable. Appendix B Figure 1 shows regressions of flow versus EC for sites where there was a regression fit of greater than $R^2 = 0.5$, and 75% of confirmation data were within the 95% prediction intervals of the calibration data. While the overwhelming general relationship was one of a decrease in EC with increasing flow, the relationship differed between sites, with some sites experiencing a much stronger decrease in EC with higher flow than others. Some sites experienced a linear decrease in EC with increasing flow, while most experienced an asymptotic decrease in EC with increasing flow. The differences between gauging stations in regards to the relationships

between flow and EC is probably as a result of differing geology within the catchments of the respective gauging stations (Figure 3.1).

Regressions of flow versus phosphate generally showed a much less clear pattern, and R^2 values were much weaker than were obtained for EC. The average R^2 was 0.06, and no regressions obtained an R^2 better than 0.42.

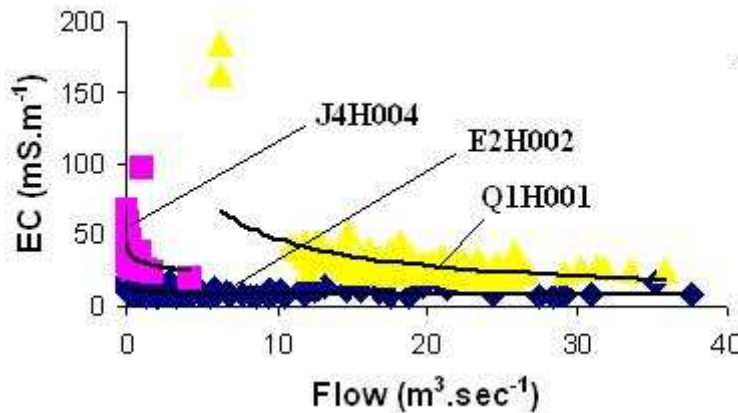


Figure 3.1: Regression of daily flow versus EC for three DWA monitoring stations occurring in different geological areas. E2H002: $9.98 \times 10^{-0.094}$, $R^2 = 0.32$; J4H004: $29.94x^{0.14}$, $R^2 = 0.41$; Q1H001: $268.76x^{-0.80}$, $R^2=0.50$.

Of all the sites investigated, 70 % of sites showed an increase of phosphate with increasing flow, indicating the possible influence of diffuse sources of phosphate. R2H010 showed a strong relationship of decreasing phosphate with increasing flow (Figure 3.2). R2H010 is downstream from two waste water treatment plants in the vicinity of King William's Town and can therefore, be expected to be influenced by point sources of phosphate (see Chapter 8).

Similar to that of phosphate, regressing flow against nitrite plus nitrate gave less clear relationships than was the case with EC. The average R^2 for regressions of flow against nitrite plus nitrate was 0.11. Only three sites showed R^2 values of greater than 0.5, and Appendix B Figure 2 shows regressions of flow versus nitrite plus nitrate for sites where

there was a regression fit of greater than $R^2 = 0.5$, and 75% of confirmation data were within the 95 % prediction intervals of the calibration data. Similar to that of phosphates, 70% of sites showed an increase of nitrite plus nitrate with increasing flow, indicating that most sites are probably influenced by diffuse sources of nitrogen. As was the case for phosphate, regressing flow against nitrite + nitrate for R2H010 showed a pattern to be expected from a reach influenced by point sources (Figure 3.3).

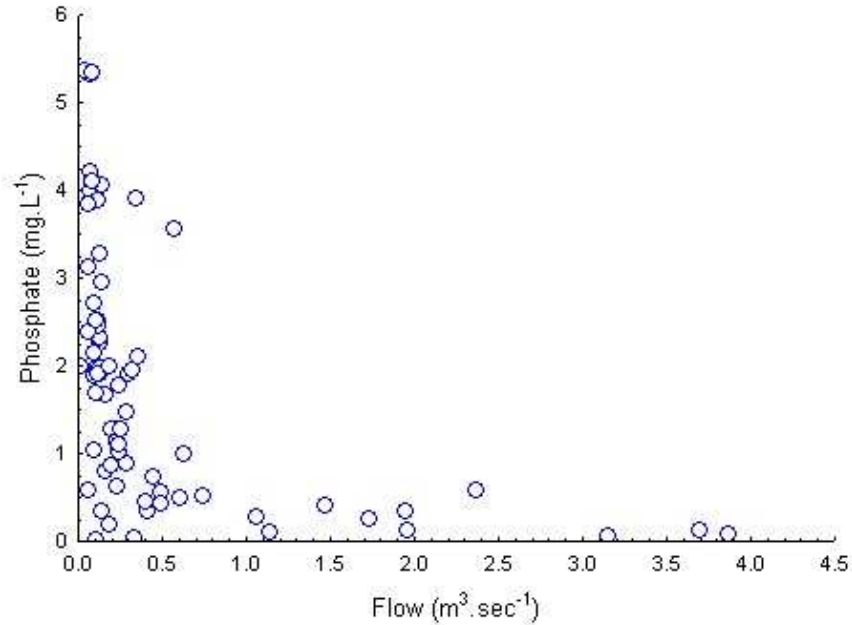


Figure 3.2: Daily flow versus phosphate for the DWA monitoring station R2H010 on the Buffalo River, within ten km of two major point sources of phosphate.

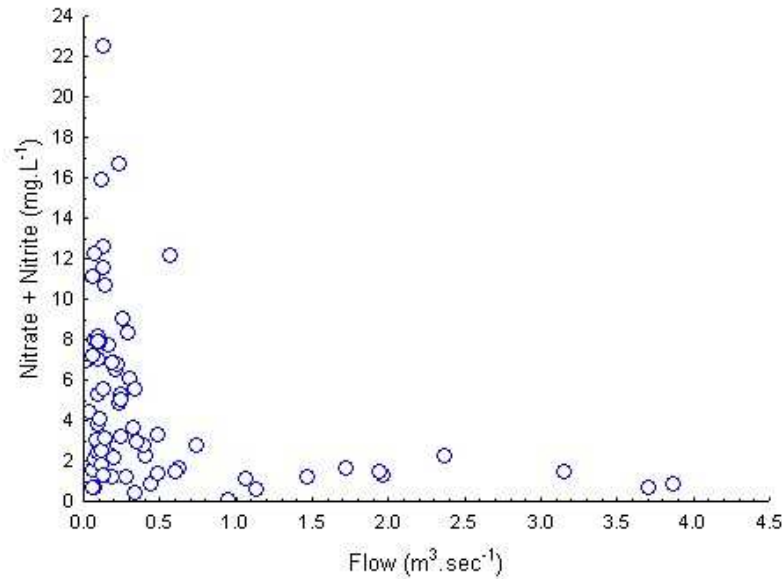


Figure 3.3: Daily flow versus nitrate + nitrite for the DWA monitoring station R2H010 on the Buffalo River, within ten km of two major point sources of phosphate.

3.4 Discussion

Malan and Day (2002a) recommended using monthly average flow and water quality values to form Q-C regressions. However, preliminary investigation in this research showed that in most cases using daily flow and available daily water quality measures allows better regression models to be developed. This chapter addresses Aim 1 and shows that Q-C model approaches to predicting water quality are limited. In this study, very few monitoring points provided data that gave adequate regression models. In addition, regression models seem not to be plausible for sites measuring outflow from reservoirs. Although the Q-C method is comparatively simple, it relies on a scenario of predicting water quality only if there is no change in the operation of the system to that of the system the data were derived from to form the Q-C relationship (Malan and Day, 2002a). For example, the construction of a dam on a river, or the introduction of outside water from an interbasin transfer scheme (IBT) into a studied river, could invalidate Q-C relationships that are based on data taken in the past. Therefore, the Q-C method is not suitable for testing different scenarios in water quality management (Malan and Day,

2002a). This chapter also in part addresses Aim 4: Although the Q-C method can use historical monitoring input data and does not require dedicated data collection as would most water quality models, the temporal extent of flow and water quality data in most cases would not be available to produce valid Q-C regressions.

Appendix B Figure 1 and Appendix B Figure 2 show linear regressions of flow versus EC and flow versus nitrates respectively, where data sets have been divided into calibration and confirmation data sets, similar to what was done by Malan and Day (2002a) who confirmed their Q-C regression relationships by determining if more than 75% of confirmation points fell within the 95% confidence intervals of the regression fitted to the calibration data set. However, in this study, 95% prediction intervals were calculated around the regression lines of the calibration data, instead of 95% confidence intervals. This was done because the 95% prediction interval is the area in which you expect 95% of all data points to fall. In contrast, the 95% confidence interval is the area that has a 95% chance of containing the true regression line. It is self evident that the confirmation criteria chosen by Malan and Day (2002a) and in this chapter (Chapter 3) would be facilitated by constructing the 95% prediction intervals around regression lines, rather than the 95% confidence intervals by the mere nature of the confirmation criteria.

Many studies have found that the relationship between flow and phosphorus is influenced by whether loading of phosphorus is dominated by either point or diffuse sources (Bowes *et al.*, 2008; Jordan *et al.*, 2007; Wood *et al.*, 2005). Loading from point sources are relatively constant over time compared to loading from diffuse sources, and independent of flow, while loadings from diffuse sources are generally highest during periods of rainfall runoff from the catchment into a river. Many sites investigated in this study showed a trend of increasing phosphorus or nitrogen concentration with increasing flow which could indicate that many rivers are influenced by diffuse sources. For example, sites G4H006 and G4H007 show a strong increase in nitrogen concentration with increasing flow (Appendix B Figure 2). The land cover within the catchments of these two sites have a large area of permanent commercial irrigated agriculture (30%) with the rest of the land cover being dominated by forest plantation (12%) and undegraded bush

(56%). The site R2H012 shows the opposite trend of a strong decrease in nitrogen concentration with increasing flow (Appendix B Figure 2). R2H012 occurs close to human settlements and one could assume that point sources of nitrogen strongly influence the water quality at this point. However, the trends shown for flow versus nutrients (phosphate and nitrite + nitrate) were not clear and in general, linear regressions obtained a bad fit to the data. The paucity of data at high flows in addition contributed to there being a weak or no clear relationship between flow and nutrients at many sites. Other sites showed a strong trend of decreasing nutrient concentration with increasing flow. For example, R2H010 on the Buffalo River showed a trend of decreasing phosphorus and nitrogen with increasing flow (Figure 3.2 and Figure 3.3). This section of the Buffalo River is influenced by various point sources of nutrients. Therefore, the trend seen here is consistent with the theory behind the models used by Bowes *et al.* (2008) and the pattern found in other studies.

It is clear that simple regressions are not sufficient to accurately and effectively model the relationship between flow and nutrients, and the method is inadequate to allow predictive modelling. The problem of modelling the effect of flow on nutrients is further explored in later chapters. Chapter 4 describes a mechanistic model that attempts to estimate the point and diffuse signatures in monitoring data by the response of the nutrient concentration to flow. Chapter 5 builds on the model developed in Chapter 4, to incorporate land cover into a model to estimate land cover effects on the diffuse signature of nutrients. Chapter 6 describes a mass-balance model that predicts the effect of agricultural return flow on in-stream salinity. Chapter 7 describes a model which utilizes sparse historical monitoring data and that estimates the fate of nutrients over time as they travel down a stretch of river. Chapter 8 describes an instream model that estimates the relationship between nutrients and flow, especially those nutrients emanating from point sources.

The relationship of flow to EC appears to be much clearer than that between flow and nutrients. It in addition appears that, unlike the case with phosphate and nitrogen, the relationship between flow and EC within simple regression is not influenced by whether sources of salt are diffuse or point source dominated. For example, the relationship of EC

versus flow for the Balfour River DWA data (Q9H019) shows a very distinctive trend of decreasing EC with increasing flow. There is no indication that there are major point sources of salt in this area, and the land cover for the Balfour upstream of the monitoring station is dominated by temporary semi commercial/subsistence cultivation. There are in addition some bush-land and forest areas upstream. The graph of flow versus EC for the Kat River at Fort Beaufort (Q9H029) in addition shows a strong relationship of decreasing EC with flow. The land cover in this area is dominated by diffuse sources such as citrus farms upstream of Fort Beaufort. The DWA monitoring point data at Pirie on the Buffalo River (R2H001) shows a strong trend of decreasing EC with increasing flow. Here, the catchment land cover is dominated by forest and one could probably expect no point sources of salts. All sites investigated showed a decreasing EC with increasing flow relationship. Some monitoring point data showed a few EC data points that were increasing with increasing flow, for example the King Williams Town (R2H010), and Mhlabati Needs Camp sites on the Buffalo River (R2H027). There were however, not many water quality observations at high flow, and these data points were not enough to affect the shape of the regression graph.

One could conclude from this that there were not enough data in most cases to detect the diffuse salt signatures, and that EC does not have the same relationship with flow as was found with flow and phosphorus by Bowes *et al.* (2008). Although the trend of decreasing EC with increasing flow is common throughout all data analyzed, the rate of decrease and shape of the regression curve most probably is a function of geological region. Figure 3.1 shows the distinct differences in the shape of the regression for three DWA monitoring points from three different geological regions. The catchment of the Elands Drift Aspoort on the Doringrivier (E2H002) occurs in the Table Mountain Series where geology is dominated by quartzite, shale and tillite. At this site, one would expect very little natural contributions to EC from the geology of the catchment, and this is reflected in the data (Figure 3.1). Langtouw River at Langfontein (J4H004) occurs in the Bokkeveld Series which is dominated by shale and sandstone geology. Here one can see that the EC within the river is fairly low but still higher than that of J4H004 as there are some natural sources of salt from the surrounding catchment geology. Katkop on Groot-Visrivier

(Q1H001) occurs in the Beaufort Series which has a geology dominated by shale, mudstone, sandstone, limestone and coal. Here one would expect a strong natural contribution to EC from the surrounding catchment geology and this is reflected in the data. One approach to take the analyses of the relationship between flow and EC further would be to extend these Q-C regressions by somehow incorporating the geology of the catchments. However, a different approach has been taken, and Chapter 6 describes a mechanistic mass-balance model that explores the relationship between flow and salinity further by incorporating the effect of pools, salt moving in and out of the river banks and irrigation return flow.

This initial investigation explored the most basic relationships between flow and various water quality variables through simple regression. This initial investigation has set the foundation for further investigation between flow and salinity, and flow and nutrients that are outlined in later chapters. It is evident from this investigation that there is a paucity of water quality measures at higher flows. This could be due to the fact that high flow events within South African rivers are generally fairly rare, as most of the country is fairly arid. The generally infrequent water quality monitoring by the DWA, combined with the rarity of high flow events, has probably resulted in there being few water quality monitoring data for higher flows. The DWA could therefore increase the utility of their monitoring data by taking more frequent water quality measures when high flow events do occur.

Due to the limitations of this type of modelling, Q-C regressions are probably of limited use for implementing IWRM within South Africa. Although the method is relatively simple, it does require a large amount of long term monitoring data to construct a regression model. The method is in addition not suitable for scenario modelling, as it does not incorporate any mechanistic understanding of processes that may influence water quality. Of concern is the fact that Q-C relationships may predict erroneous simulations, with a high degree of confidence, in cases where land use in a catchment has changed, or developments such as new dams have been constructed. There would have to be recognition of these limitations and risks with any use of Q-C regressions within management of water resources.

Chapter 4: A simple mechanistic model to relate flow to water quality

4.1 Introduction

The introduction of nutrients into aquatic systems through point and diffuse sources, caused by an increase in urbanization and agriculture, has led to a range of environmental, social and economic problems (Withers and Jarvie, 2008). Environmental problems include an increase in periphyton growth in shallow, fast running streams and a reduced abundance of macrophytes, while slower moving streams have been affected by surface algal scum, low oxygen conditions and low light penetration (Withers and Jarvie, 2008), and in very slow moving streams and impoundments, a high abundance of floating macrophytes (van Wyk and van Wilgen, 2002).

Water quality models provide the link between observed environmental problems in rivers, data observed from the field and laboratory, and current scientific understanding (Thomann, 1998). A water quality model is a tool that is used to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data (Rouch *et al.* 1998), and can provide some understanding of the underlying processes (Glaser and Bridges, 2007). It is not feasible to observe how rivers react for all pollutant loading scenarios, and models can provide a way of investigating hypothetical scenarios (Glaser and Bridges, 2007). There is therefore, a need for models that can simulate the effects of diffuse and point source inputs on in-stream nutrient concentrations, so as to act as a management tool for decision makers.

There has been some debate in the literature regarding the usefulness of large complex deterministic models in relation to management of water resources, with many authors arguing for the use of simpler models that include some estimate of uncertainty, for example Beck (1987), McIntyre *et al.* (2003), Reckhow (1994) and Young *et al.* (1996). While in the past, water quality models have ignored uncertainty, there has been an

increasing momentum to incorporate uncertainty into water quality models, which is partly a reflection of the maturation of the science underlying water quality modelling (Beck, 1987). It is true that complex deterministic models that attempt to simulate many natural processes can be more accurate than simpler deterministic models. However, in reality, the large amount of data required to accurately calibrate large models, and the expertise required to operate these complex models, effectively excludes the use of these models in management in most cases (Reckhow, 1994). Complex models with many parameters are in addition prone to the problem of equifinality (McIntyre *et al.*, 2003), where multiple sets of parameter values will give model results that are similar to observed results, resulting in possibly inaccurate model simulations when the model is applied to future scenarios. It is in addition extremely difficult to incorporate uncertainty into large complex models. Complex models are archives of hypotheses that attempt to simulate as many of the cause effect relationships in natural processes as possible and are therefore impossible to falsify (Beck, 1987). As model complexity increases, the ability to evaluate uncertainty in these models will decrease due to the large number of uncertain model components (McIntyre *et al.*, 2003). Therefore, relatively simple models that give approximate solutions may be more appropriate than extremely complex models, as it is possible to incorporate an indication of uncertainty around predictions (McIntyre *et al.*, 2003).

Water quality models require measured nutrient data so as to be accurately calibrated (Beck, 1981; Chapra, 2003; Oreskes *et al.*, 1994; Shanahan *et al.*, 1998; Thomann, 1998). Unfortunately, while many countries have reasonably good flow data for main river reaches, there is often a paucity of water quality data (McDonnel, 2008). However, models that can be considered useful from a management perspective, would be required to accurately simulate in-stream nutrient concentrations using the available data, as time and budgetary constraints often preclude the option of dedicated field measures being undertaken.

Bowes *et al.* (2008) created models based on an understanding of the responses of phosphate to flow. Their understanding was that phosphate introduced primarily through

point sources into a river, would show a decreasing concentration with increasing flow. This is because the load of point sources is generally relatively constant over time compared to that emanating from diffuse sources, and higher natural flows dilute effluent from point sources, leading to lower in-stream nutrient concentrations. In contrast, Bowes *et al.* (2008) found that rivers dominated by diffuse sources of phosphate, would show an increasing concentration of phosphate with increasing flow. This is because the mobilization of phosphate is dependant on flow processes, such as surface runoff from urban areas (Hughes and van Ginkel, 1994), or soil water drainage from agricultural areas (Malan and Day, 2002a). Their models in addition, sought to separate the diffuse and point source phosphate signatures in rivers that were influenced by both point and diffuse sources using a non-linear regression equation.

The South African Department of Water Affairs (DWA) historical flow and water quality monitoring data were investigated to determine if there were any simple relationships evident when regressing measured flow data against measured nutrient data. However, there is a paucity of water quality data in South Africa. The DWA maintains a hydrological database that provides daily flow data for measuring gauges, but only provides some of the data that would be required for nutrient modelling (Wimberley and Coleman, 2005). In addition, the DWA nutrient data has temporal gaps between measures of up to multiple years in some extreme cases, while some gauges have as much as two nutrient measures per week. While the data that Bowes *et al.* (2008) used showed a clear asymptotic decrease in phosphate concentrations with increasing flow in point source dominated catchments, the DWA nutrient concentration data investigated (see Appendix A, Table 1) show considerable scatter at low flows, with concentrations ranging from close to zero to very high concentrations at low flow. This could be as a consequence of point sources within South Africa releasing effluent that has highly variable nutrient concentration, and/or a highly variable flow rate. Possibly, this could be related to overflow from the final settling ponds of wastewater treatment works (WWTWs) within South Africa. In addition, the DWA data have very few nutrient concentration measures taken at high flow conditions, which make quantifying the diffuse source nutrient signature very difficult. For these reasons, the use of the non-linear regression models

proposed by Bowes *et al.* (2008) to the DWA nutrient data (Appendix A, Table 1) in the initial investigation, met with little success and an alternative approach has been adopted in this study. The concept of the method was to make use of the same underlying mechanisms that are the basis of the Bowes *et al.* (2008) approach, but to apply a combined mechanistic/statistical approach that may be more appropriate for South African conditions. This model was applied to phosphate as well as nitrite plus nitrate data, with the assumption that nitrite plus nitrate signatures would display the same response to flow as phosphate.

This chapter partly addresses Aim 2, in that the model investigated is fairly simple, with a simple mechanistic component and a statistical component. If the model proves accurate in its predictive ability to describe the relationship between flow and nutrients within rivers, then this chapter will demonstrate that relatively simple models can be used to model the relationship between flow and water quality. Since the model uses solely historical monitoring data, the success or failure of this model will contribute into answering Aim 4.

4.2 Data and methods

4.2.1 Data

A subset of the data from the DWA monitoring points outlined in the Appendix A (Table 1) were used for this analysis. Analyses for this chapter (Chapter 4) and Chapter 5 on relating land cover to water quality were performed together and the same selection criteria for monitoring points was used for both chapters. Only flow and water quality data measured after 1990 were used for the analysis, so as to minimize the temporal disparity between the monitoring data and the land cover data database that was published in the year 2001. The land cover database used was derived from the DWA Groundwater Resource Directed Measures database (Parsons *et al.*, 2006), which will be expanded on in Chapter 5. Only monitoring points were selected where there were greater than 50 sampling dates after 1990. Flow data and corresponding water quality data were

ignored where flow was zero, as the aim of the model is to relate changes in flow to changes in water quality. Only monitoring points with a catchment of one quaternary or greater were considered. In addition, since the model outlined here is a simple mechanistic model, monitoring points on large rivers with very large amounts of flow were avoided as to minimize the effects of other processes that the model does not attempt to explain. The data for monitoring points were in addition analyzed for seasonal bias, and gauges where data were biased more than 70:30 for either summer: winter or winter: summer were rejected.

4.2.2 The model used

The model was implemented in Microsoft Office 2003 Excel. One model for each monitoring point/gauging station was constructed, to fit the daily flow data, and the corresponding available phosphate or nitrogen (nitrate + nitrite) data. The model simulates the point source signature of the data using four parameters: Q_{pmax} , Q_{pmin} , C_{pmax} , C_{pmin} where Q_{pmax} and Q_{pmin} represent the maximum and minimum possible flow contributions from all point sources influencing the data of that particular monitoring point in $m^3.sec^{-1}$, and C_{pmax} and C_{pmin} represent the maximum and minimum possible concentration of either phosphate or nitrate + nitrite of the effluent being released from the point sources in $mg.L^{-1}$. The model generates two random numbers for each observed data point using the Rand() function in Excel. This was incorporated into the model because of the apparent variability of point sources in relation to effluent flow and effluent concentration that can evidently vary independently. One random number is used to generate a simulated estimation of point source flow Q_{psim_i} ($m^3.sec^{-1}$) for each observed data point:

$$Q_{psim\_i} = (Rand() * (Q_{pmax} - Q_{pmin})) + Q_{pmin} \quad \text{(Equation 4.1)}$$

A separate random number is used to generate a model simulated estimation of point source concentration C_{psim_i} ($mg.L^{-1}$) for each observed data point:

$$C_{psim\_i} = (Rand() * (C_{pmax} - C_{pmin})) + C_{pmin} \quad (\text{Equation 4.2})$$

The use of the Rand() function in excel incorporates a very basic form of uncertainty into the model. The model estimated concentration of either phosphate or nitrate + nitrite within the river due to point sources is then estimated:

$$C_{sim\_i} = (C_{psim\_i} * Q_{psim\_i})/Q_i \quad (\text{Equation 4.3})$$

where C_{sim_i} represents the simulated concentration of phosphate or nitrate + nitrite in the river due to point sources in $mg.L^{-1}$ and Q_i represents the observed flow in the river in $m^3.sec^{-1}$. The model estimated C_{sim_i} for each observed flow is then plotted on the same graph as the observed concentration, C_i . In the majority of cases, actual values of parameters from observational data are not available, and the user then adjusts the parameters Q_{pmax} , Q_{pmin} , C_{pmax} and C_{pmin} until a visual assessment of the model simulated point source signature is similar to the perceived point source signature in the observed data. This is illustrated in Figure 4.1 which shows a series of trial and error parameter fitting steps to estimate the point source signature for the monitoring point data from R2H010, until a satisfactory reproduction of the observed variability is obtained.

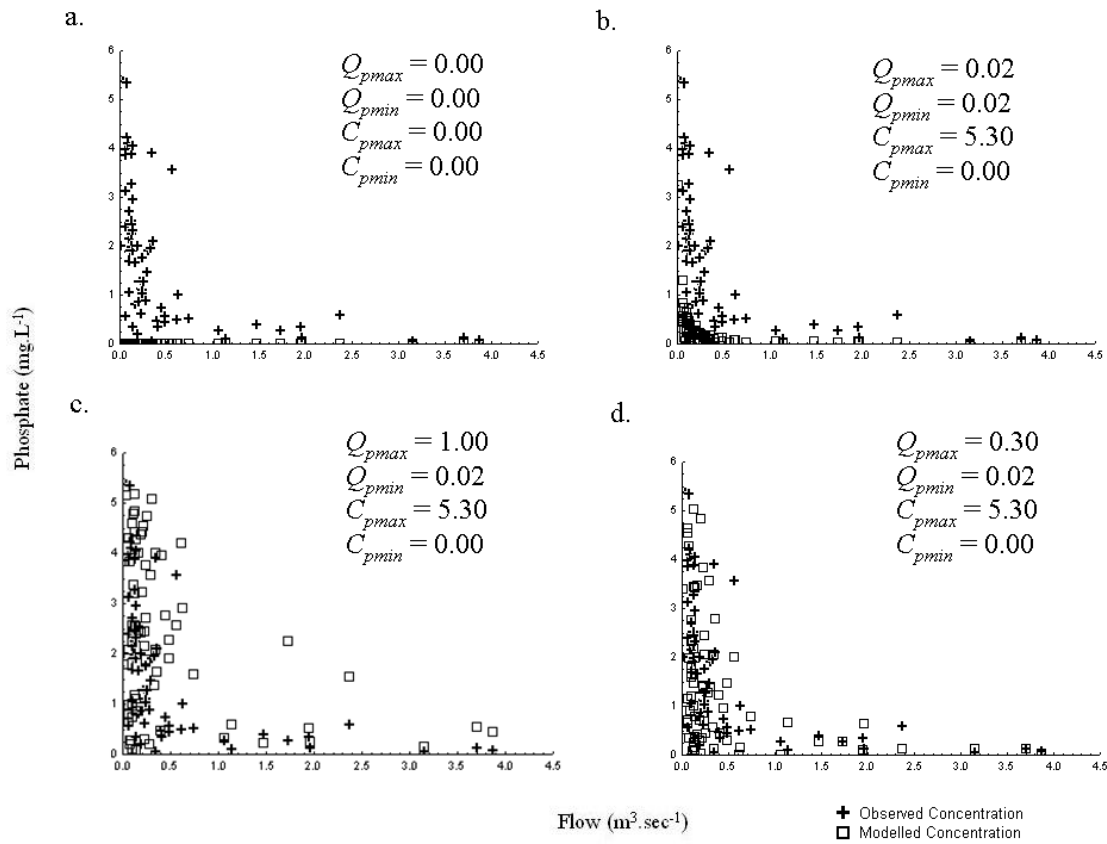


Figure 4.1: Example calibration process for estimating the point source signature in the historical data for DWA monitoring point R2H010.

Figure 4.1a illustrates the visual fit of model estimated point source influence to observed data when no point source is estimated. Figure 4.1b shows the visual fit of model estimated point source influence with a small amount of estimated point source input, which is obviously too small to obtain the same degree of variability as the observed data. Figure 4.1c shows the visual fit of model estimated point source influence to observed data, where the degree of simulated variability is greater than that of the observed data. Figure 4.1d shows a simulated point source influence that mirrors the variability of the perceived point source influence in the observed data.

The highest and lowest nutrient concentration in the historical data set is chosen for C_{pmax} and C_{pmin} respectively, while the lowest flow in the historical data set is chosen for Q_{pmin} .

The value of Q_{pmax} is then adjusted until a visual fit between the observed and simulated data is obtained. The basis for the visual fit is to achieve a similar degree of scatter on the observed and simulated concentrations, as well as similar maximum concentrations for different in-channel flow rates.

It was found that the observed data show a high variation in nutrient concentrations at low flow. It is assumed that this result is a consequence of flow and nutrient concentrations from point sources varying independently so that low flows in a river show high variations in the final concentration of nutrients. A method was required to separate the diffuse source signature from the point source signature, bearing in mind that the point source signature would have a high deviation at low flows but a low deviation at high flows as effluent becomes diluted.

The residual concentration of each simulated data point is then calculated:

$$C_{res\_i} = C_i - C_{sim\_i} \quad (\text{Equation 4.4})$$

where C_{res_i} is the residual concentration of either phosphate or nitrate + nitrite in mg.L^{-1} , and C_i is the observed concentration of the nutrient in the river in mg.L^{-1} .

When developing this model, it was found that the positive residuals or $\text{abs}(C_{res\_i})$, when regressed against flow, had a decreasing value with increasing flow in a power relationship with a power approximating -0.60. This assumption was tested with a number of sites that are influenced predominantly by point sources (Figure 4.2).

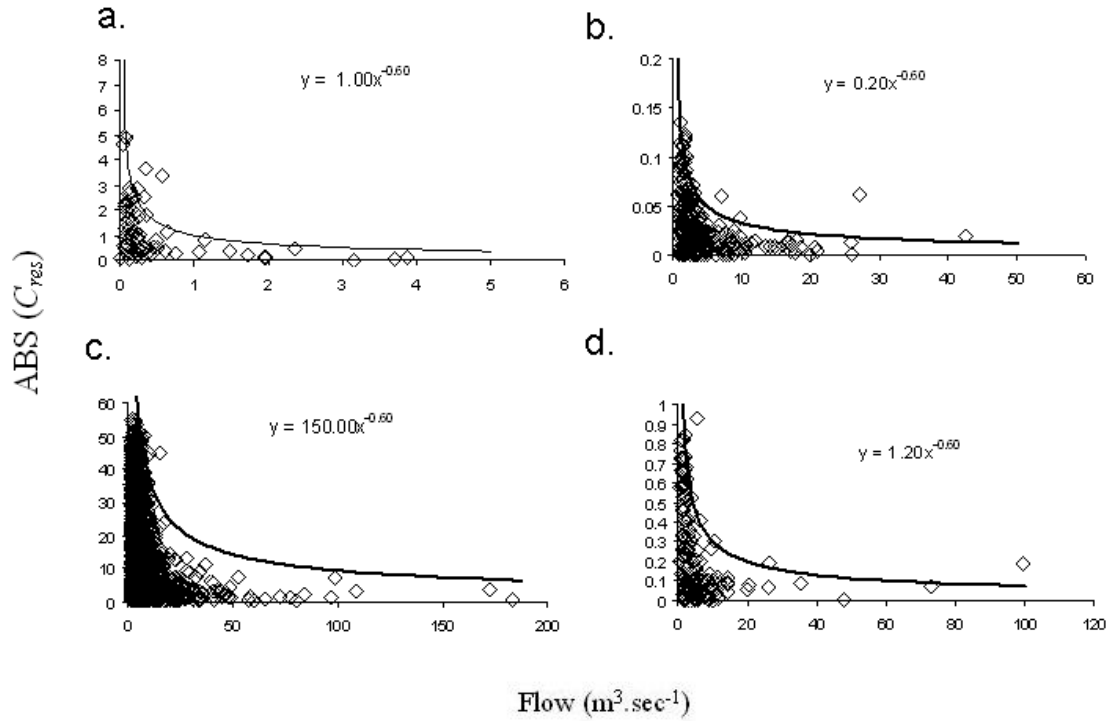


Figure 4.2: Flow ($\text{m}^3.\text{sec}^{-1}$) versus the absolute residuals (observed – simulated water quality) generated by a simple conceptual model that predicts the point source signature in the relationship between flow and nutrient concentration. a. monitoring point R2H010 for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}); b. monitoring point B6H001 for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}); c. A2H012 for $\text{NO}_3^{-}\text{-N} + \text{NO}_2^{-}\text{-N}$ (mg.L^{-1}); d. X1H001 for $\text{NO}_3^{-}\text{-N} + \text{NO}_2^{-}\text{-N}$ (mg.L^{-1}).

An estimation of the maximum range for each observed data point of the nutrient concentration in the river due to point sources (C_{sim_i}), and scaled by flow (the range should decrease with increasing flow) is made, using the general relationship between residuals and flow:

$$\text{Range}_i = A * Q_i^{-0.60} \quad (\text{Equation 4.5})$$

Where Range_i is an estimate of the range of C_{sim_i} of any observed flow Q_i .

The maximum possible range $\text{Range}_{\max}$ would be the Range_i at $Q_{\min}$ and can be estimated as

$$\text{Range}_{\max} = (C_{p\max} * Q_{p\min})/Q_{\min} \quad (\text{Equation 4.6})$$

In addition according to Equation 4.5

$$\text{Range}_{\max} = A * Q_{\min}^{-0.6}$$

Therefore

$$A = \text{Range}_{\max} * Q_{\min}^{0.6} \quad (\text{Equation 4.7})$$

or

$$A = (C_{p\max} * Q_{p\min})/Q_{\min} * Q_{\min}^{0.6} \quad (\text{Equation 4.8})$$

Therefore to calculate the maximum range scaled by the observed flow

$$\text{Range}_i = (((C_{p\max} * Q_{p\min})/Q_{\min}) * Q_{\min}^{0.6}) * Q_i^{-0.60} \quad (\text{Equation 4.9})$$

An absolute value of C_{res_i} compared to the scaled range for each data point is then estimated:

$$Y_i = \text{abs}(C_{\text{res}_i})/\text{Range}_i \quad (\text{Equation 4.10})$$

Figure 4.3 shows the values of Y_i in relation to flow and observed nutrient data for a point source dominated monitoring point as well as a monitoring point that has some diffuse source input.

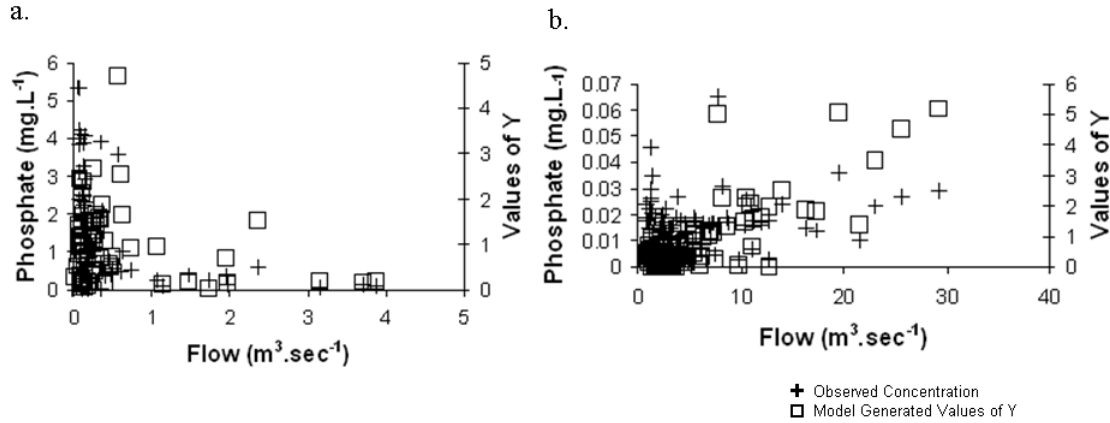


Figure 4.3: Values of Y (Equation 4.10) in relation to flow and observed phosphate concentration. Graph 4.3a shows the point source dominated DWA monitoring point R2H010 and graph 4.3b shows the diffuse source influenced X3H006.

Figure 4.3a demonstrates that the model generated values of Y_i generally mirror the variation of the observed phosphate concentrations in point source dominated catchments. The gauge R2H010 occurs along the Buffalo River just before Laing Dam, and is influenced by sewage effluent release from two WWTWs. Figure 4.3b shows that values of Y_i tend to increase with higher flow in catchments that show some diffuse input of phosphate. The gauge X3H006 occurs within a catchment dominated by forest plantations (> 60%) and some irrigated farmland (7%), and therefore, one could expect the load of nutrients coming into a river at this point due to diffuse sources to be relatively high.

If there is some perceived diffuse source input in the historical monitoring data of a gauging station, a linear regression line of observed flow Q_i versus the Y_i values is fitted.

$$Y_i' = \text{slope} * Q_i + \text{intercept} \quad (\text{Equation 4.11})$$

where Y_i' is the estimate of Y_i from fitting a linear regression to Y_i regressed against flow.

A positive estimation of the residuals is then calculated by:

$$C'_{\text{res}_i} = Y_i' * \text{Range}_i \quad (\text{Equation 4.12})$$

Where C'_{res_i} is an estimation of the positive values of C_{res_i}

The concentrations of the nutrient associated to the diffuse signature can then be estimated by:

$$C_{\text{dsim}_i} = C'_{\text{res}_i} - C_{\text{sim}_i} \quad (\text{Equation 4.13})$$

The positive values of C_{dsim_i} are then regressed against flow using a power model:

$$C'_{\text{dsim}_i} = A.Q_i^B \quad (\text{Equation 4.14})$$

Where C'_{dsim_i} is the estimation of C_{dsim_i} by fitting a power model to C_{dsim_i} versus flow.

The A and B parameters therefore quantify the relationship between the diffuse signature of nutrients and flow at particular monitoring points.

4.3 Results

4.3.1 A case study of a point source dominated monitoring point

R2H010 is a monitoring point on the Buffalo River. The Buffalo River is situated in the Eastern Cape, South Africa. The monitoring point R2H010 is situated approximately 15 km downstream of King Williams Town. This stretch of river is subject to two point sources, the King Williams Town wastewater treatment works (WWTW), and a few km further downstream, the Zwelitsha WWTW. The DWA has some historical monitoring data on the concentrations of phosphate that are released from these two WWTWs (Table 4.1). Additional data on the effluent flow rates and concentrations were collected as part of another study (see Chapter 8) and are listed in Table 4.2.

Table 4.1: Summary of DWA monitoring data for $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}) for two sewerage treatment works (WWTWs) on the Buffalo River

Point Source	Dates		n	Mean	Min	Max	Std Dev
	From	To					
King Williams Town WWTW	20-Apr-00	03-Mar-09	74	3.36	0.11	13.60	2.54
Zwelitsha WWTW	23-Jan-02	03-Mar-09	69	1.52	0.03	4.61	1.34

Table 4.2: Flow and nutrient measures taken in grab samples from effluent from two sewerage treatment works (WWTWs) along the Buffalo River

King Williams Town WWTW				Zwelitsha WWTW		
Sample Date	Flow ($\text{m}^3.\text{sec}^{-1}$)	$\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1})	$\text{NO}_2^{-}\text{-N} + \text{NO}_3^{-}\text{-N}$ (mg.L^{-1})	Flow ($\text{m}^3.\text{sec}^{-1}$)	$\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1})	$\text{NO}_2^{-}\text{-N} + \text{NO}_3^{-}\text{-N}$ (mg.L^{-1})
26-Aug-09	0.295	3.774	3.78	0.06	5.37	4.23
12-Oct-09	0.295	3.574	7.73	0.27	6.28	5.09
18-Nov-09	0.094	3.967	10.78	0.13	5.08	1.94

The historical DWA data for the monitoring point R2H010 appears to show that both phosphates, and nitrates + nitrites, show a strong decreasing concentration with increasing flow (Figure 4.4) with no indications of increasing concentration with increases of flow.

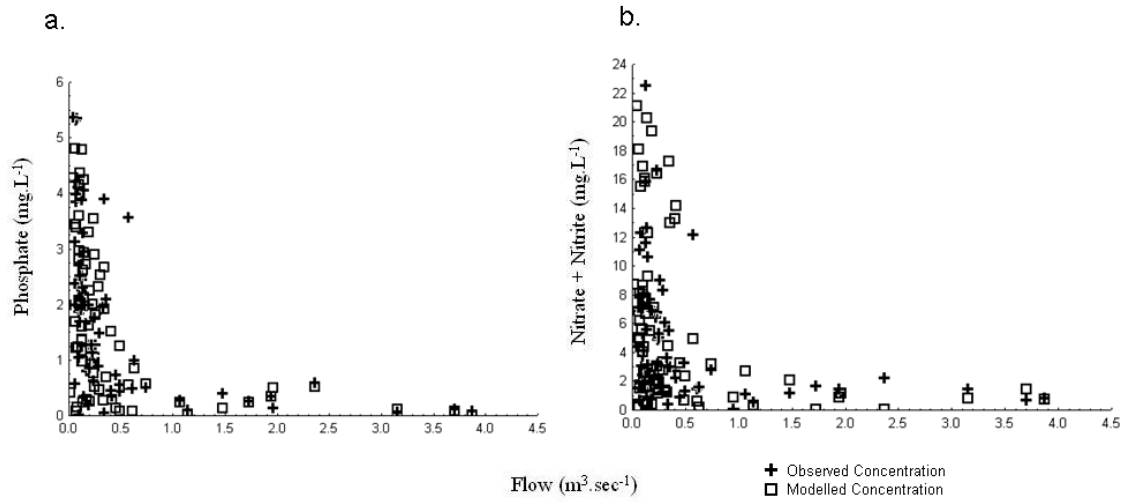


Figure 4.4: Graph a shows flow ($\text{m}^3.\text{sec}^{-1}$) versus $\text{PO}_4^{3-}\text{-P}$ (mg.L^{-1}) observed data, as well as model simulated data for the DWA monitoring point R2H010. Graph 4.4b shows flow ($\text{m}^3.\text{sec}^{-1}$) versus $\text{NO}_3^{-}\text{-N} + \text{NO}_2^{-}\text{-N}$ (mg.L^{-1}) observed data, as well as model simulated data for the DWA monitoring point R2H010.

The model estimated parameters for phosphates were:

$$Q_{\text{pmax}} = 0.3 \text{ m}^3.\text{sec}^{-1}; Q_{\text{pmin}} = 0.016 \text{ m}^3.\text{sec}^{-1}; C_{\text{pmax}} = 5.36 \text{ mg.L}^{-1}; C_{\text{pmin}} = 0.003 \text{ mg.L}^{-1}$$

The model estimated parameters for nitrates + nitrites were:

$$Q_{\text{pmax}} = 0.3 \text{ m}^3.\text{sec}^{-1}; Q_{\text{pmin}} = 0.016 \text{ m}^3.\text{sec}^{-1}; C_{\text{pmax}} = 22.50 \text{ mg.L}^{-1}; C_{\text{pmin}} = 0.02 \text{ mg.L}^{-1}$$

The values of Q_{pmax} for both the phosphate and nitrate + nitrite models are similar to those of observed effluent flows if one were to add the average daily effluent flow values taken from the King Williams Town WWTW and the Zwelitsha WWTW (Table 4.2). The fact that both models in addition generated the same Q_{pmax} is encouraging and indicates that the DWA historical monitoring data for R2H010 shows that the same point sources are influencing concentrations of both phosphate and nitrate + nitrite, as one would expect from WWTWs. The value of C_{pmax} for phosphate is similar to that of the max

phosphate value measured at the Zwelitsha WWTW (Table 4.1). This WWTW is closer to the R2H010 monitoring site than the King Williams Town WWTW and one would expect the concentration of phosphate in the effluent of this WWTW to have more of an effect on the concentrations at R2H010. The value of C_{pmax} for phosphate is in addition similar in value to that measured during grab samples (Table 4.2) for both WWTWs. The value of C_{pmax} for nitrate + nitrite is higher than any values measured in grab samples from either WWTW (Table 4.2) where the range for the King Williams Town WWTW is 3.78 – 10.78 mg.L⁻¹ and the range for the Zwelitsha WWTW is 1.94 – 5.09 mg.L⁻¹. However, the high variability of concentrations of nitrate + nitrite from these grab samples indicates that the concentration of nitrates + nitrites from both WWTWs has high temporal variability, and high concentrations, as estimated by the model of 22.50 mg.L⁻¹, may well occur in the effluents.

4.3.2 A case study of a diffuse source dominated monitoring point

The DWA monitoring point X3H006 occurs on the Sabie River. Land cover information for the monitoring site shows that land cover is dominated by forest plantation (61%), undegraded bush (16%), degraded natural areas (11%) and cultivated permanent commercial irrigation (7%). One would expect some diffuse nitrogen input from forest plantations as there is a high concentration of leaf litter associated with plantations. Some natural sources of nitrogen may arise from the undegraded bush land cover, and the cultivated land cover may in addition contribute some diffuse nitrogen as fertilizer is often applied to cultivated land.

The observed DWA historical monitoring data for the monitoring point X3H006 shows a trend of increasing nitrate + nitrite concentration with increasing flow (Figure 4.5a).

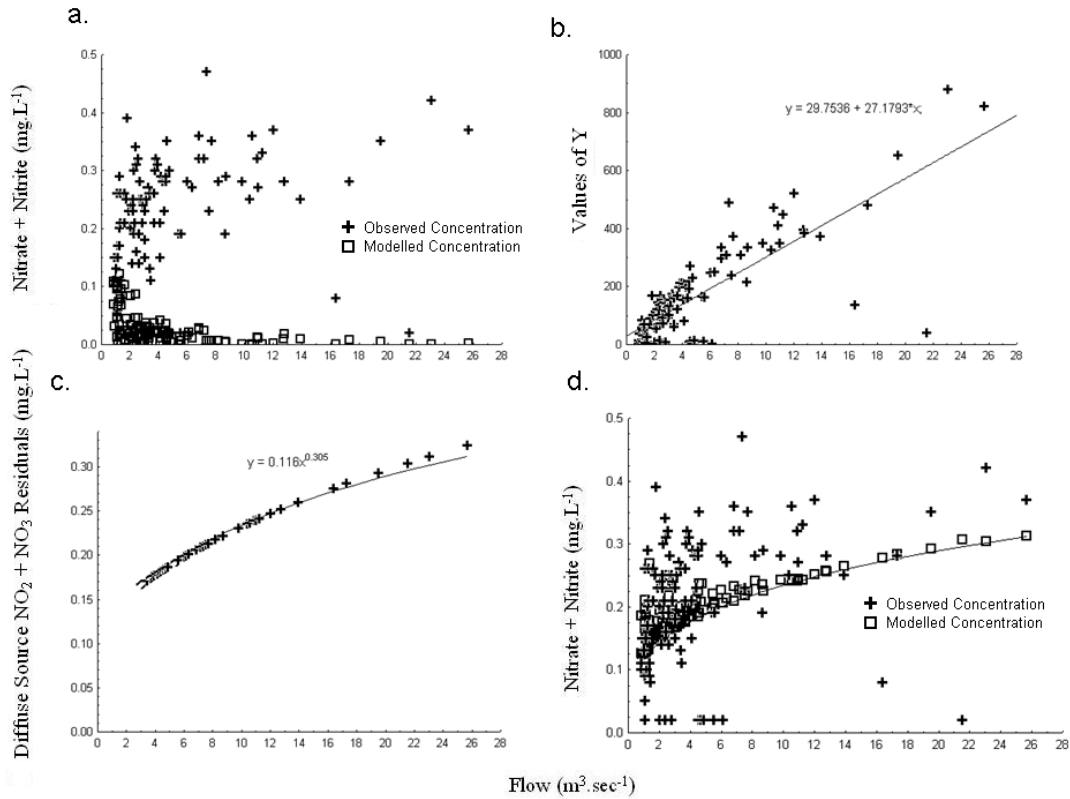


Figure 4.5: Diagram demonstrating the steps in a simple mechanistic model to separate the point source and diffuse source signatures in relation to flow in historical nutrient water quality modelling. This example is for the DWA monitoring point X3H006.

The following model parameters fitted the observed data for the point source signature (Equation 4.1 – 4.3):

$$Q_{\text{pmax}} = 0.88 \text{ m}^3 \cdot \text{sec}^{-1}; Q_{\text{pmin}} = 0.001 \text{ m}^3 \cdot \text{sec}^{-1}; C_{\text{pmax}} = 0.30 \text{ mg} \cdot \text{L}^{-1}; C_{\text{pmin}} = 0.02 \text{ mg} \cdot \text{L}^{-1}$$

The observed data shown in Figure 4.5a display an overwhelming trend of increasing nitrogen with increasing flow. A small amount of point source influence is estimated, which can be seen in Figure 4.5a. Figure 4.5b (Equation 4.4 – 4.11) shows the regression of flow versus residuals scaled by Range_i . Working back from the regression equation shown in Figure 4.5b and going through the process defined by Equations 4.12 – 4.14, Figure 4.5c shows the power function equation fitted to the residuals that can be

associated with diffuse source input. Figure 4.5d shows observed nitrogen data, as well as the added point and diffuse influences as determined by the model.

Once the point source signature was separated from the perceived diffuse source signature, the parameters for the diffuse signature were estimated using equation 4.14 as: $A = 0.116$ and $B = 0.305$ (see Figure 4.5c and 4.5d).

4.3.3 Results of model applied to all data

Appendix A Tables 2 and 3 show the estimated parameters from the simple mechanistic model applied to flow versus phosphate and flow versus nitrate + nitrite data respectively for approximately 140 monitoring sites. Figures 4.6 and 4.7 show some examples of the model applied to DWA monitoring sites for phosphate and nitrate + nitrite respectively. The relationship between flow and phosphate and between flow and nitrate + nitrite show similar patterns for individual monitoring points. The data from some sites show a strong point influence with no real diffuse influence, while some sites show both a point and diffuse signature. At a few sites, the opposite is evident with a strong diffuse influence and no real point influence. Point influences for both phosphate and nitrate + nitrite typically have a much stronger effect on the concentration of nutrients in rivers than do diffuse influences, especially at very low flows. A greater number of monitoring points show diffuse influences for nitrate + nitrite than is the case for phosphate.

The monitoring point A7H001 (Figure 4.6a) shows a moderate amount of point source phosphate signature, and a small amount of diffuse source phosphate signature. B3H021 (Figure 4.6b) shows a small amount of point and diffuse source phosphate signature. R2H027 (Figure 4.6c) shows a relatively large point source signature of phosphate, with no discernable diffuse signature. W5H026 (Figure 4.6d) shows a moderate point source signature of phosphate and no discernable diffuse signature. X3H004 (Figure 4.6e) shows a small point and diffuse phosphate signature. X3H008 (Figure 4.6f) shows a relatively large point source signature and a small diffuse signature for phosphate.

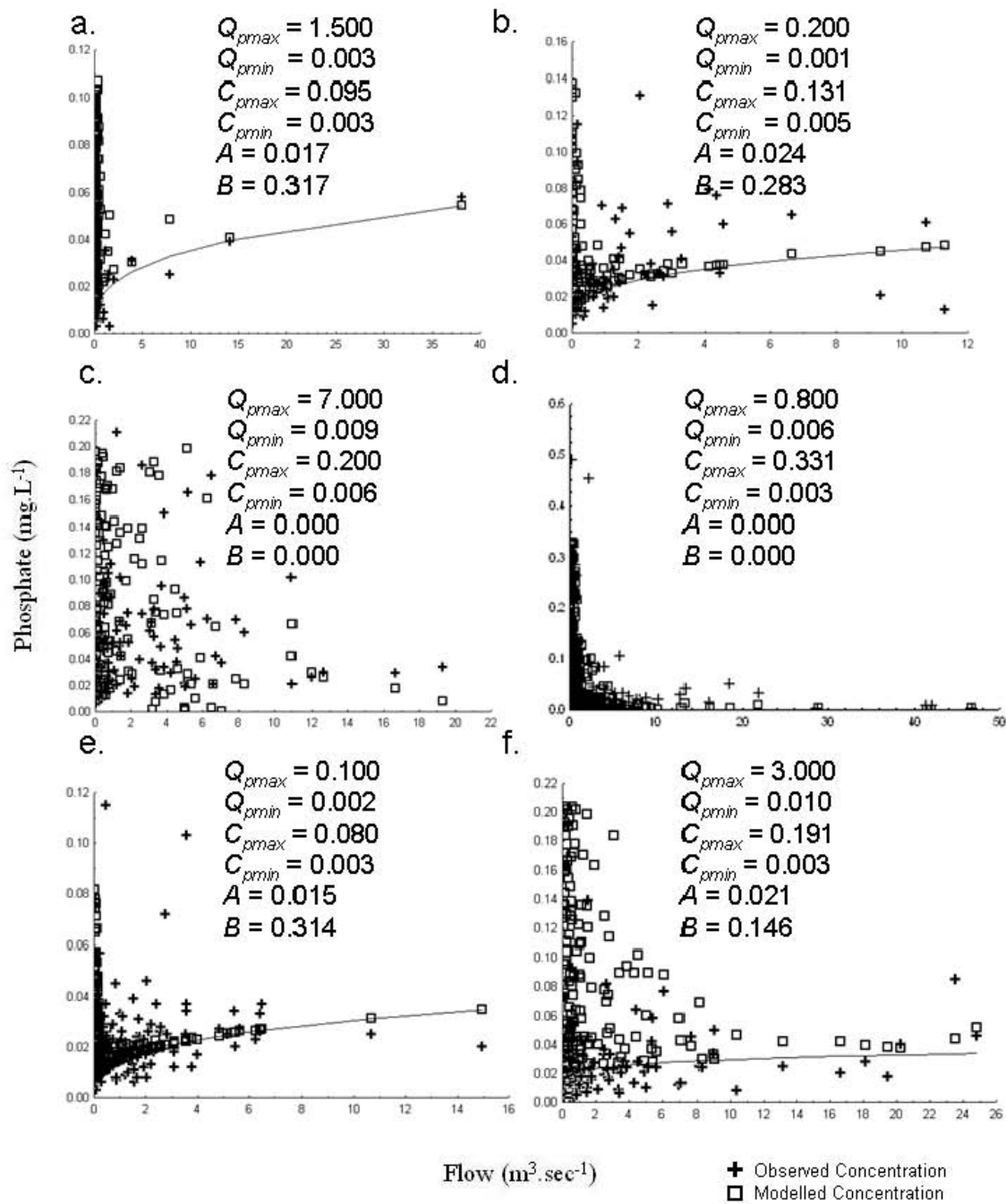


Figure 4.6: Examples of a simple mechanistic model applied to phosphate historical monitoring data of various DWA monitoring sites. a – A7H001; b – B3H021; c – R2H027; d – W5H026; e – X3H004; f – X3H008.

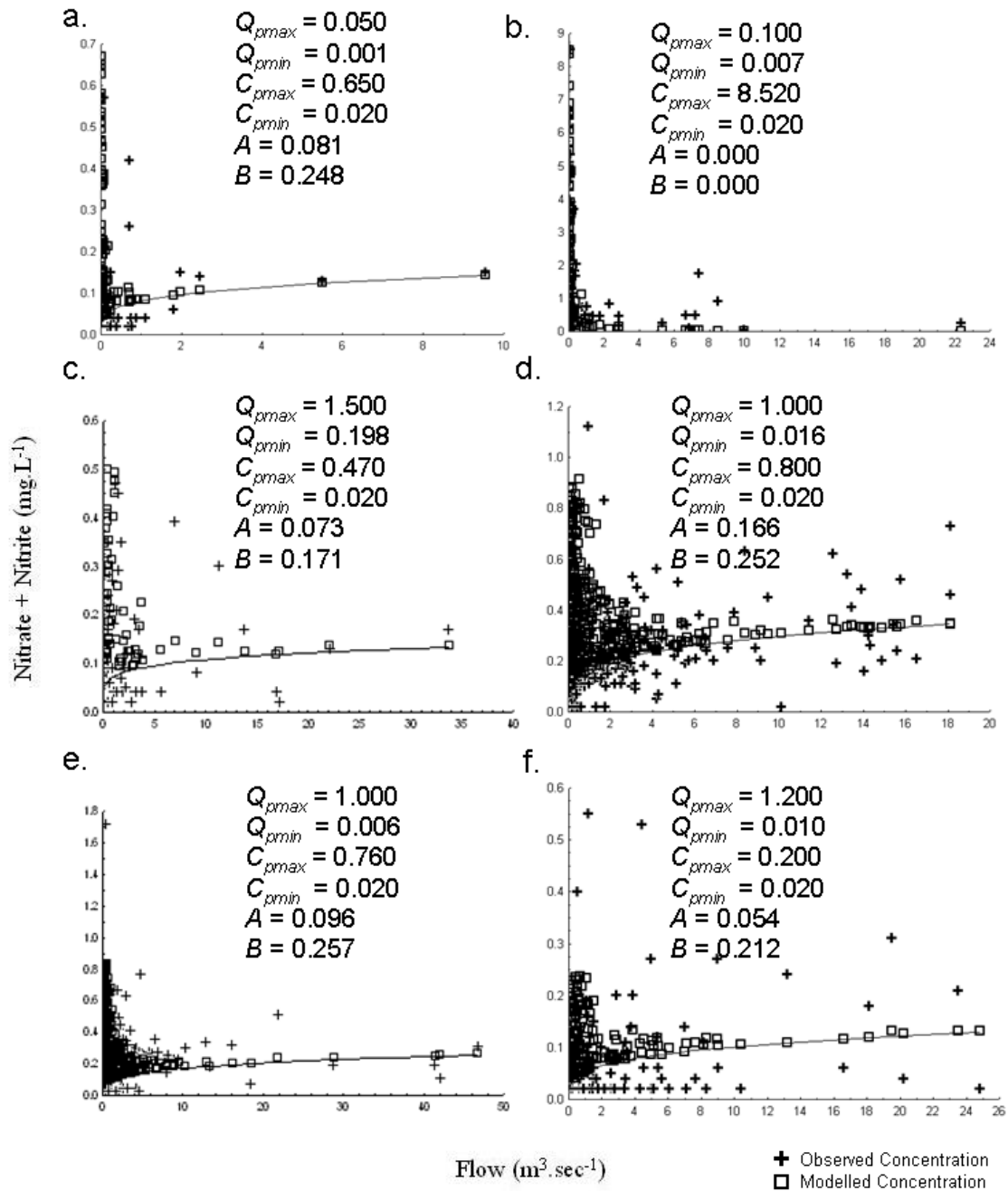


Figure 4.7: Examples of a simple mechanistic model applied to nitrate + nitrite historical monitoring data of various DWA monitoring sites. a – D3H015; b – S7H001; c – T1H001; d – V2H006; e – W5H026; f – X3H008.

D3H015 (Figure 4.7a) shows a small point source nitrogen signature and a small diffuse

source nitrogen signature. S7H001 (Figure 4.7b) shows a small point signature with no discernable diffuse source signature of nitrogen, with the highest point source concentration being relatively high, and consequently concentrations of phosphate at low flow tend to be excessively high. T1H001 (Figure 4.7c) shows a moderate point source signature of nitrogen, and a small diffuse source signature. V2H006 (Figure 4.7d) shows a moderate point source signature of nitrogen, and a small diffuse source signature. W5H026 (Figure 4.7e) similarly shows a moderate point source signature and a small diffuse signature of nitrogen. X3H008 (Figure 4.7f) shows a moderate point source signature of nitrogen and a small diffuse source signature.

4.4 Discussion

Due to the way this model is constructed, the model cannot be confirmed in the conventional way. Usually, mechanistic models are calibrated to one data set and confirmed against an independent data set. This model however, uses a random generator to generate the point source influence within the model which means that no attempt is made to accurately simulate individual observed data values. This is justified by the assumption that much of the scatter of the observed data is related to the random nature of the point source output, in both quantity of effluent flow, and nutrient concentrations. Although the model cannot be tested in the conventional sense, the model parameters can be compared to measured point source data as was done earlier in this chapter.

While the model attempts to simulate the variability of in-stream nutrient concentrations due to point source input, the data in addition show considerable scatter in the perceived diffuse source signature at many monitoring points for example Figures 4.6b & 4.6f and Figures 4.7d and 4.7f. The model attempts to account for the diffuse source signature by applying a regression line. In this way, the model combines mechanistic and statistical components. There are various reasons why the diffuse source signature should show variability, however, no mechanistic understanding in this regards was built into the model because of lack of information. For example, the model does not attempt to account for antecedent rainfall in the recent past i.e. a lack of rainfall for a period may lead to a build up of nutrients in the catchment, and unusually high concentrations of

nutrients flowing into a river at the next high rainfall event. Simpson and Stone (1988) in a study of runoff pollution within an urban catchment in South Africa, found that there was a peak in load export of many pollutants within rainfall events following a dry year, which they attributed to a 'first flush' effect. Antecedent rainfall may be the reason why some monitoring point data show a scatter of nutrient concentrations at high flows. The effect of antecedent rainfall could possibly be included in a more mechanistic model of the diffuse source input, while the research here attempts only to fit a regression line to the diffuse signatures within the nutrient data. An attempt was made in this research to try and account for antecedent rainfall, but it is difficult to determine how far in the past to account for antecedent rainfall, and it was decided in this research to rather point out this problem as an issue for future research. High flow processes in larger rivers could re-introduce nutrients to the water column through scouring of the bottom sediments, thereby accounting for some scatter in nutrient concentrations at high flow. To limit the effect of this process as far as possible, it is advisable that this model be applied only to small rivers and streams of order 1 to 3 (Strahler, 1952). The scatter of nutrient concentrations at high flows could in addition be due to seasonal influences, for example, seasonal application of fertilizer to agricultural land, causing a large load of nutrient input into a river during a rainfall event. The scatter of nutrient concentrations at high flow could in addition be due to a variable nature of the diffuse sources affecting a river. Perhaps there are some land use activities within a catchment that occur randomly, or seasonally, that affect diffuse inputs of nutrients to a river. Nutrients are in addition subject to in-stream modification, such as nitrification of nitrogen species (Chapra, 1997), and nutrients are taken up by aquatic flora. These processes could be more pronounced at certain times of the year, resulting in a scatter of nutrient concentrations at high flow within the data set. An initial attempt was made to develop relationships between the A and B parameters of the diffuse signatures, and land cover data (see Chapter 5). Unfortunately, it was found that there is not a sufficiently strong relationship between land cover data in South Africa, and the diffuse signature parameters related to nutrient inputs, and consequently, the models developed did not have good predictive power.

The case study of the model applied to data collected at the point source dominated

R2H010, shows that the parameters Q_{pmax} , and C_{pmax} , estimated in the model, are reasonably representative when compared to measured data. A case study of the model applied to the monitoring point X3H006, and an investigation of land cover within the quaternary catchment containing the monitoring point, shows that the model indication of a strong diffuse source influence is supported by land cover information. The land cover within the catchment around the monitoring point X3H006 is dominated by forest plantations and some permanently irrigated cultivated land, which are both land cover types that are associated with diffuse sources of nutrients into rivers. These two case studies indicate that while the mechanistic model is simple, it is based on solid conceptual grounds. The accuracy of the model is of course influenced by the accuracy of the DWA data used.

The Mechanistic/Statistical Nutrient Model uses the same underlying mechanistic understanding as that of the Bowes *et al.* (2008) model. However, the Bowes *et al.* (2008) model is a purely statistical model, and therefore, is not suitable for South African conditions for reasons I have made clear in the introduction of this chapter. The Mechanistic/Statistical Nutrient Model however, does incorporate some mechanistic understanding in an effort to be more suitable for South African conditions. While the Bowes *et al.* (2008) model was applied only to phosphate, this research shows that the same model can be applied to simulate $NO_2-N + NO_3-N$. The Mechanistic/Statistical Nutrient Model differs from other mechanistic models in that there are a limited number of processes simulated, as the model attempts so simulate purely the relationships between flow and nutrient concentration.

This chapter partly answers Aim 2. Although this is a relatively simple model, the model does seem to be able to mechanistically predict the effect of flow on nutrient concentrations taking into account point sources. However, since the diffuse component of the model is predicted by a statistical regression, this part of the model suffers from the same shortcomings as that of the Q-C regression approach. Models constructed on past data, may be inaccurate when predicting future diffuse inputs of nutrients, as land use/cover may change in the future. So while the mechanistic component of this model

proves that relatively simple models can accurately describe the relationship between flow and water quality, this model is not sufficiently descriptive to accurately predict diffuse inputs of nutrients under changing land use/cover. Chapter 5 describes the Land Cover Model which builds on the Mechanistic/Statistical Nutrient Model, by attempting to statistically describe the relationship between land cover and the diffuse input component of the Mechanistic/Statistical Nutrient Model component. This chapter (Chapter 3) also addresses Aim 4, since the Mechanistic/Statistical Nutrient Model uses solely historical monitoring data, and demonstrates that to a limited extent, available historical monitoring data can give an accurate description of the relationship between flow and water quality.

4.5 Conclusion

This investigation shows that it is possible to separate nutrient concentrations in South African rivers according to whether they originate from point and diffuse sources, by their relationship with flow. Therefore, this simple mechanistic/statistical model could provide a useful tool to managers who want to model either, or both the influences of point or diffuse sources on water quality. This model has advantages over a simple statistical model, in that parameters estimated, especially those for the point source influences such as Q_{pmax} and C_{pmax} , can be changed in ‘what if’ management scenario investigations for point sources, so as to determine the best strategy of controlling the influence of point sources on water quality. Further research is needed to account for the scatter of nutrient concentrations at high flow. This model could be extended by further research into linking land activities within a catchment, and the in-stream diffuse source signatures of nutrients.

Chapter 5: A simple model to relate land cover and flow to water quality

5.1 Introduction

Chapter 3 provides a simple statistical method to relate water quality to flow. Since the regressions used in Chapter 3 are based on historical monitoring data and incorporate no conceptual understanding of the processes involved, the regression models are subject to a number of limitations. Most importantly, the regressions listed in Chapter 3 model the relationship between flow and water quality based on data taken in the past, from as early as 1990. Using these regressions to model the relationship between flow and water quality in the future may be inaccurate, as land cover may have changed drastically since 1990. These regressions in addition do not allow managers to investigate management scenarios, such as a change in land cover. The simple mechanistic model outlined in Chapter 4 does incorporate a simple conceptualization of the difference in relationship between flow and water quality depending on whether nutrients are introduced to rivers through point or diffuse sources. While the model outlined in Chapter 4 allows the user to investigate different scenarios in terms of point source concentration and flow, the model is lacking in incorporating the effect of land cover on the diffuse signature of nutrients coming into rivers.

This chapter (Chapter 5) aims to investigate the relationship between the diffuse signatures in historical monitoring data identified in Chapter 4 for various water quality monitoring points, and the land cover in the catchment of the monitoring points influencing these data. By using historical flow and water quality data, as well as land cover data, the intention of this part of the study was to develop a model that can predict the water quality of a stretch of river, given that land cover in the catchment is measured or predicted, and daily flows within the river stretch are measured or predicted. This chapter (Chapter 5) attempts to address Aim 2, as the proposed model is relatively simple, and the results of this exercise will indicate whether a relatively simple model such as this one is capable of describing the relationship between flow and water quality. The

development and validation of the Land Cover Model proposed in this chapter will also indicate the conditions under which models are required to consider land cover/use, so as to give accurate representations of the relationship between flow and water quality. Therefore, this chapter (Chapter 5) goes some way in addressing Aim 3.

5.2 Methods

5.2.1 Data

This chapter builds on the work done in Chapter 4. The Department of Water Affairs (DWA) historical monitoring data used is a subset of the data described in Appendix A Table 1, with the monitoring points chosen listed in Appendix A Table 2 and Appendix A Table 3. The simple mechanistic model outlined in Chapter 4 was used to generate parameters A and B for a diffuse nutrient input signature for the monitoring points chosen. These parameters are listed in Appendix A Table 2 for phosphate and Appendix A Table 3 for nitrite plus nitrate (nitrogen).

Criteria for selecting monitoring points are listed in Chapter 4. Land cover fractions for the catchments of the selected monitoring points were determined using the DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006). For each monitoring point, the catchment was delineated in ArcMap 9.3 (ESRI, Inc.) using 1:50000 river and relief coverages. The land cover coverage was then clipped by the catchment to define the land cover for the water quality monitoring point. The clipped land cover shape file was converted to a raster file using a cell size of 0.0002° (approximately 20m x 20m) and the number of cells for each land cover category was enumerated. The fractions of total land cover for each category were then determined for the catchment of each monitoring point. The process was repeated for each monitoring point. The final land cover categories chosen are listed in Table 5.1. Some categories were grouped together to make new categories, and are indicated in Table 5.1.

In addition to determining the land cover fractions for the catchment of each selected

monitoring point, the land cover fractions for a riparian zone 1 km wide on each side of the river in the catchment of the monitoring point were determined.

The monitoring points used were in addition grouped into water quality management regions within South Africa (Table 5.2, Figure 5.1). These management regions were taken from Day *et al.* (1998). Day *et al.* (1998) based their proposed management regions on the natural water chemistry differences found in rivers in different regions.

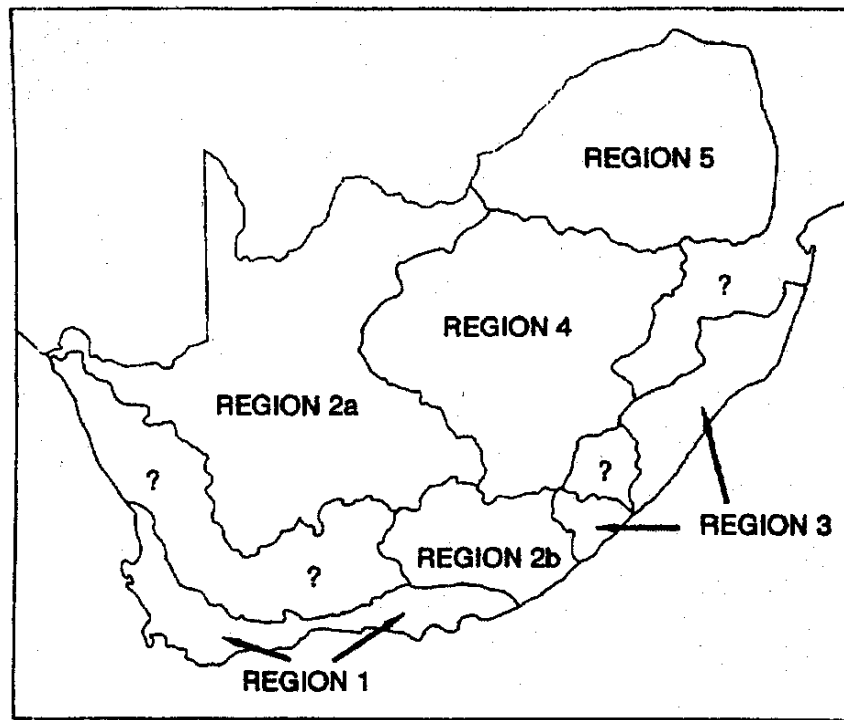


Figure 5.1: Water quality management regions according to Day *et al.* (1998). Diagram taken from Day *et al.* (1998). Question marks indicate unclassified subcatchments.

Table 5.1: Land cover categories used from the Department of Water Affairs (DWA) Groundwater Resource Directed Measures database to develop a simple model to relate land cover to flow and water quality in rivers

Final Land Cover Categories	Code	Consisting of original land cover categories
Barren Rock	BR	Barren Rock
Cultivated: permanent - commercial dryland	C:PCD	Cultivated: permanent - commercial dryland
Cultivated: permanent - commercial irrigated	C:PCI	Cultivated: permanent - commercial irrigated
Cultivated: temporary - commercial dryland	C:TCD	Cultivated: temporary - commercial dryland
Cultivated: temporary - commercial irrigated	C:TCI	Cultivated: temporary - commercial irrigated
Cultivated: temporary - semi - commercial/subsistence dryland	C:TCSD	Cultivated: temporary - semi - commercial/subsistence dryland
Degraded natural areas	DNA	Degraded: shrubland and low Fynbos; Degraded: thicket and bushland (etc); Degraded: unimproved grassland; Unimproved grassland
Dongas and sheet erosion scars	DSES	Dongas and sheet erosion scars
Undegraded forest natural areas	UFNA	Forest; Forest and woodland
Forest plantations	FP	Forest plantations
Improved grassland	IG	Improved grassland
Mines and Quarries	MQ	Mines and Quarries
Undegraded Bush	UB	Shrubland and low fynbos; Thicket and bushland (etc)
Urban - commercial/industrial	U:CI	Urban/built up land: commercial; Urban/built up land: industrial/transport
Urban /built up land: residential	U:R	Urban /built up land: residential
Waterbodies*	WB	Waterbodies
Wetlands	W	Wetlands

*- Standing water bodies such as impoundments

Table 5.2: Water management regions based on natural water chemistry as determined by Day *et al.* (1998)

Region	Subcatchments
Southern and western coast (1)	G, H, J4, K, L7 - L9, M, N4, P
Arid interior (2a)	D3 - D8
Eastern Cape drought corridor (2b)	N1 - N3, Q, R, S
East Coast (3)	T (excluding T3), U, V2, V4 - V5, W1 - W3
Upper Orange/Vaal (4)	C, D1 - D2
North- East (5)	A, B, X

5.2.2 Model development

Chapter 4 developed a mechanistic model that could separate point and diffuse signals of nutrients in relation to flow. The diffuse signature was specified as a statistical regression of the form:

$$C_{\text{diffuse}} = A.Q^B$$

Where C_{diffuse} is the in-stream concentration of a nutrient (mg.L^{-1}) that can be attributed to nutrient input from diffuse sources. The flow is represented by Q in $\text{m}^3.\text{sec}^{-1}$. The parameters A and B define the regression line that is representative of the diffuse input of nutrients in relation to flow.

Land cover fractions for monitoring points and the A and B parameters of the diffuse source model discussed in Chapter 4, were analysed in Statistica (StatSoft, 2007), using Principle Component Analysis (PCA). PCA allows the identification of generalities across a large data set and reduces the dimensionality of data to orthogonal axes with high variance, thereby allowing the development of hypotheses concerning patterns within the data. PCA was used to determine if there was any correlation between land cover categories and the diffuse signatures, indicated by the values of A and B , within particular catchments. The correlation biplot diagrams as well as the variable contributions based on correlations were the results of the PCA that were used to determine the land cover categories that explain the variance in the parameters. Figure 5.2 for example, is the correlation biplot for PCA axis 1 and PCA axis 2, for phosphate

data for region 3. It shows that both the A and B parameters have a strong correlation with PCA axis 1, as they are both lying close to the axis. Therefore, land cover categories that are in addition positioned in the same axis can be regarded as having a correlation with A and B, with the length of the line indicating the correlation strength. However, land cover categories shown in the biplot that are in opposite directions to A and B in this case would have negative correlations. In this example, cultivated temporary commercial irrigated land (C:TCI), degraded natural areas (DNA) and water bodies (WB) can be regarded as having a positive correlation on the values of the A and B parameters, while cultivated semi-commercial subsistence dryland can be regarded as having a negative correlation with the parameter values.

Land cover categories that were found to explain the variance in either A or B or both parameters, within the PCA axes 1 to 3, were then used to construct models. Models were constructed for both phosphate and nitrogen. For each nutrient, models were constructed to represent all regions using all the available data. Models were in addition constructed using data from specific water quality management regions to represent those specific regions. This process was repeated using only the land cover in the riparian zone. There were no monitoring points within the water quality management region 2a (see Table 5.2 and Figure 5.1).

The models were constructed in Microsoft Excel 2003 using Solver. Monitoring point information that was entered into the model included the A and B parameters relating to diffuse source inputs (as determined in Chapter 4), and land cover information for the catchment of each monitoring point, as a fraction of the total land cover. A model estimate of A and B, based on land cover fractions was then estimated by the models.

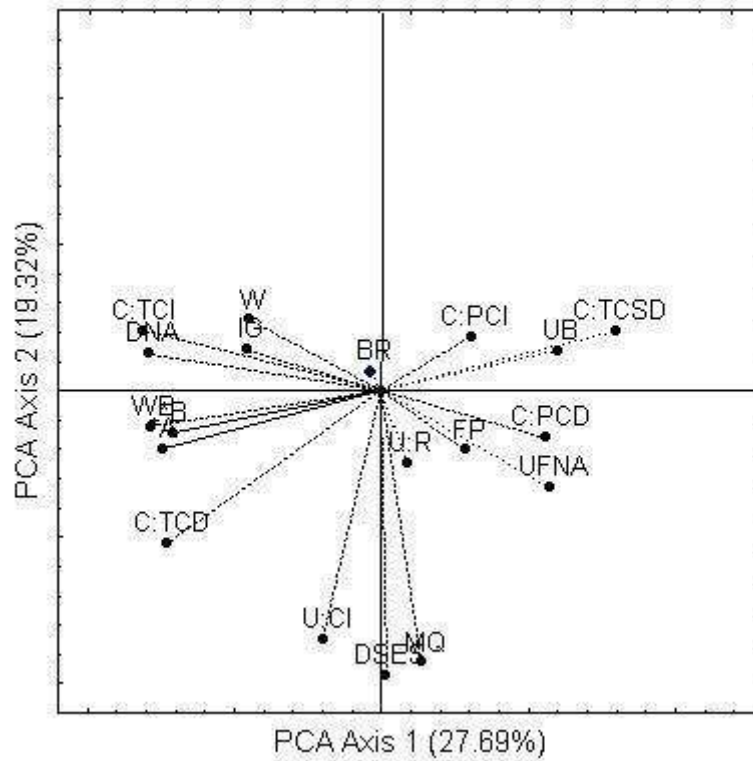


Figure 5.2: PCA correlation biplot for PCA Axis 1 and PCA axis 2 for PCA applied to phosphate data for region 3. (Explanation of the abbreviations can be found in Table 5.1).

For each land cover that was determined to explain the variation to parameter A in the first 3 PCA axes:

$$A_{\text{land}} = (\alpha_1 * \text{land\_coverA}_1) + (\alpha_2 * \text{land\_coverA}_2) + \dots (\alpha_n * \text{land\_coverA}_n) + \alpha C$$

(Equation 5.1)

For each land cover that was determined to explain the variation to parameter B:

$$B_{\text{land}} = (\beta_1 * \text{land\_coverB}_1) + (\beta_2 * \text{land\_coverB}_2) + \dots (\beta_n * \text{land\_coverB}_n) + \beta C$$

(Equation 5.2)

Where $\alpha_1, \dots, \alpha_n$ and $\beta_1, \dots, \beta_n$ are parameters to be determined via maximum likelihood techniques using Solver, $\text{land\_coverA}_1 - \text{land\_coverA}_n$ are the land cover fractions of

particular categories that were found to explain the variation in parameter A within the first 3 PCA axes, and $\text{land\_coverB}_1 - \text{land\_coverB}_n$ are the fraction land covers of particular categories that were found to explain the variation to parameter B. A_{land} and B_{land} are the model estimated values of A and B based on land cover fractions.

For each data entry, the Chi-square difference between A and A_{land} , and B and B_{land} was determined as a goodness of fit statistic for the model:

$$\chi^2 = (A - A_{\text{land}})^2 / A_{\text{land}} \quad (\text{Equation 5.3})$$

$$\chi^2 = (B - B_{\text{land}})^2 / B_{\text{land}} \quad (\text{Equation 5.4})$$

Solver was used to determine the best α and β values in the model that would minimize the sum of the chi-square values within the model.

Upper and lower 95 % prediction limits for A_{land} and B_{land} were in addition estimated:

$$A_{\text{land}} \pm 1.96 * SD_A * (1-R^2)^{0.5} \quad (\text{Equation 5.5})$$

$$B_{\text{land}} \pm 1.96 * SD_B * (1-R^2)^{0.5} \quad (\text{Equation 5.6})$$

where SD_A is the standard deviation of the A parameter values, SD_B is the standard deviation of the B parameter values, and R^2 is the coefficient of determination providing a measure of the variability in the A and B parameter data sets explained by the model.

Independent data from sites not used to construct the land cover models were used to confirm the land cover models. These sites were originally rejected from the land cover analysis only because there were not enough water quality data points available (<50) at each monitoring site. The stipulation of sites requiring at least 50 water quality monitoring points was decided for the point and diffuse source mechanistic model developed in Chapter 4. Although the number 50 is rather arbitrary, any number less than that would not give an accurate reflection of the relationship between flow and nutrients. The point and diffuse signature model outlined in Chapter 4 was applied to the data from these sites. The diffuse signatures estimated in these data using the model from Chapter 4 was then compared to the diffuse signature estimated from the land cover models

developed in this chapter (Chapter 5), so as to determine whether the diffuse signature simulations obtained from the land cover models were comparable in relation to the diffuse signature obtained from the model in Chapter 4.

5.3 Results

Tables 2 and 3 in Appendix A show the land cover fractions for all monitoring sites for the entire catchment and 1 km riparian zone respectively. Appendix B Figure 3 - 8 and Appendix B Figure 9 - 14 show the results of PCA applied to the phosphate and nitrogen data respectively while Tables 5.3 and 5.4 are a summary of the PCA results for phosphate and nitrite plus nitrate respectively. PCA could find no correlation between land cover and the A parameter values for region 5 for both the entire catchment and the riparian zone for the phosphate data (Table 5.3). PCA could find no correlation between land cover and the B values for region 4 for nitrite plus nitrate data (Table 5.4). Tables 5.5 and 5.6 list the final land cover models for phosphate and nitrogen data respectively.

The final models as determined through the use of Solver in Excel are shown for phosphate and nitrogen in Tables 5.5 and 5.6 respectively. In many cases, solver could not assign a parameter value to some land cover types that PCA determined to explain variance to A and B parameter values, and therefore, these land cover types are not used in the final models. In some cases, for instance the models for the east coast (3), upper Orange/Vaal (4) and north east region, no parameter values could be assigned to land cover categories that would explain either or both parameters A or B, and in these cases, only a constant value was assigned to the model.

Table 5.3: Land cover categories determined by PCA to have a correlation with either the A or B parameters from a diffuse signature model for phosphates. All categories have a positive correlation unless indicated by a '-' symbol.

Region	Entire Catchment			Riparian Zone		
	A	B	*	A	B	*
All Regions	UB; U:R; U:CI; W(-); C:TCSD(-); DNA(-)	C:TCSD; UFNA; U:R; U:CI; DNA(-)	40	UB; IG; U:R; U:CI; DNA(-); W(-)	U:R; U:CI; UB; C:TCSD; W(-);	38
Southern and western coast (1)	C:PCD; DNA; C:TCSD; W(-)	C:PCD; DNA; C:TCSD; W(-)	63	W(-); IG(-); C:TCSD(-)	W(-); IG(-); C:TCSD(-)	54
East Cape drought corridor (2b)	WB; U:R; UB(-)	WB; U:R; UB(-)	59	U:R; C:TCSD; DSES; DNA; UB(-); UNFA(-)	U:R; C:TCSD; DSES; DNA; UB(-); UNFA(-)	56
East coast (3)	C:TCI; DNA; WB; C:TCSD; C:TCSD(-)	C:TCI; DNA; WB; C:TCSD; C:TCSD(-)	61	C:TCSD; C:TCI; DNA; C:TCSD(-)	C:TCSD; C:TCI; DNA; C:TCSD(-)	60
Upper Orange/Vaal (4)	C:TCI; UB; IG(-); C:TCSD(-)	C:TCI; UB; DNA; IG(-); C:TCSD(-); C:PCD(-)	53	UB; C:TCI; C:TCSD(-); BR(-)	UB; C:TCI; C:TCSD(-); BR(-)	56
North east (5)		C:TCSD; W; UB(-); IG(-)	58		UB(-)	56

* - Percentage variance explained within the first 3 PCA Axes

Table 5.4: Land cover categories determined by PCA to have a correlation with either the A or B parameters from a diffuse signature model for nitrites plus nitrates. All categories have a positive correlation unless indicated by a '-' symbol.

Region	Entire Catchment			Riparian Zone		
	A	B	*	A	B	*
All Regions	UB; C:TCD(-); W(-); DNA(-)	UB; C:TCD(-); W(-); DNA(-)	40	UB; IG; DNA(-); W(-)	UB; IG; DNA(-); W(-)	38
Southern and western coast (1)	W; BR; DSES; C:PCD(-); DNA(-); C:TCSD(-); IG(-); UNFA(-)	C:PCI; U:CI; MQ; U:R; UB(-)	63	FP; U:CI; C:PCI; BR; DSES; UB(-); C:TCSD(-); UNFA(-)	FP; U:CI; C:PCI; UB(-); IG; W; C:TCD; C:TCI	59
East Cape drought corridor (2b)	UB; UNFA; WB(-); DNA(-)	C:TCD; FP;	59	UNFA; FP; UB; DNA(-); C:TCD(-)	UNFA; FP; DNA(-); C:TCD(-)	57
East coast (3)	DNA; C:TCI; WB; DSES; MQ	DNA; C:TCI; WB; DSES; MQ; FP; C:PCD(-)	63	BR; U:R; DNA; FP	BR; U:R; DNA; FP	60
Upper Orange/Vaal (4)	C:TCI; UB		53	UB; C:TCI; C:TCD; C:PCD(-)	UB; C:TCI; C:TCD; C:PCD(-)	56
North east (5)	UB; C:TCD(-); W(-)	UB; C:TCD(-); W(-)	58	FP; UNFA; C:TCSD(-)	FP; UNFA; C:TCSD(-)	56

* - Percentage variance explained within the first 3 PCA Axes

Table 5.5: Results of land cover model for phosphates, including land cover categories that correlate with diffuse model parameters, the final model, and an indication of model goodness of fit

Model Run	A	± 95% Prediction Limits	sum χ^2	B	± 95% Prediction Limits	sum χ^2	degrees of freedom	Tabulated χ^2
All regions	(0.01 * UB) + (-0.08 * C:TCD) + (-1.00 * DNA) + 0.02	0.02	3.41	(0.10 * C:TCSD) + 0.16	0.24	18.47	143	116.4
All regions – riparian zone	(-0.04 * DNA) + (0.02 * UB) + (1.60 * IG) + (0.14 * U:R) + (0.51 * U:CI) + (-0.63 * W) + 0.02	0.02	2.68	(0.08 * U:CI) + (-1.97 * W) + (0.06 * UB) + (0.04 * C:TCD) + 0.15	0.08	17.96	143	116.4
Southern and western coast (1)	(-0.76 * W) + 0.02	0.02	0.25	(-7.09 * W) + 0.2	0.12	1.81	19	10.12
Southern and western coast - riparian zone (1)	(-0.97 * IG) + (-0.03 * C:TCD) + 0.03	0.02	0.47	(-2.97 * W) + 0.21	0.13	1.82	19	10.12
East Cape drought corridor(2b)	(-0.11 * UB) + 0.04	0.03	1.11	(-0.34 * UB) + (10.10 * WB) + 0.16	0.17	2.88	16	7.96
East Cape drought corridor - riparian zone (2b)	(-0.06 * UB) + (0.06 * U:R) + (0.06 * C:TCSD) * (0.77 * DSES) + (0.10 * DNA) - 0.06	0.03	1.12	(6.81 * DSES) + (0.02 * DNA) + 0.11	0.14	2.11	16	7.96
East coast (3)	(-0.09 * C:TCSD) + (0.02 * DNA) + 0.01	0.01	0.11		0.2	1.77	14	6.57
East coast - riparian zone (3)		0.01	0.11		0.2	1.77	14	6.57
Upper Orange/Vaal (4)		0.02	0.48	(4.42 * C:TCI) + (1.33 * UB) + (-1.50 * C:TCD) + (1.12 * DNA) + (-1.04 * C:PCD) + 0.56	0.16	3.12	31	19.28
Upper Orange/Vaal - riparian zone (4)	(0.01 * UB) + (0.14 * C:TCI) + (- 0.90 * C:PCD) + (-0.76 * BR) + 0.02	0.02	0.46	(-0.90 * C:TCD) + (10.92 * C:TCI) + 0.11	0.21	5.4	31	19.28

Table 5.5 continued: Results of land cover model for phosphates, including land cover categories that correlate with diffuse model parameters, the final model, and an indication of model goodness of fit

Model Run	A	$\pm 95\%$ Prediction Limits		sum χ^2	B	$\pm 95\%$ Prediction Limits		sum χ^2	degrees of freedom	Tabulated χ^2
North east (NE) (5)	0.01	0.01	0.01	0.59	$(-10.39 * IG) + 0.15$	0.16	0.16	5.41	42	28.14
NE-riparian zone (5)	0.01	0.01	0.01	0.59	$(0.17 * C:TCD) + 0.15$	0.14	0.14	5.98	42	28.14

Table 5.6: Results of land cover model for nitrates + nitrites, including land cover categories that correlate with diffuse model parameters, the final models, and an indication of model goodness of fit

Model Run	A	± 95% Prediction Limits	sum χ^2	B	± 95% Prediction Limits	sum χ^2	degrees of freedom	Tabulated χ^2
All regions	$(0.13 * UB) + (-0.38 * C:TCD) + (-0.16 * DNA) + 0.21$	0.21	16.58	$(0.01 * UB) + (-0.18 * C:TCD) + (-0.99 * W) + (-0.04 * DNA) + 0.22$	0.12	15.24	143	116.4
All regions - riparian zone	$(-0.09 * DNA) + (0.20 * UB) + (-1.29 * W) + 0.13$	0.18	15.12	$(0.05 * UB) + (-3.07 * W) + 0.18$	0.12	15.21	143	116.4
Southern and western coast (1)	$(-6.59 * IG) + (0.10 * DSES) + 0.34$	0.31	4.3	$(13.78 * U:R) + (0.37 * UB) - 0.1$	0.45	3.98	19	10.12
Southern and western coast - riparian zone (1)	$(4.5 * U:R) + 0.23$	0.34	4.33	$(1.11 * C:TCI) + 0.17$	0.09	1.6	19	10.12
East Cape drought corridor (2b)	$(0.16 * UB) + (-1.14 * WB) + (0.80 * UFNA) + 0.09$	0.09	1.91	no valid solution			16	7.96
East Cape drought corridor - riparian zone (2b)	$(0.21 * UB) + (0.40 * UFNA) + (0.86 * FP) + 0.07$	0.16	1.85	$(-0.02 * DNA) + (2.42 * FP) + 0.16$	0.19	1.89	16	7.96
East coast (3)	0.18	0.09	0.72	$(0.24 * C:TCI) + (0.77 * MQ) + (0.05 * FP) + 0.2$	0.05	1.37	14	6.57
East coast - riparian zone (3)	0.18	0.09	1.37	0.21	0.05	0.73	14	6.57
Upper Orange/Vaal (4)	$(0.37 * UB) + 0.02$	0.04	1.17	0.13	0.11	3.59	31	19.28
Upper Orange/Vaal - riparian zone (4)	0.07	0.07	2.35	$(0.16 * UB) + (4.39 * C:TCI) + 0.06$	0.13	3.06	31	19.28

Table 5.6 continued: Results of land cover model for nitrates + nitrites, including land cover categories that correlate with diffuse model parameters, the final models, and an indication of model goodness of fit

Model Run	A	$\pm 95\%$ Prediction Limits	sum χ^2	B	$\pm 95\%$ Prediction Limits	sum χ^2	degrees of freedom	Tabulated χ^2
North east (5)	$(-0.24 * C:TCD) + (0.33 * UB) + (-13.50 * W) + 0.05$	0.12	3.86	$(-0.17 * C:TCD) + (0.20 * UB) + (-8.24 * W) + 0.18$	0.14	5.45	42	28.14
NE - riparian zone (5)	$(-0.57 * IG) + (0.28 * FP) + (-0.50 * UFNA) + (-0.36 * C:TCSD) + 0.08$	0.14	5.15	$(0.12 * FP) + (-0.21 * UFNA) + (-0.15 * C:TCSD) + 0.22$	0.15	5.32	42	28.14

The 95% prediction limits for the A and B parameters are in addition fairly large in value indicating a high degree of variance in the A and B parameters, and decreasing the confidence in which the models can predict diffuse signatures.

The final land cover models obtained (Tables 5.5 and 5.6) were applied to the independent data, as outlined in the methods section of this chapter, so as to confirm the land cover models. The diffuse signatures within the data (parameters A and B) were first determined using the model outlined in Chapter 4. The results of this analysis are listed in Table 5.7. Land cover fractions for the confirmation sites for the full catchments and the riparian zone are shown in Appendix A Table 4 and Appendix A Table 5 respectively. The results of the confirmation for phosphate and nitrogen are shown in Figures 5.3 and 5.4 respectively.

The phosphate land cover models applied to the confirmation data from the monitoring point A6H009 performed very well. The ‘all region riparian zone’, ‘region’ and ‘region riparian’ models all simulated accurate estimations of the diffuse phosphate signature. The ‘all region’ model did not estimate any diffuse signature, although the observed data shows a weak observed signature. The land cover models applied to the phosphate data from the monitoring point B8H033 in addition all performed very well except for the ‘all region’ model which once again did not estimate a diffuse signature even though there was a weak signature indicated in the observed data. There was no observed diffuse signature in the phosphate data for the monitoring point C4H017, and none of the land cover models estimated a diffuse signature. The land cover models all performed very well compared to the observed phosphate data from the monitoring point K4H001. The land cover models applied to the phosphate monitoring data from N2H007 all underestimated the diffuse signature, with all land cover models estimating no diffuse signature, except for the ‘region riparian’ model which simulated a small diffuse signature.

Table 5.7: Point and diffuse signature model parameters and water quality regions for monitoring sites used to confirm the land cover model

Monitoring Point	Nutrient	Point Model				Diffuse Model		Land Cover Model Region
		Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B	
A6H009	$NO_2^- + NO_3^-$	5.000	0.011	0.670	0.020	0.078	0.372	North east
A6H009	PO_4^{3-}	12.500	0.011	0.066	0.003	0.006	0.206	North east
B8H033	$NO_2^- + NO_3^-$	1.000	0.025	0.150	0.020	0.074	0.460	North east
B8H033	PO_4^{3-}	1.000	0.012	0.043	0.011	0.013	0.307	North east
C4H017	$NO_2^- + NO_3^-$	0.800	0.001	1.820	0.020			Upper Orange/Vaal
C4H017	PO_4^{3-}	1.000	0.009	0.444	0.003			Upper Orange/Vaal
K4H001	$NO_2^- + NO_3^-$	0.200	0.122	0.060	0.020	0.048	0.527	Southern and western coast
N2H007	$NO_2^- + NO_3^-$	3.000	0.008	1.600	0.020	0.181	0.142	Eastern Cape drought corridor
N2H007	PO_4^{3-}	1.500	0.008	0.450	0.070	0.103	0.278	Eastern Cape drought corridor
Q1H001	$NO_2^- + NO_3^-$	10.900	10.900	0.600	0.020	0.034	0.781	Eastern Cape drought corridor
Q1H001	PO_4^{3-}	10.900	109.000	0.035	0.003	0.001	0.979	Eastern Cape drought corridor
T5H003	PO_4^{3-}	0.400	0.113	0.610	0.020			East Coast

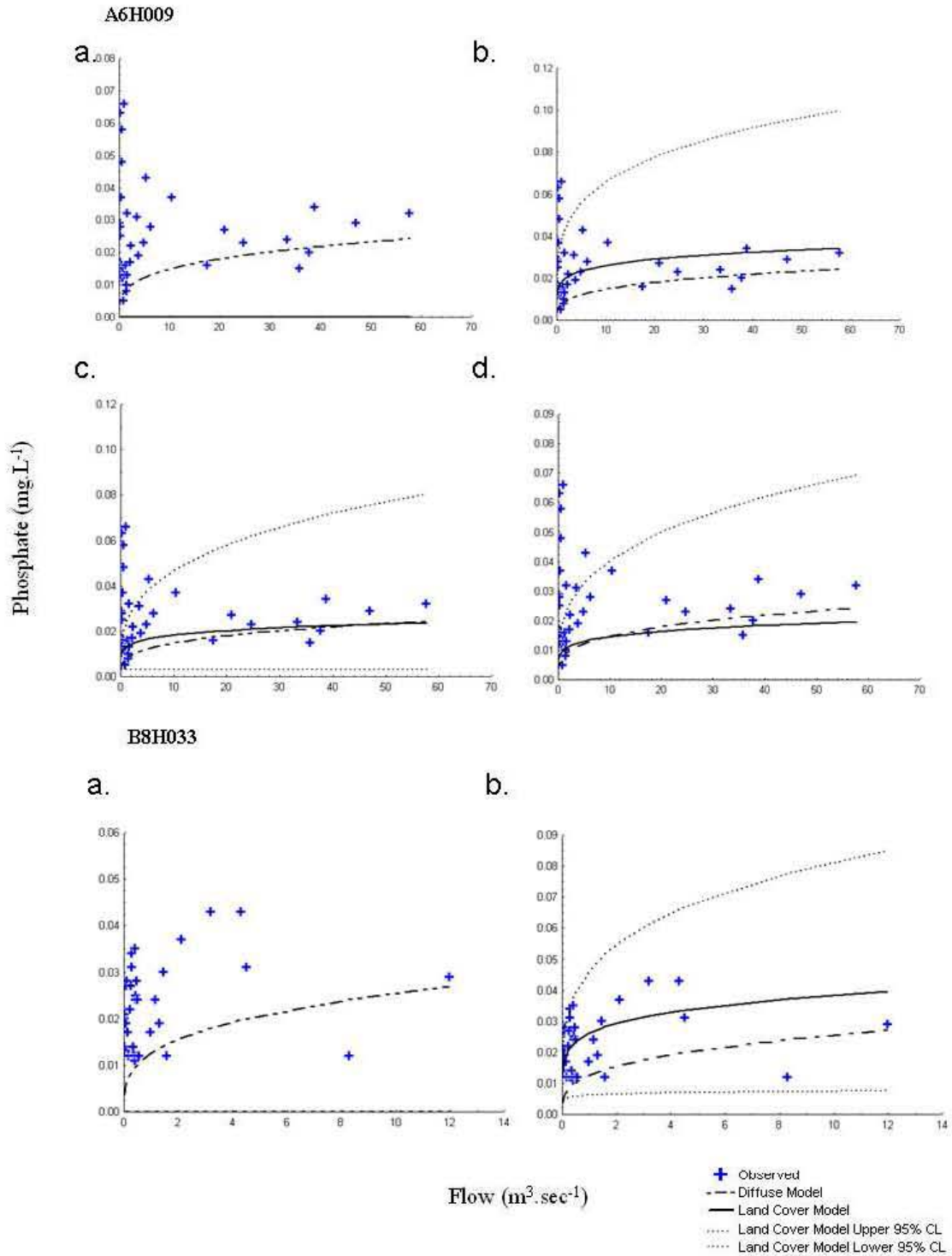


Figure 5.3: Land cover estimations of the diffuse source signature in historical monitoring data for phosphate. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

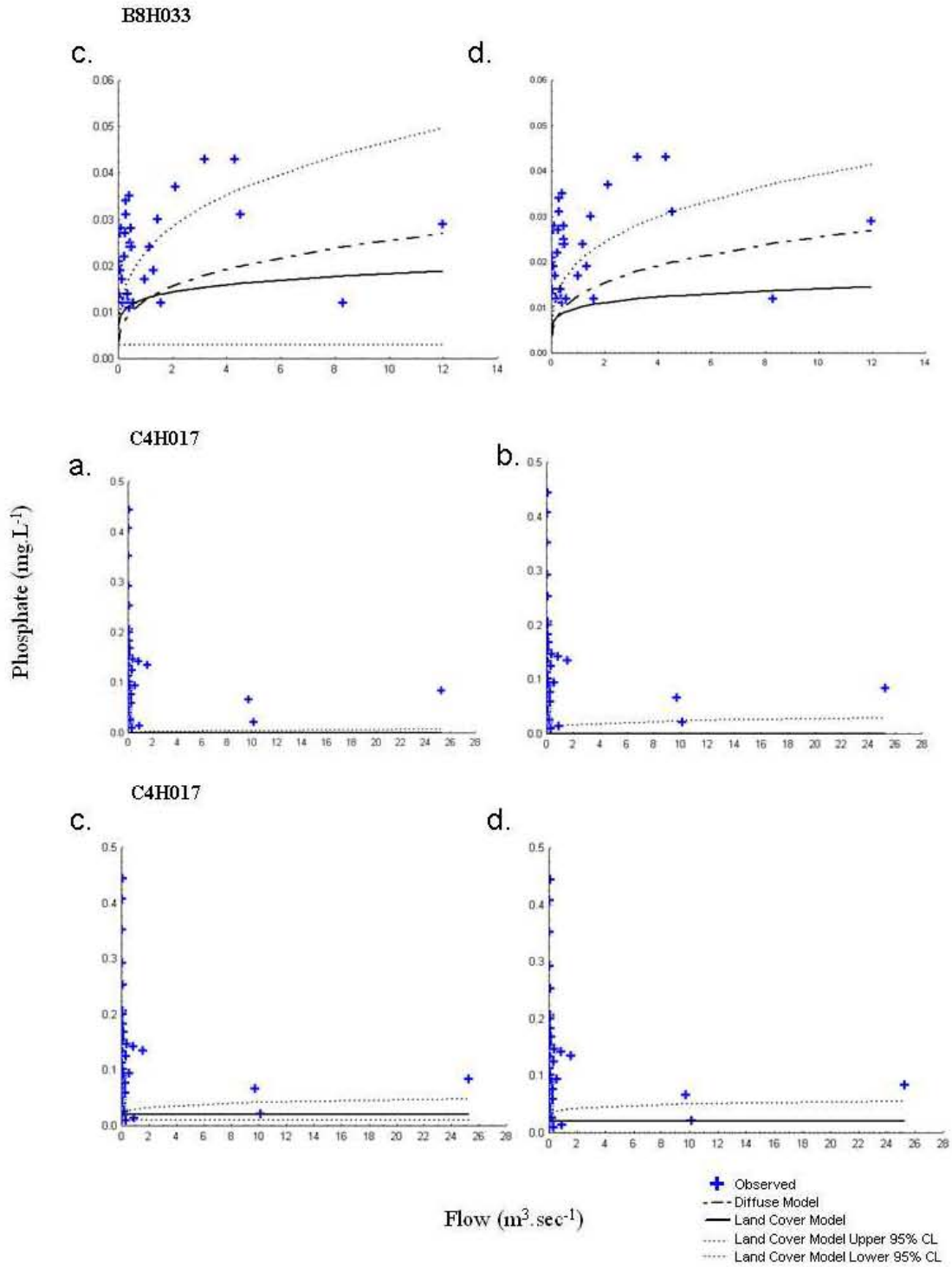


Figure 5.3 continued: Land cover estimations of the diffuse source signature in historical monitoring data for phosphate. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

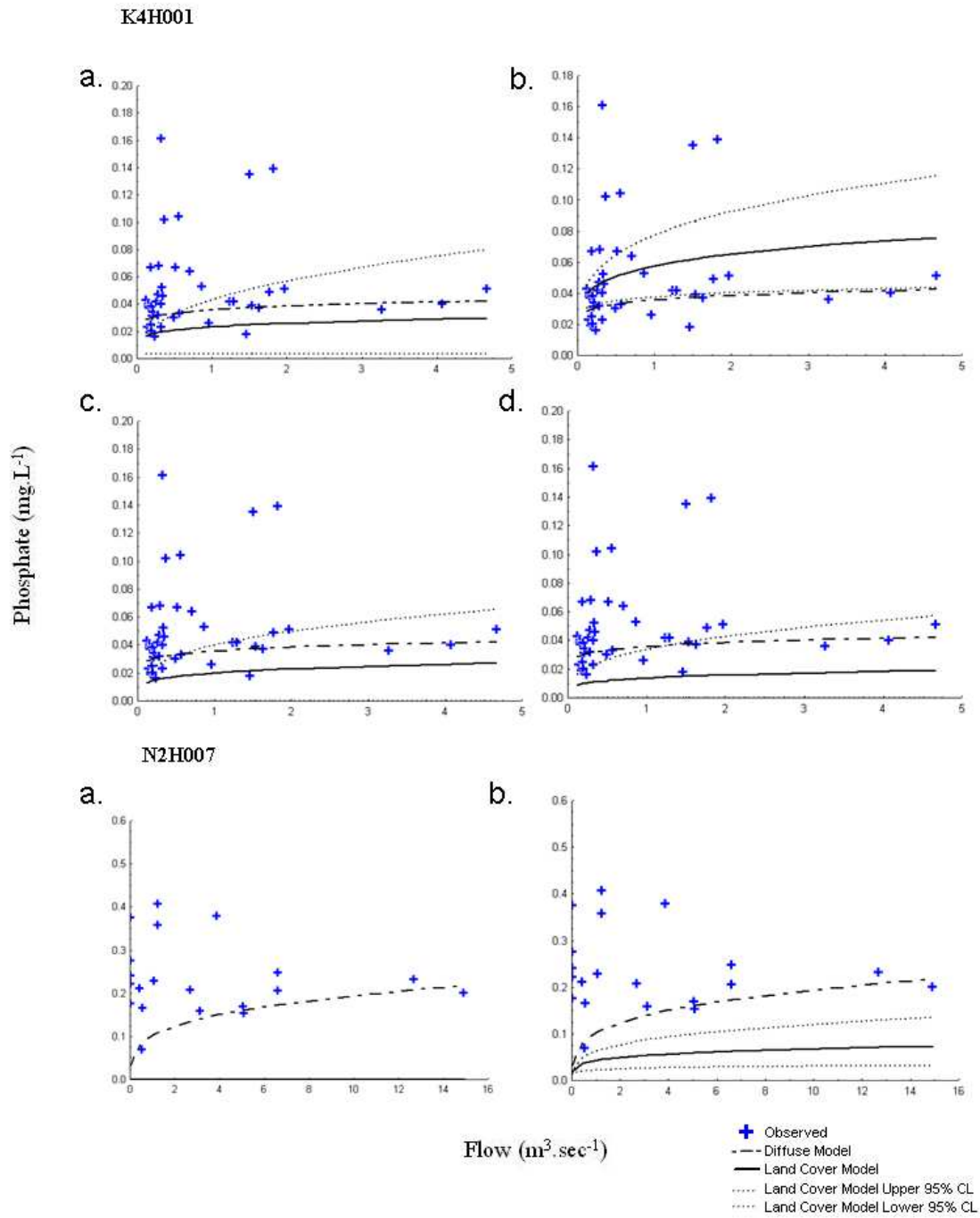


Figure 5.3 continued: Land cover estimations of the diffuse source signature in historical monitoring data for phosphate. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

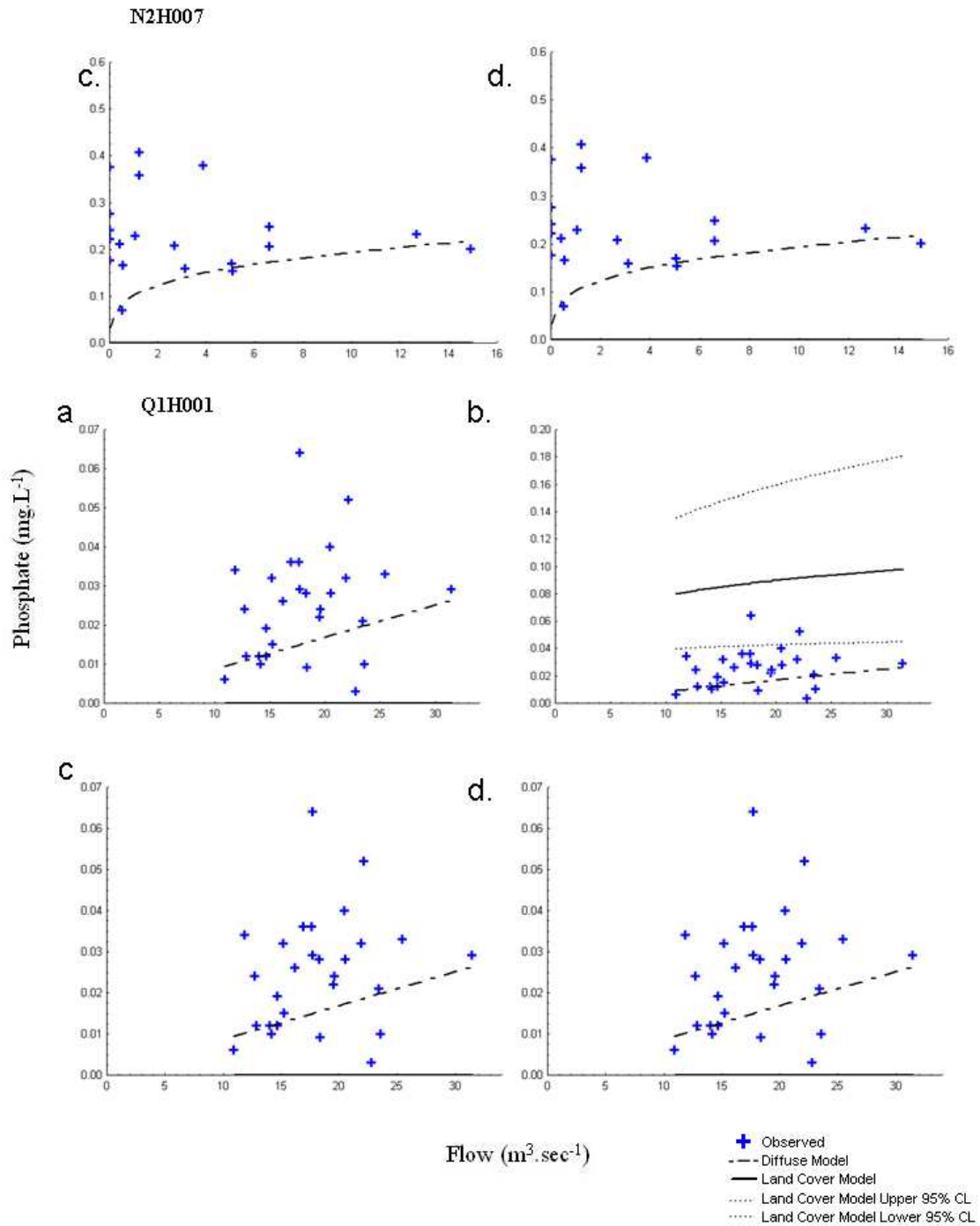


Figure 5.3 continued: Land cover estimations of the diffuse source signature in historical monitoring data for phosphate. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

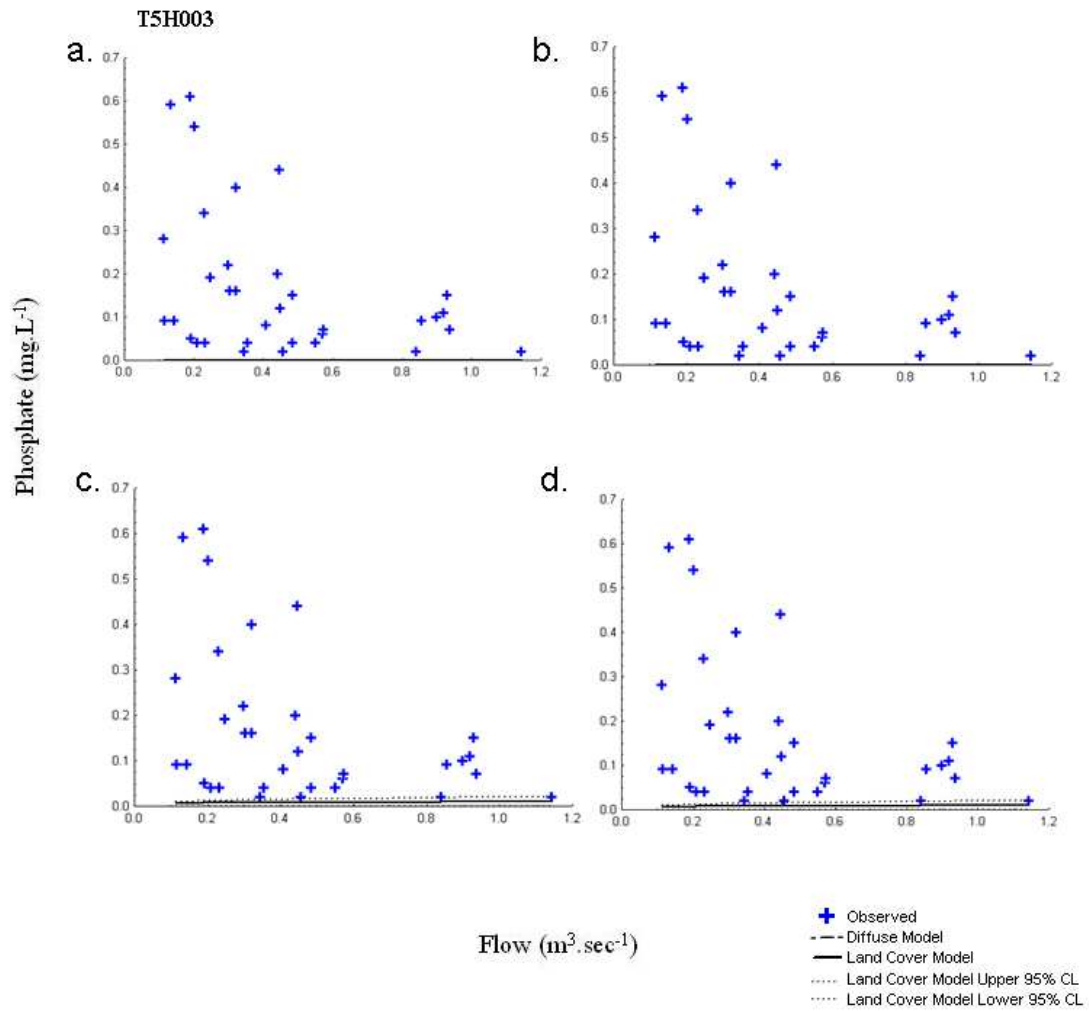


Figure 5.3 continued: Land cover estimations of the diffuse source signature in historical monitoring data for phosphate. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

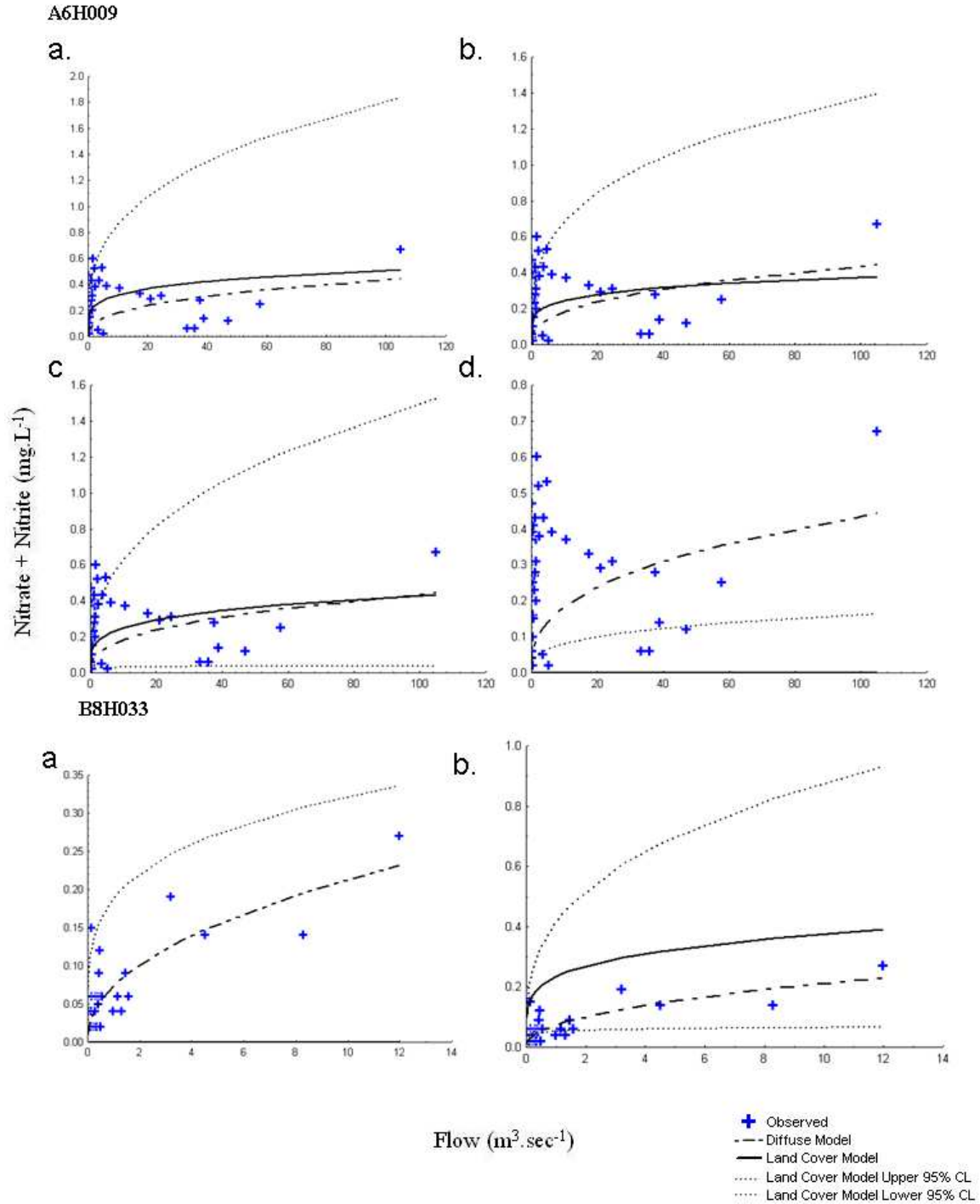


Figure 5.4: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

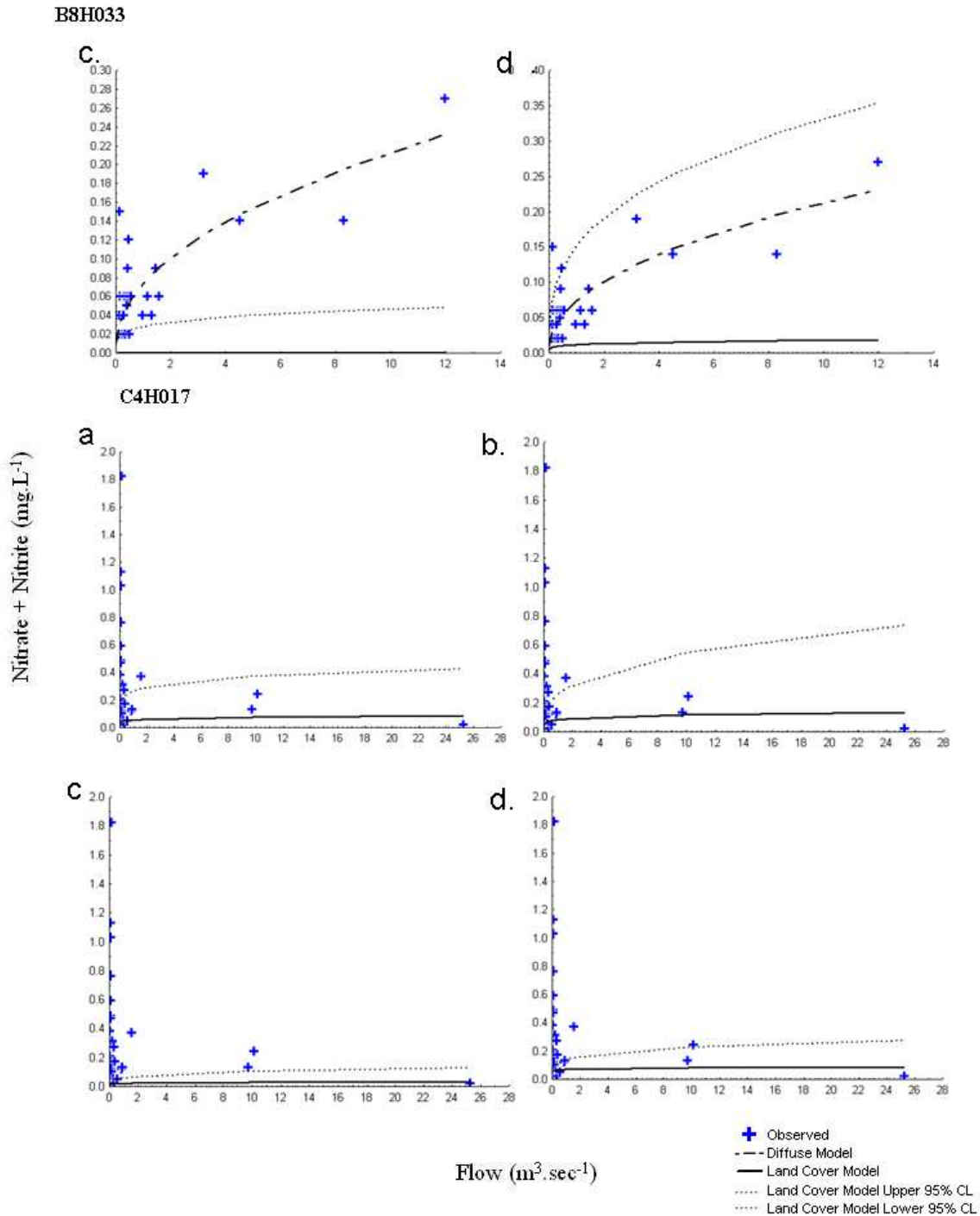


Figure 5.4 continued: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

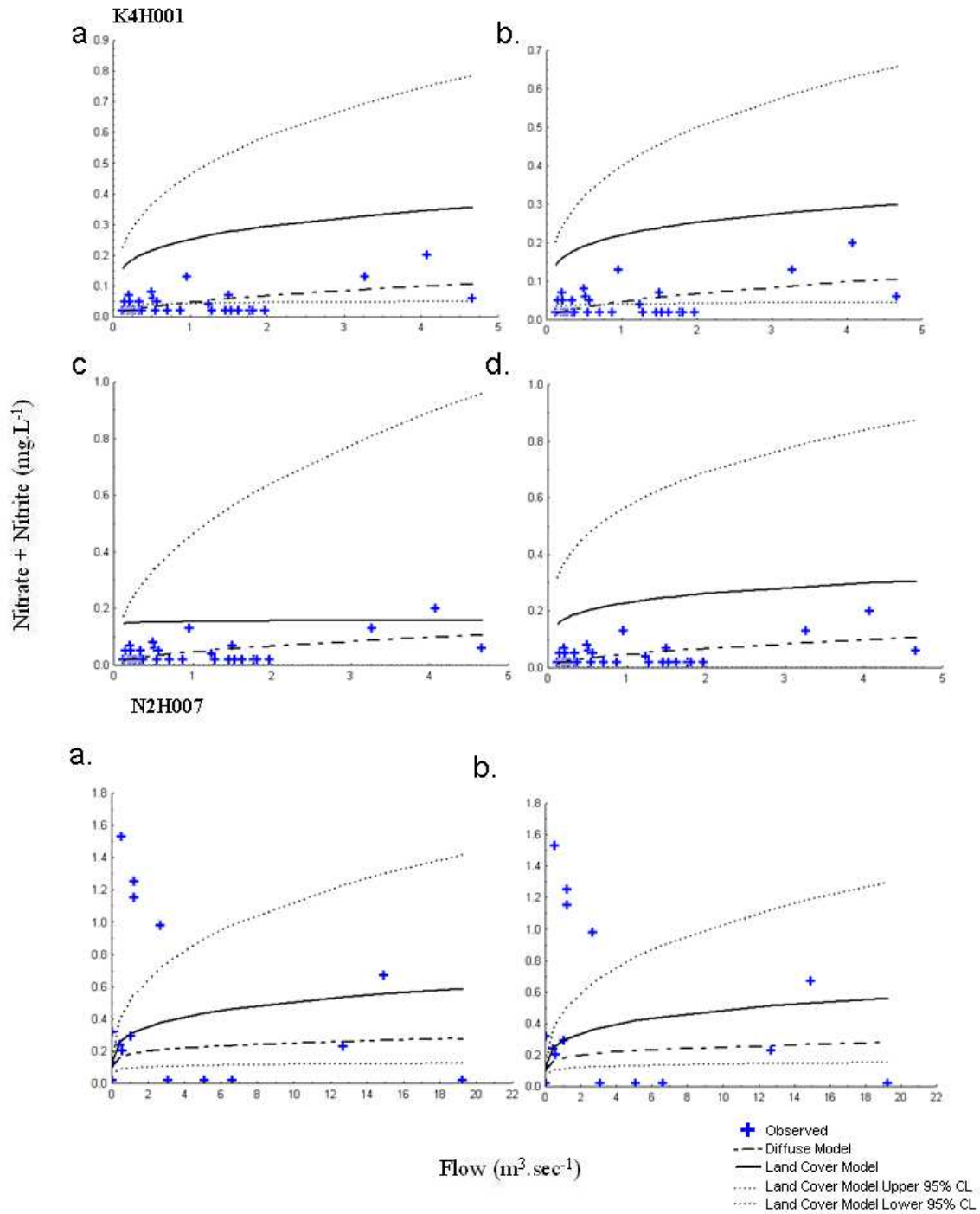


Figure 5.4 continued: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

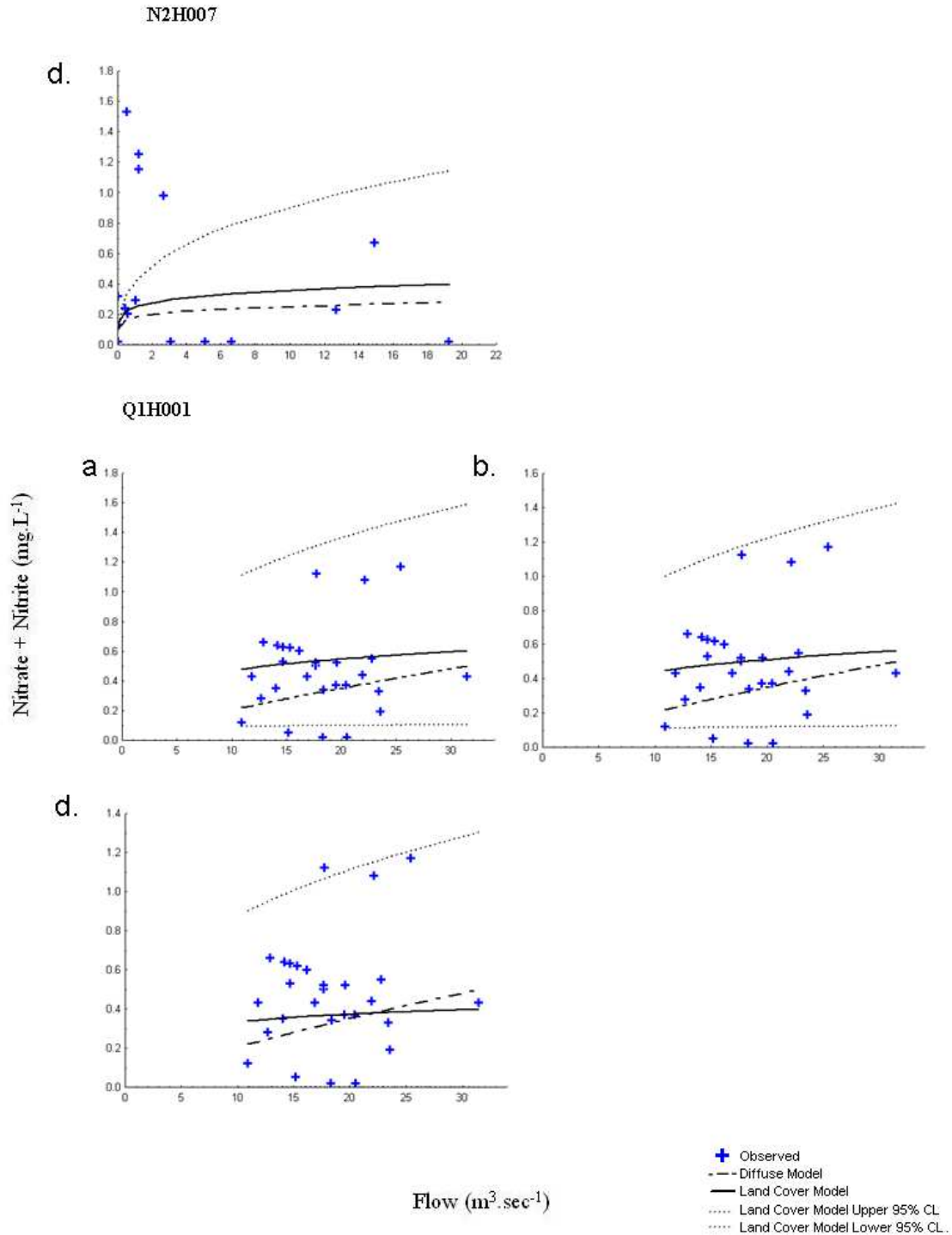


Figure 5.4 continued: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

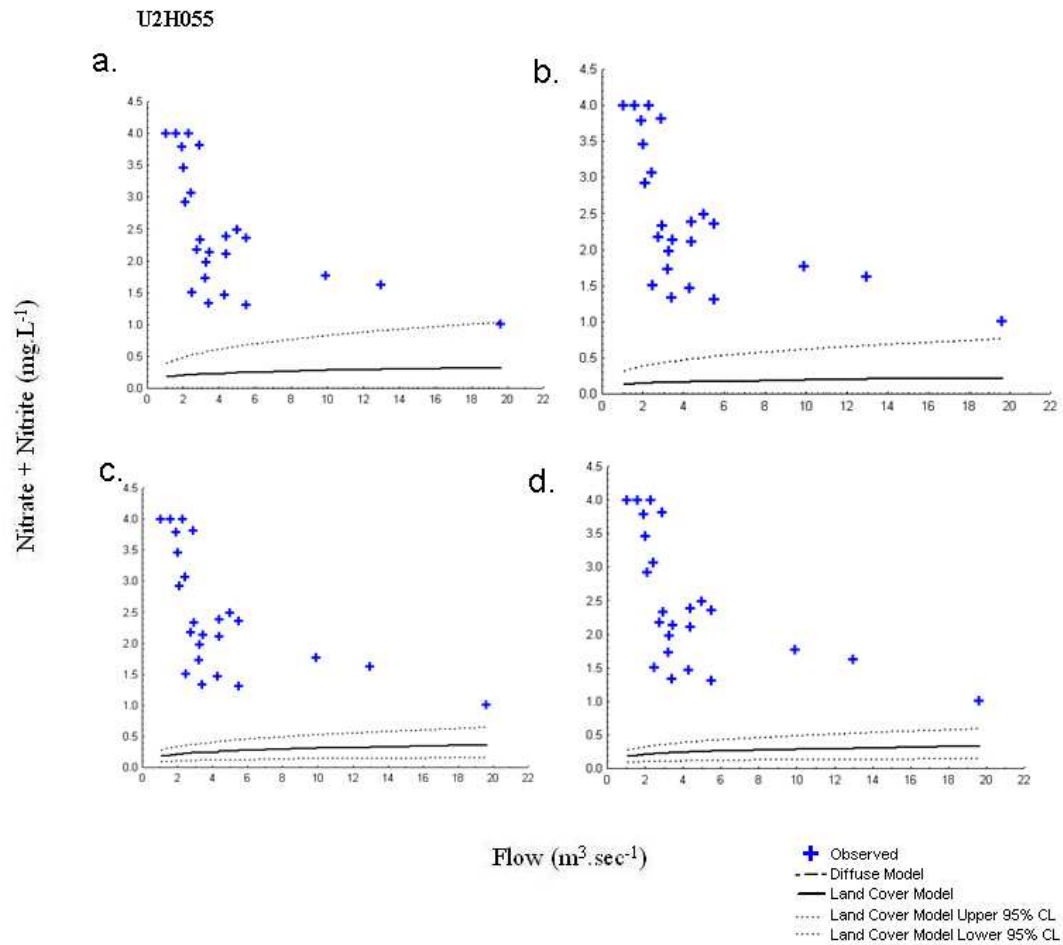


Figure 5.4 continued: Land cover estimations of the diffuse source signature in historical monitoring data for nitrogen. Four models were run on each confirmation data set: a- all regions; b-all regions riparian, c-region; d-region riparian.

The land cover models for Q1H001 simulated phosphate concentrations that were below the observed diffuse trend, although it is hard to detect any trend, diffuse or otherwise in the observed phosphate data. The land cover models did not simulate a diffuse signature for this monitoring point except for that of the ‘all region riparian zone’ model which simulated too high a result. The land cover models applied to the observed phosphate data for the monitoring point T5H003 all performed well, as all estimated no or a weak diffuse signature, which is reflected by the observed data which shows a decrease in phosphate concentration with increasing flow.

The land cover models applied to the observed nitrogen data for the monitoring point A6H009 all performed well, except for the 'region riparian' model which did not estimate a diffuse signature. The land cover models applied to observed nitrogen data for B8H033 all underestimated the diffuse signature except for the 'all region riparian' model which was fairly accurate. The observed nitrogen data for the monitoring point C4H017 showed no diffuse signature, which was accurately estimated by the land cover models. The diffuse signature in the observed data for K4H001 was slightly overestimated in the 'all region', and 'all region riparian' models, but fairly accurately estimated in the 'region' and 'region riparian' models. A 'region' land cover model could not be applied to the observed nitrogen data from N2H007, as there was no valid model for the East Cape drought corridor region, however, the other three land cover models estimated the diffuse signature very accurately. As was the case with N2H007, a 'region model' could not be applied to the observed nitrogen data from Q1H001, but the other three land cover models estimated the diffuse signature very accurately. The observed nitrogen data from the monitoring point U2H055 shows a very weak or no diffuse signature, and this was accurately estimated by all four land cover models.

The χ^2 difference between the land cover model estimations, and the diffuse signatures estimated by the model in Chapter 4, were calculated, and are listed in Table 5.8 and Table 5.9 for phosphates and nitrates plus nitrites respectively. What is evident from the tabulated χ^2 values, is that the land cover models simulated nutrient concentrations that were not significantly different ($p < 0.05$) from the Chapter 4 model estimations of the diffuse signature, except in cases where the land cover models estimated no diffuse signature.

5.4 Discussion

The values of the parameters A and B in the flow-quality model described in Chapter 4 determine the diffuse signature input at various DWA monitoring points.

Table 5.8: χ^2 values indicating model fit between the land cover model prediction of the diffuse signature and the diffuse signature predicted by the model from Chapter 4 for Phosphate data.

DWA Station	Land Cover Models				Degrees of Freedom	Tabulated χ^2
	All Regions	All Regions Riparian Zone	Region	Region Riparian Zone		
	sum χ^2	sum χ^2	sum χ^2	sum χ^2		
A6H009	NR	0.22	0.07	0.02	40	26.51
B8H033	NR	0.27	0.03	0.04	36	24.07
C4H017	0	0	1.18	1.2	57	40.65
K4H001	0.31	0.28	0.6	1.58	41	27.33
N2H007	NR	2.18	NR	NR	18	9.39
Q1H001	NR	1.68	NR	NR	26	15.38
T5H003	0	0	0.3	0.29	33	20.87

NR - Land cover model predicted no diffuse signature

Table 5.9: χ^2 values indicating model fit between the land cover model prediction of the diffuse signature and the diffuse signature predicted by the model from Chapter 4 for nitrite plus nitrate data.

DWA Station	Land Cover Models				Degrees of Freedom	Tabulated χ^2
	All Regions	All Regions Riparian Zone	Region	Region Riparian Zone		
	sum χ^2	sum χ^2	sum χ^2	sum χ^2		
A6H009	2.64	1.4	1.01	NR	41	27.33
B8H033	NR	3.63	NR	11.16	32	20.07
C4H017	2.41	3.4	0.89	3.44	58	41.5
K4H001	6.57	5.47	3.79	5.89	41	27.33
N2H007	1.21	1.05	NA	0.37	17	8.67
Q1H001	2.4	1.83	NA	0.33	26	15.38
U2H055	5.62	3.95	5.94	5.7	22	12.34

NR - Land cover model predicted no diffuse signature

NA - Not Applicable

The PCA analysis aimed to explain the variation in these two parameters according to the land cover types and percentage coverage of these types within the catchment of these monitoring points.

Generally, the results of the PCA analysis made sense, as land cover types one would generally associate with diffuse source input, were found in many regions to explain the variation in A or B or both parameters in a positive direction. In many regions, urban residential, urban commercial and cultivated land was found to positively explain the variation in the A and B parameters. In all cases, cultivated irrigated land cover types were found to positively explain the variation, while in some cases, cultivated dryland was found to negatively explain the variation. While intuitively, the role of irrigated cultivated land in the positive contribution of diffuse input makes sense, the negative influence of temporary or permanent cultivated dryland on diffuse inputs requires a bit more thought. Possibly, cultivated dryland that has become fallow for many years, may not have much influence on diffuse inputs of nutrients, and vegetation on these lands may absorb nutrient wash-off from higher up the catchment.

The PCA analysis showed that cultivated irrigated land cover categories explained some of the variation in the A and B parameters for the Upper Orange/Vaal region as well as the north east region. These are the regions where the majority of cultivated land is located (Figure 5.5). This makes sense as cultivated land is known to be a source of nutrients, especially where fertilizer is applied to cultivated land.

The PCA analysis found that the mines and quarries land cover type explained some of the variation of the B parameter values for the east coast region for nitrogen. Again, this is the region where some mines are located, although most mines occur in the north east region (Figure 5.6). The PCA analysis found that the mines and quarries land cover type explained the variation in the diffuse parameters in the east coast(3), and southern and west coast (1) regions, but did not make the association with the north east region. It is not immediately evident why this occurred, unless for a lack of data.

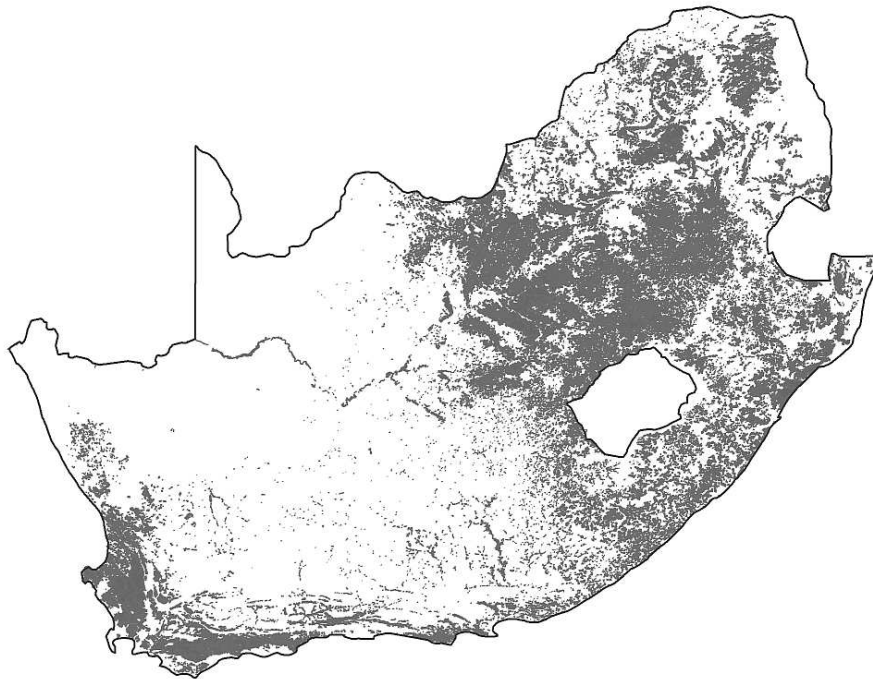


Figure 5.5: Location map of cultivated land in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006)



Figure 5.6: Location map of mines in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006)

The land cover models for nitrogen found the forest plantation land cover type to be a factor influencing the diffuse signature in the East Cape drought corridor, east coast and north east regions. These are the regions where most forestry takes place (Figure 5.7 is a location map of forest plantations). This makes sense as forest plantations have a dense concentration of plant matter debris covering the catchment surface soil which would be a source of nitrogen during rainfall runoff events.

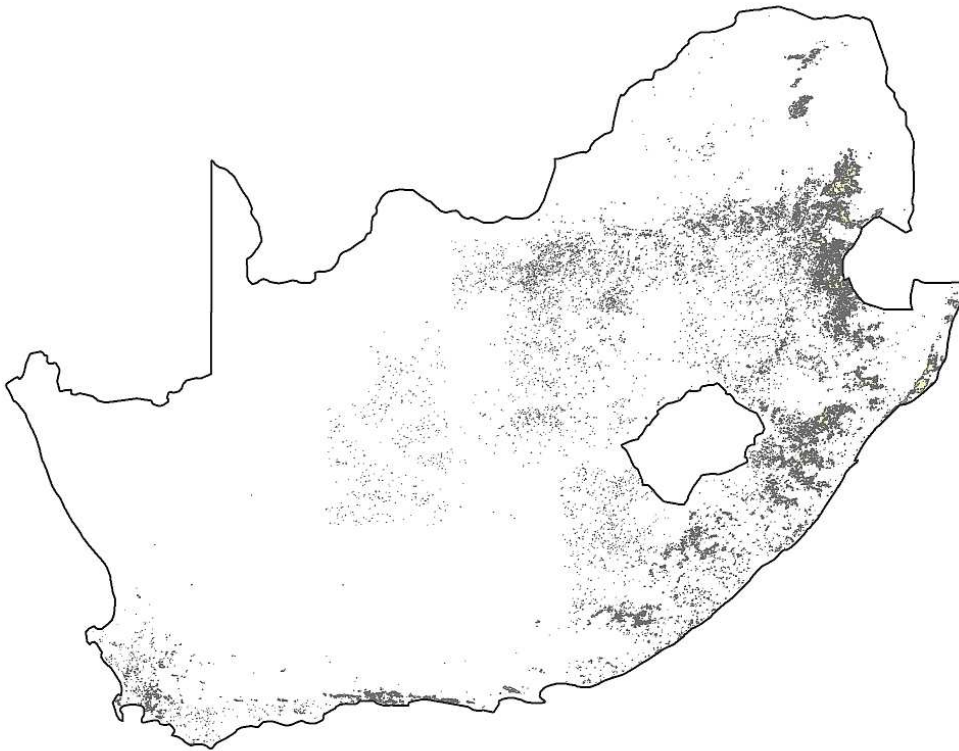


Figure 5.7: Location map of forest plantation in South Africa from DWA Groundwater Resource Directed Measures database (Parsons and Wentzel, 2006)

In some cases, PCA found wetlands to negatively explain the variation in the parameters A and B. This in addition makes sense as wetlands are known to be a nutrient sink. In some cases, the undegraded bush or improved grassland land cover categories positively explain the variation to the diffuse signature parameters. This could indicate that these land cover types are responsible for a natural nutrient signature in some regions.

The process of building the models using solver in Excel, resulted in many land cover types that were found by PCA to explain variation in the A and B parameters, being left out of the final models. This could be because some land cover types have a much stronger influence on the values of the A and B parameters, resulting in the other land cover types not being assigned a weight by the maximum likelihood process that Solver employs. For some regions, solver did not assign weights to any land cover types, and the model in these cases effectively became a generic model of constants for a particular region to explain the diffuse inputs.

This analysis does have some shortcomings. Generally, there was a paucity of data on which to do the analysis, especially after breaking monitoring points into regions, where some regions have less than 15 monitoring points. In addition, the observed water quality monitoring data provided by the DWA has very few observations at high flows. This lack of water quality data at high flows effectively means that in many data sets, the point source signature is over-represented, while only a few points taken at high flow show the effects of runoff from the catchment on nutrient signatures. In this analysis, the regionalization scheme might not be sufficiently geographically specific to pick up regional trends. There are alternative regionalization schemes for South Africa, such as ecoregions (Kleynhans and Hill, 1999) or bioregions (Eekhout *et al.*, 1996). The bioregion regionalization scheme is based on the broad distributions of macroinvertebrates and fish, while the ecoregions regionalization scheme is based on physiography, climate, rainfall, geology and potential natural vegetation. The regionalization scheme as proposed by Day *et al.* (1998) is based on natural water quality for rivers, and was therefore deemed the most appropriate regionalization scheme for the Land Cover Model. One must in addition consider that the land cover information obtained might not have a very strong link to diffuse signatures. Perhaps information on population density for urban land and fertilization rates and cattle density for cultivated land may have shown a stronger link to diffuse signatures, but that information is not readily available. The models in addition show a high degree of uncertainty with 95% prediction limits being very wide in some cases. This is as a result of the high variation in observed A and B parameters indicating the diffuse source signatures, and the

shortcomings in the data mentioned above.

The confirmation process had some mixed results with the land cover model estimations mirroring the diffuse signatures in the observed data fairly well in many cases, but in some cases the land cover models did not perform well. Some reasons why there were some isolated cases of non-confirmation may be because of some upstream influence or unique land cover not considered in the analysis. The land cover models applied to the DWA monitoring points, Q1H001 and N2H007, both estimated phosphate diffuse signatures that were well below the observed signatures. Q1H001 is the DWA gauge at Katkop on the Fish River while N2H007 is a gauge on the Sundays River. Both occur in region 2b, and both the Sundays River and the Fish River in this region are used extensively for irrigating fields adjacent to the river reach. This can be confirmed by studying satellite images of the catchments of these two gauging stations, and in addition by looking at the land cover fractions in Appendix A Table 4. Both Q1H001 and N2H007 have relatively large areas of their catchment used for cultivated temporary irrigated land. The PCA analyses did not find a correlation between irrigated cultivated land and the values of the A and B parameters for region 2b (Table 5.3) for phosphate data. This is probably as a consequence of a paucity of monitoring sites within this region on which to do the PCA analysis. Therefore, the use of land in the catchments of Q1H001 and N2H007 as cultivated irrigated land was most likely the reason why the land cover models did not perform well in these two cases. A similar argument can be made for the monitoring point B8H033, where the land cover models estimated concentrations of nitrite plus nitrate that were well below the observed diffuse signature. This is a gauge on the Klein Letaba River, and once again, the land in the catchment of this monitoring site is used for irrigated cultivated land. However, the PCA analysis for region 3 for nitrite plus nitrate, did not find a correlation between irrigated land and the values of the A and B parameters (Table 5.4). This is probably the reason why the land cover models did not perform well in this case. These results would indicate that perhaps the land cover models in their present form do not account for diffuse signatures from cultivated irrigated land adequately.

Although in some cases, the ‘all region’ models performed better than the ‘region’ models in the confirmation process, it is suggested that use of the regionalized models would be preferable, as they are more specific to the region. The riparian zone regionalized models, in addition, would most likely explain diffuse signatures better than the regionalized models as land cover types in the riparian zone would have a greater impact on diffuse signatures.

The models show some usefulness if one wanted to obtain an idea of what the diffuse signature might be in a catchment where no water quality data were available, but data on land cover were available. This research in addition shows what kind of approach could be used in future research, if better information on land cover or land use became available. Methods of predicting water quality in ungauged catchments has become an international research priority (Visapalan *et al.*, 2003). The Water Research Commission (WRC) in South Africa has also identified this as a research priority i.e. Key Strategic Area 1 (KSA 1) or Water Resource Management, Thrust 1: Water Resource Assessment and Planning, and Programme 3: Water resource planning, where the WRC website states: ‘(this program is) focused on the development of tools that will address planning gaps such as the absence of reliable information in ungauged areas and the persistent record gaps which exist in present data sets’ (<http://WWTW.wrc.org.za/Pages/KSA1-Thrust1.aspx>, 16 November 2010). Lack of reliable data and scientific knowledge concerning catchment processes has also been identified as one of the key barriers preventing Integrated Water Resource Management (IWRM) policies from being implemented (Biswas, 2008). This model is an initial attempt to link land cover categories with diffuse source signatures of nutrients within rivers. This model could be used as a preliminary tool with which to obtain some indication of water quality due to diffuse sources in ungauged catchments.

An alternative approach to quantifying diffuse source loads of pollutants is that of export coefficients. In South Africa, there have been a few studies that have attempted to quantify export coefficients for various water quality variables and various land use types (Grobler and Silberbauer, 1985; Simpson and Stone, 1988; Simpson, 1991) and Pegram

and Gorgens (2001) give a summary of export coefficients calculated in South Africa. The export coefficient approach has several disadvantages that this study attempted to address. Export coefficients work on an annual scale, and don't account for variation within that scale. The Land Cover Model attempts to link land cover and diffuse source inputs at a daily scale. It was explicitly mentioned in the studies by Grobler and Silberbauer (1985), Simpson and Stone (1988) and Simpson (1991) that values for export coefficients calculated for the same catchment over different years showed wide variation, and this variation was linked to rainfall. In the summary of export coefficients given by Pegram and Gorgens (2001), it was noted that there is generally more variation in loading within a land use category, than between categories. These studies recommended long term monitoring of study catchments so as to obtain a more general idea of export coefficients, taking into account annual variation in rainfall. However, the approach taken with regards to the Land Cover Model is much more useful, as the model attempts to find a mechanistic/statistical relationship between flow and the diffuse source signature, and then to statistically relate this diffuse source signature to land cover. In this way, the model attempts to simulate the effect of rainfall, and therefore flow, on the diffuse source signature for specific land cover categories at a daily scale, whereas the export coefficient approach relates land use to diffuse pollutant export at an annual scale, and even this coefficient may be inaccurate, disregarding the problem of gross generalization and averaging, due to variation in rainfall from year to year, which the export coefficient approach does not explicitly account for. In addition, while it is possible using the export coefficient approach to relate diffuse source loads to catchments with predominant land uses, the Land Cover Model approach is capable of calculating diffuse source loads for combinations of land cover categories at any combination of ratios. For example, while it would be difficult to calculate the annual diffuse source load from a catchment that is $1/8^{\text{th}}$ urban residential, $3/8^{\text{th}}$ permanently irrigated and $1/2$ natural forest using the export coefficient approach and past studies, it should be perfectly possible to find an approximation of the diffuse source signature, and relate that to flow at a daily scale, using the Land Cover Model. It is clear that the export coefficient approach is extremely limited, and some mechanistic/statistical model approach at at least a monthly scale, or even better at a daily scale as this model attempts, is more useful.

Previous modelling exercises in South Africa have tried to model the effect of land use and diffuse source inputs on water quality. Herold and van Eeden (2001) report on a low cost modelling methodology called NACL for estimating diffuse load inputs in ungauged catchments. Their approach has some similarities to the approach taken in the Mechanistic/Statistical Nutrient Model detailed in Chapter 4 and the Land Cover Model reported here, in that the investigators investigated relationships between flow and water quality for specific land uses. However, the regressions relationships used in their model to relate water quality to flow are too simple, especially for relating non-conservative variables to flow. The ACRU (Agricultural Catchments Research Unit) model (Tarboton and Schulze, 1991) has been applied to the Mgeni catchment (Kienzle *et al.*, 1997) to simulate the effect of land use on water quality. The ACRU model seems to work with a fundamentally different approach by simulating movement of soil particles on a catchment scale.

Internationally, catchment scale models such as INCA (Jarvie *et al.*, 2002; Whitehead *et al.*, 1998) and SWAT (Arnold *et al.*, 1998) are designed to simulate land use effects on river water quality. Both these models are fairly complicated and would require setting many parameters. INCA in addition is limited to simulating nitrogen fluxes within a catchment, and the land use classes used in the INCA model are not entirely appropriate for southern Africa.

This chapter (Chapter 5) partly addresses Aim 2, in that it shows that a relatively simple model, such as the Land Cover Model presented here, is capable of giving an accurate representation of the relationship between flow and water quality, if used in combination with the Mechanistic/Statistical Nutrient Model. Due to a lack of data, the confidence limits around predictions of diffuse inputs within catchments determined using the Land Cover Model, are very broad. The Mechanistic/Statistical Nutrient Model and the Land Cover Model show that within the context of modelling the relationship between flow and nutrients within rivers in a general context, it is important to consider the input of diffuse sources originating from land cover/use within the catchment. Therefore, this

chapter goes some way in addressing Aim 3.

Chapter 6: Extending a mechanistic mass-balance model linking flow to salinity to account for the effect of saline agricultural return flow

6.1 Introduction

The models presented in Chapter 3, 4 and 5, are statistical models, although Chapter 4 does incorporate a mechanistic component. The models presented in the previous chapters also increase in complexity with successive chapters. Chapter 3 showed that salinity does not have the same relationship with flow as the relationship that nutrients have with flow, therefore, it is impossible to distinguish the diffuse signature of salinity within historical monitoring data in the same way that was done with nutrients in Chapter 4. Chapter 5 presented a model that can link land cover to diffuse nutrient signatures within historical monitoring data. This chapter (Chapter 6) attempts to model the relationship between a diffuse source of salinity, i.e. saline irrigation return flow, and instream flow. However, the model presented in this chapter (Chapter 6), differs from the models presented in the previous chapters in that it is a purely mechanistic mass- balance model. While the model presented here is relatively simple for a mechanistic model, it is presented after the models in Chapters 3 to 5, as generally mechanistic models are considered more complex than statistical models, and the model simulates the effect of a diffuse source of salinity, making it a logical choice for presentation in this thesis after the land cover model in Chapter 5.

Salinity is a conservative water quality constituent, i.e. the inorganic salt ions that affect salinity remain relatively unchanged in their chemical composition throughout their movement along a river channel (Malan and Day, 2002a). Although the input of salts into surface waters is to a certain extent a natural process (Day, 1993; Herczeg *et al.*, 2001; Pillsbury, 1981; Smedema and Shiati, 2002), anthropological activities are causing unacceptable levels of salinity in surface waters in many arid parts of the world including

parts of the United States of America (Kaushal *et al.*, 2005; Williams 2001), Australia (Williams, 2001), South Africa (Davies and Day, 1998; DWAF, 1991) and central Asia (Williams, 2001). Anthropological causes include flow reduction in rivers, evaporative losses in surface waters, irrigation return flow, runoff from dry-land agriculture, saline industrial effluents, urban development contributions of point and non-point sources and atmospheric deposition (Kefford *et al.*, 2006; Kirchner *et al.*, 1997). Salinization of freshwater resources has a direct economic cost as water with a salinity of higher than 1000 mg.L⁻¹ becomes unsuitable for agriculture, human consumption and most industrial purposes, unless treated (Williams, 2001). Anthropogenically caused salinization in addition has negative effects on aquatic biota. The salinity levels of impacted rivers are on average higher than natural levels with less temporal variability (Kefford *et al.*, 2002), which leads to a decrease in biodiversity and the dominance of halotolerant biota within these systems (Williams, 2001).

It is clear that salinization of surface waters needs to be managed and controlled to alleviate the impacts caused by the problems listed above. Therefore, there is much value in modelling salinity in rivers, as a salinity model is a tool to be used to estimate how salinity will change over temporal and spatial scales in the absence of observed data (Rouch *et al.*, 1998), and can be used to investigate the consequences of different potential management options (Glaser and Bridges, 2007). It must also be considered that simpler models that simulate a few key processes may be more appropriate for management of water resources than large complex models, especially within the context of Integrated Water Resource Management (IWRM). The integrated approach to modelling for sustainable water resource management is different from a comprehensive approach which may not be either necessary or feasible (Liu *et al.*, 2008). An integrated approach to modelling salinity in rivers should instead focus on key processes that account for the most variability in salinity in the river investigated.

The salinization of surface water has been recognized as a major water quality problem in South Africa (DWA, 1991), and therefore, the development of a salinity model is especially relevant for management of water resources in South Africa. In addition,

observed salinity data is readily available, as the Department of Water Affairs (DWA) maintains a hydrological database that provides much of the data that would be needed for salinity modelling (Wimberley and Coleman, 2005). Many rivers in South Africa are ephemeral, therefore, it is important that the development of a salinity model for South African conditions should consider the fact that many rivers will consist of static pools during certain periods. Agricultural return flow has been shown to be a major cause of salinization of surface waters, for example Farber *et al.* (2004), Kirchner *et al.* (1997) and Lee and Howitt (1996). Therefore, there is value in developing a salinity model that simulates the effect of saline agricultural return flow on in-stream salinity. Hughes (2008) described a simple mass-balance water quality model that accepts hydrological output from either the monthly Pitman model with revised surface – ground water routines (Hughes, 2004), or the daily VTI model (Hughes and Sami, 1994). The water quality model simulates the salinity of flowing or static water within channel pools and is therefore relevant for modelling salinity in ephemeral or perennial streams and rivers. This research describes how the Hughes (2008) model has been extended to account for saline agricultural return flow. Uncertainty around predictions given by the model has been identified as an important model component, however, uncertainty has not yet been incorporated at this stage of the model development. In addition, other processes affecting in-stream salinity, such as input from point sources, are left for future research.

This chapter (Chapter 6), attempts to use a relatively simple mass – balance model to determine the effect of natural geology, as well as saline irrigation return flow, on in-stream salinity concentrations. Consequently, the development and validation of the Mass-Balance Salinity Model attempts to address Aim 2.

6.2 Model description and studied areas

6.2.1 Model description

The model described by Hughes (2008) simulates the salinity of ephemeral or perennial rivers. Ephemeral rivers often consist of static pools during periods of low rainfall, and salinity in the river is a function of flow from one pool to another as well as their storage

levels, as pools with no flow will experience evaporation and increasing salinity. The water quality model is able to use two different rainfall runoff models as the hydrological module in the model, the one being the revised monthly time step Pitman Model (Hughes, 2004) and the other being the daily VTI Model (Hughes and Sami, 1994). The output from the hydrological models include simulations of surface runoff depth, interflow runoff depth, ground water volume, upstream inflow volume, direct abstractions, pool volume, abstractions from dam volume, and downstream flow volume. In the modelling exercise, it is important that the hydrological model accurately simulates the flow components in an investigated system, as it will be difficult to accurately simulate the salinity of the investigated system unless the hydrology is correct. The water quality module simulates the salinity mass-balance in a relatively simple way. TDS concentrations of both flow and water stored in pools are simulated by accepting the different runoff components from the hydrological model and calculating the change in storage. The salinity model assigns fixed TDS concentrations to the inflow components and calculates changes in TDS load within a river reach based on the water quantity (volumetric balance):

$$\Delta S = UI - DO + SQ + IQ + GQ - PE - ABS \quad (\text{Equation 6.1})$$

where ΔS is the change in storage between the start and end of the period, UI is the inflow from upstream, DO the outflow to downstream, SQ, IQ, and GQ are the surface, interflow and ground water discharge additions to pool storage respectively from the local sub – basin, PE is the evaporation loss from the pool surface and ABS the total abstraction volume. The water quality model includes parameters for the TDS concentrations for the three inflow components:

CGW is the salinity concentration of groundwater discharge;

CINT is the salinity concentration of interflow discharge;

CSUR is the salinity concentration of surface discharge.

Other required parameters include maximum pool depth, width, and length as well as the

maximum bank storage salinity and the bank storage release rate. The water quality model simulates the exchange of salts between the water column and the soil of the banks surrounding the channel. The dynamics of salt movement into and out of the banks are determined by the ratio of wetted to un-wetted bank area. This was done by adding a simple pool bed and bank storage function which exchanges salt from the water to the bank during drying and moves salt from the bank to the water during wetting. This part of the model was developed specifically for ephemeral rivers and was found to be necessary to prevent excessive pool water TDS concentrations during zero inflow and pool drying conditions.

The water quality model described in Hughes (2008) has been extended to take into account the effect of irrigation abstraction and return flow. Presently, this is restricted to the monthly time step model. The hydrology model includes outputs that specify the volume of abstraction (from the river channel) and volume of return flows (drainage back to the channel as a direct consequence of irrigation) (see Figure 6.1). The assumptions of the irrigation extension to the water quality model are:

- The TDS concentration of the abstracted water is the same as the channel water TDS concentration in any given time interval.
- The TDS load added to the irrigated portion of the catchment is the product of the volume (from the hydrology model) of abstraction and its TDS concentration.
- The TDS load removed from the irrigated portion is the product of the return flow volume (from the hydrological model) and the TDS concentration of water in the irrigated soil profile.
- The TDS concentration in the irrigated soil profile is estimated from the load (updated through the mass-balance calculations) divided by the assumed water contents of the soil profile (product of irrigated area, soil depth and field capacity).
- Groundwater recharge (from the hydrology model) is assumed to transfer part of the irrigated soil profile TDS load to the groundwater body below the irrigated area.
- Part of the interflow and groundwater discharge to the river is assumed to be

affected by the TDS load in the irrigated soil zone and underlying groundwater zone (Figure 6.1 and Figure 6.2). This means that the fixed concentration applicable to these flow components in the earlier version of the model are now modified in each time interval by the TDS concentration of the water in the irrigated soil zone and underlying groundwater zone (see Figure 6.2 and Equations 6.2 and 6.3).

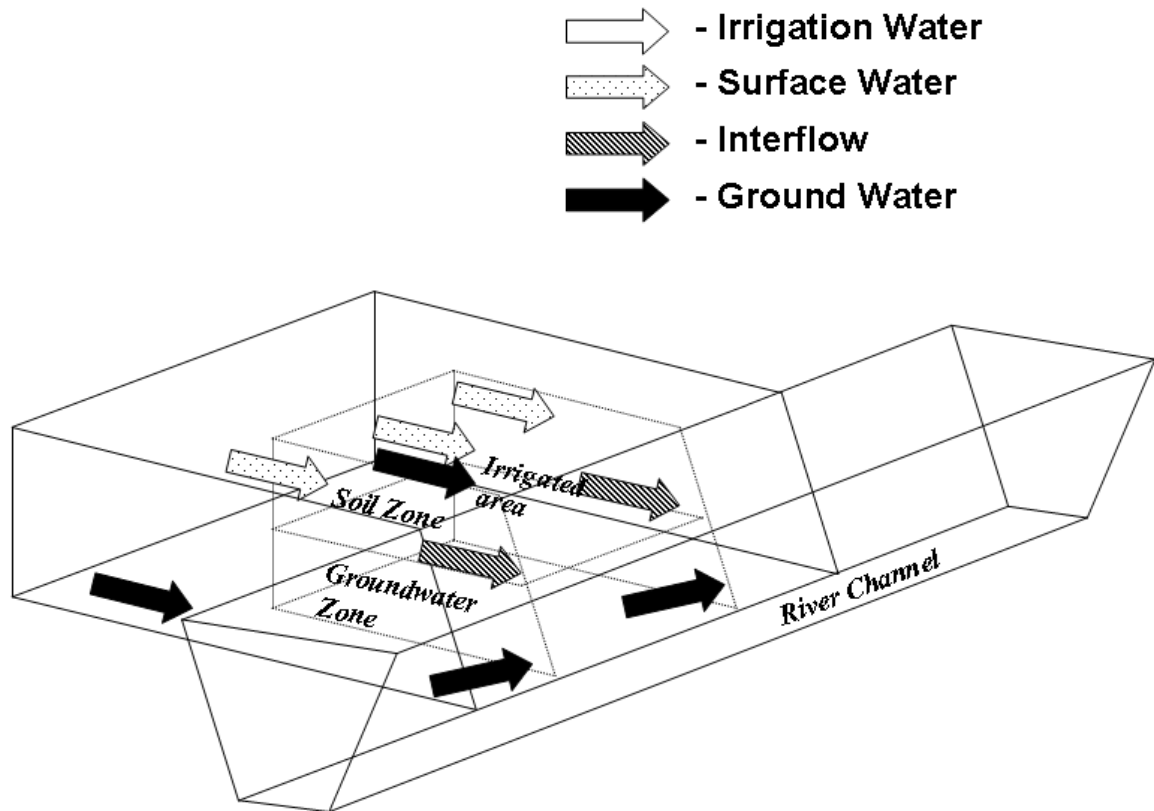


Figure 6.1: Diagram representing a conceptual cross section of catchment and the movement of flow components through the catchment. The salinity signatures of the components of flow shown in the diagram are modelled by the mass-balance water quality model.

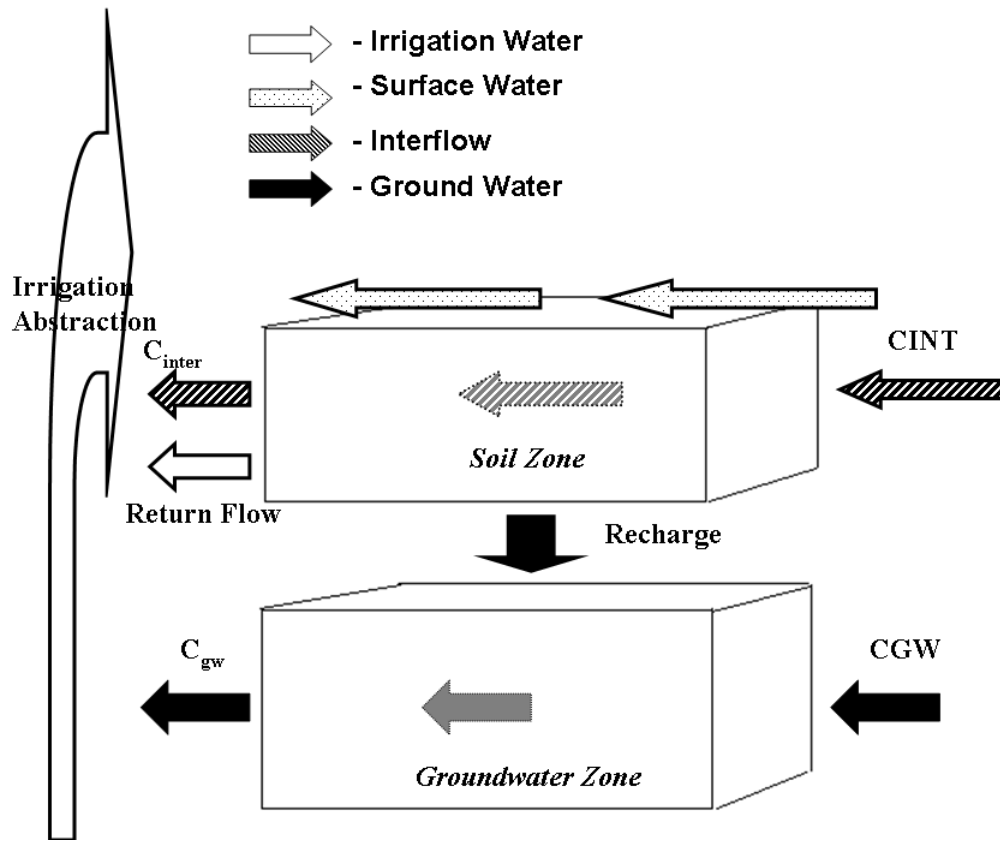


Figure 6.2: A conceptual diagram showing the partitioning of the catchment into two zones which represent irrigated area within a catchment. The salinity water quality model treats the two zones as separate units, with the top soil zone conducting interflow, and the bottom ground water zone conducting ground water flow. Water flows from the soil zone to the groundwater zone as groundwater recharge.

Figure 6.2 demonstrates how the model treats the irrigated part of the catchment as two zones, with interflow conducted through the soil zone and ground water through the groundwater zone, while recharge occurs from the soil zone to the groundwater zone. In the earlier version of the model the interflow and groundwater concentrations were fixed (CINT and CGW). In the extended model that considers irrigation, CINT and CGW are modified to account for the effects of irrigation based on the assumption that some of the interflow and groundwater drainage will occur from the irrigated area. The model therefore updates CINT and CGW in proportion to the ratio of irrigated area to total area

in the modelled catchment:

$$C_{inter} = ((1-Prop_{irrig}) * CINT) + (Prop_{irrig} * (Load_{irrig}/(Area_{irrig} * Depth_{inter} * FieldCapacity)))$$

(Equation 6.2)

$$C_{gw} = ((1-Prop_{irrig}) * CGW) + (Prop_{irrig} * (Load_{gw}/Area_{irrig} * Depth_{gw} * Stor))$$

(Equation 6.3)

Where $Prop_{irrig}$ = the proportion of irrigated land area to total modelled catchment area.

$Load_{irrig}$ = the load of salt within the upper layer of irrigated land.

$Area_{irrig}$ = the area of irrigated land.

$Depth_{inter}$ = an assumed depth of the upper layer through which interflow is conducted.

$FieldCapacity$ = field capacity of the soil in the upper layer.

$Depth_{gw}$ = assumed depth of bottom layer conducting ground water.

$Stor$ = storativity of the rock in the lower layer.

Values of $Depth_{inter}$, $FieldCapacity$, $Depth_{gw}$ and $Stor$ as set as parameters of the model.

The model calculates the change in river salt load using Equation 6.4 (ignoring bank storage effects that do not apply in a flowing river)

$$\Delta Load = (Q_{sur} * CSUR) + (Q_{inter} * C_{inter}) + (Q_{gw} * C_{gw}) + (Q_{rf} * C_{irrig}) + Load_{upstream} - (Q_{abs} * C_{ab}) - Load_{downstream}$$

(Equation 6.4)

Where

Q_{sur} = surface flow.

Q_{inter} = interflow flow.

Q_{gw} = groundwater flow.

Q_{rf} = return flow.

C_{irrig} = salt concentration of irrigation water.

$Load_{upstream}$ = load of salt coming into the river from upstream.

Q_{abs} = abstraction flow.

C_{ab} = salt concentration of abstraction water.

$Load_{downstream}$ = load of salt leaving the modelled river downstream.

The current river concentration is calculated from its salt load and the river pool storage volume. The concentration and downstream flow volumes are used to calculate the downstream load (equal to upstream load for the next sub catchment in the routing system). A similar mass-balance equation (involving inflows and outflows) is used to update the TDS loads in the irrigated soil and ground water zones.

Because historical monitoring data measured by the Department of Water Affairs (DWA) measures salinity in electrical conductivity (EC), but not TDS, DWA observed data in EC were converted to TDS for comparison to model output using the following equation taken from DWA (1996):

$$\text{TDS (mg.L}^{-1}\text{)} = \text{EC (mS.m}^{-1}\text{ at 25 C}^{\circ}\text{)} * 6.5 \quad (\text{Equation 6.5})$$

6.2.2 Study Areas

At this stage of the model development, the model was applied to two river reaches. A preliminary sensitivity analysis of the model was performed by application to a section of the Balfour River. The model also needed to be tested on a reach of river known to be heavily affected by saline agricultural return flow, and this is why the model was in addition applied to the middle reaches of the Breede River.

6.2.2.1 The Balfour River

A preliminary sensitivity analysis of the model was performed by applying the model to the Balfour River. The Balfour River is a small tributary (approximately 9 km) of the Kat River with a catchment area of about 120 km² and is situated in the Eastern Cape, South Africa (Hosking and du Preez, 2002; Gordon *et al.*, 2009) (Figure 6.3). The Balfour River is classed as a naturally perennial river, although judging from the flow record of the gauging station Q9H019, there are periods of no flow and extended periods of minimal flow (<0.01 m³.sec⁻¹). The Kat River catchment of which the Balfour River is a tributary, is part of the Amatola escarpment and the topography of this area is made up of the Cape

Fold mountains (Hosking and du Preez, 2002). The geology of the area is part of the Beaufort Series consisting of shale, mudstone, sandstone and limestone. The catchment receives a mean annual precipitation of 950 mm (Hosking and du Preez, 2002) and the mean annual discharge of the Balfour River is $10.38 \times 10^6 \text{ m}^3 \cdot \text{yr}^{-1}$ (Gordon *et al.*, 2009). The river is a low order stream consisting of riffles and pools where depth generally does not exceed 1 m (Gordon *et al.*, 2009). Detailed land cover categories are shown in Figure 6.3, and land use is described by Gordon *et al.* (2009) as broadly consisting of subsistence livestock and agriculture.

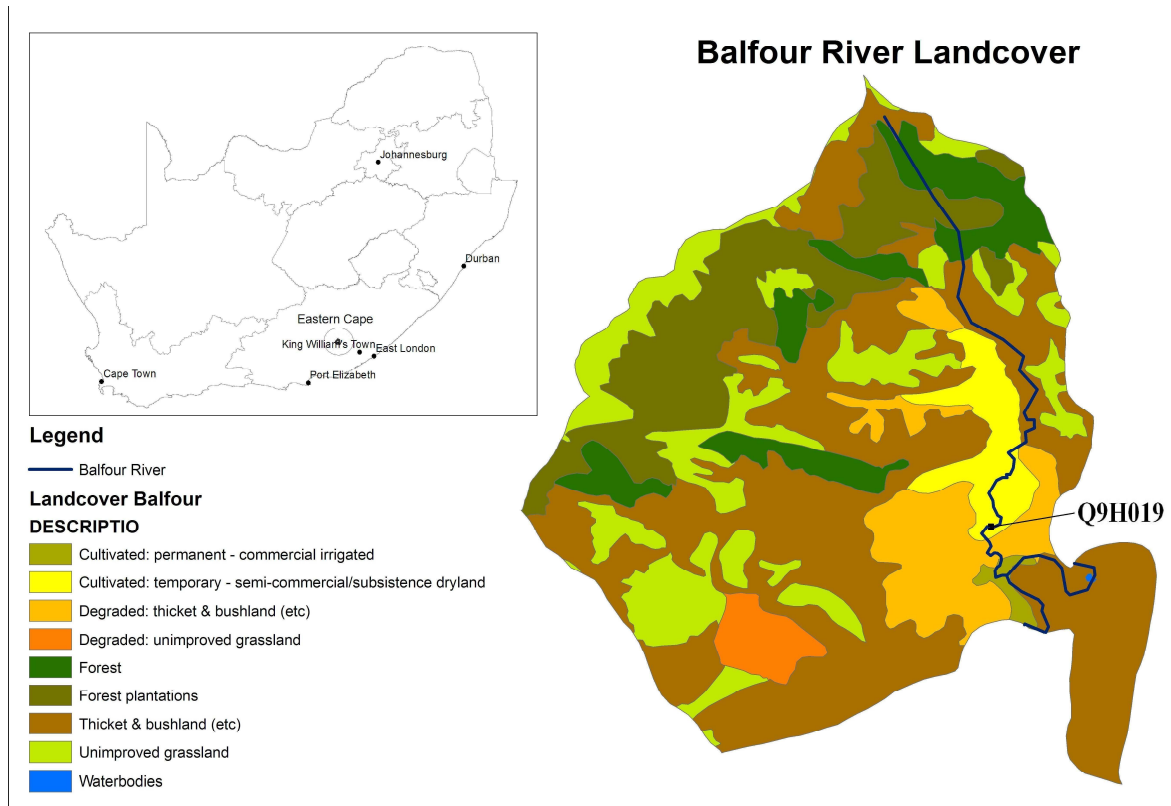


Figure 6.3: Diagram showing the location of the Balfour River catchment within South Africa, and the dominant land cover types within the catchment. Water quality data were obtained from the weir Q9H019, indicated on the map.

Commercial citrus farmers that belong to the Kat River Irrigation Board are situated further downstream (Hosking and du Preez, 2002). The potential irrigation area adjacent to the Balfour River was approximated by viewing satellite images of the area. Simulated

flow and simulated TDS data were compared to historical monitoring data from the DWA gauging site Q9H019 for the years 1977 to 1990.

6.2.2.2 The Breede River Catchment

The Breede River originates in the Ceres Valley in the Western Cape, South Africa (Figure 6.4). The river flows in a south east direction for approximately 320 km before reaching the Indian Ocean (Kirchner *et al.*, 1997). The area of the catchment of the Breede River investigated is that between the DWA monitoring points H4H017 and H5H004. This segment of the river forms part of the middle reaches of the river.

The middle reaches of the Breede River occur in a valley, with the Riviersonderend Mountains to the south, and the Langeberg Mountains to the north (Kirchner *et al.*, 1997). The region receives winter rainfall between 1600 mm.year⁻¹ to 2000 mm.year⁻¹. The mountain ranges on each side are of the Table Mountain Group (Flugel and Kienzle, 1989), and consequently, runoff and groundwater originating from these regions are typically low in salinity. Formations of the Bokkeveld Group, Dwyka and Enon Formations underlie the slopes of the valley. These deposits are of marine origin with a high salt load (Flugel and Kienzle, 1989). The plain of the river and its tributaries are underlain by alluvial sediment (Kirchner *et al.*, 1997).

The section of the Breede River investigated, including the tributaries are extensively used for irrigation (Flugel and Kienzle, 1989; Kirchner *et al.*, 1997). In addition, the water from the Brandvlei Dam upstream of H4H017 is used to irrigate farmland in the investigated catchment as part of an irrigation scheme (Kirchner *et al.*, 1997). Brandvlei Dam was constructed in 1922 to provide reliable irrigation water, is an off-channel reservoir adjacent to the Breede River, and intercepts water from two tributaries of the Breede River (Kirchner *et al.*, 1997). The dam is in addition used by DWA to provide freshening releases to the Breede River in summer to ensure that salinity levels remain within a certain limit (Kirchner *et al.*, 1997).

Most of the irrigated land in the investigated catchment is used for vineyards (65%), while there is in addition some cultivation of peaches and apricots, vegetables and pasture land (Kirtchner *et al.*, 1997). Farmers typically collect water in farm dams in winter and irrigate in summer using the stored water, water from the irrigation scheme or abstraction from the Breede River or its tributaries (Kirtchner *et al.*, 1997). Because of the low levels of the Breede River in summer, and high volumes of saline irrigation return flow coming into the river, the TDS signature in the middle Breede River shows a seasonal trend (Flugel and Kienzle, 1989; Kirtchner *et al.*, 1997). The average salinity signature in the Breede River shows a dramatic increase between the sites H4H017 and H5H004, which Kirtchner *et al.* (1997) attributed primarily to saline irrigation return flow. From a review of previous studies, Kirtchner *et al.* (1997) concluded that natural groundwater discharge is probably not a major cause of salinization. Kirtchner *et al.* (1997) concluded that excessive leaching from irrigation, as well as the mobilization of salts caused by the preparation of new land for irrigated winelands within the marine deposits, as the cultivated area of land expands, are the primary causes of salinization of the Breede River.

Observed data from the upstream site H4H017 were compared to simulated flow and TDS data, although a thorough calibration of the model was not attempted, since the aim of the research was not to simulate the irrigation processes upstream of the study area. Rather, a rough calibration to obtain flow and TDS simulations in the same approximate range as the observed data was attempted, so that the model could more accurately simulate flow and TDS concentrations within the study area downstream. Within the study area, observed flow data from H5H004 were compared to the simulated flow from the model. Observed TDS data from H5H002 and H5H004 were combined for comparison to the model simulated TDS estimates, as the two gauging stations are close to each other (< 1 km), and combining the TDS data reduces the temporal gaps between the observed measures. Observed data from 1980 to 1990 were compared to model simulated data for both the upstream and downstream sites.

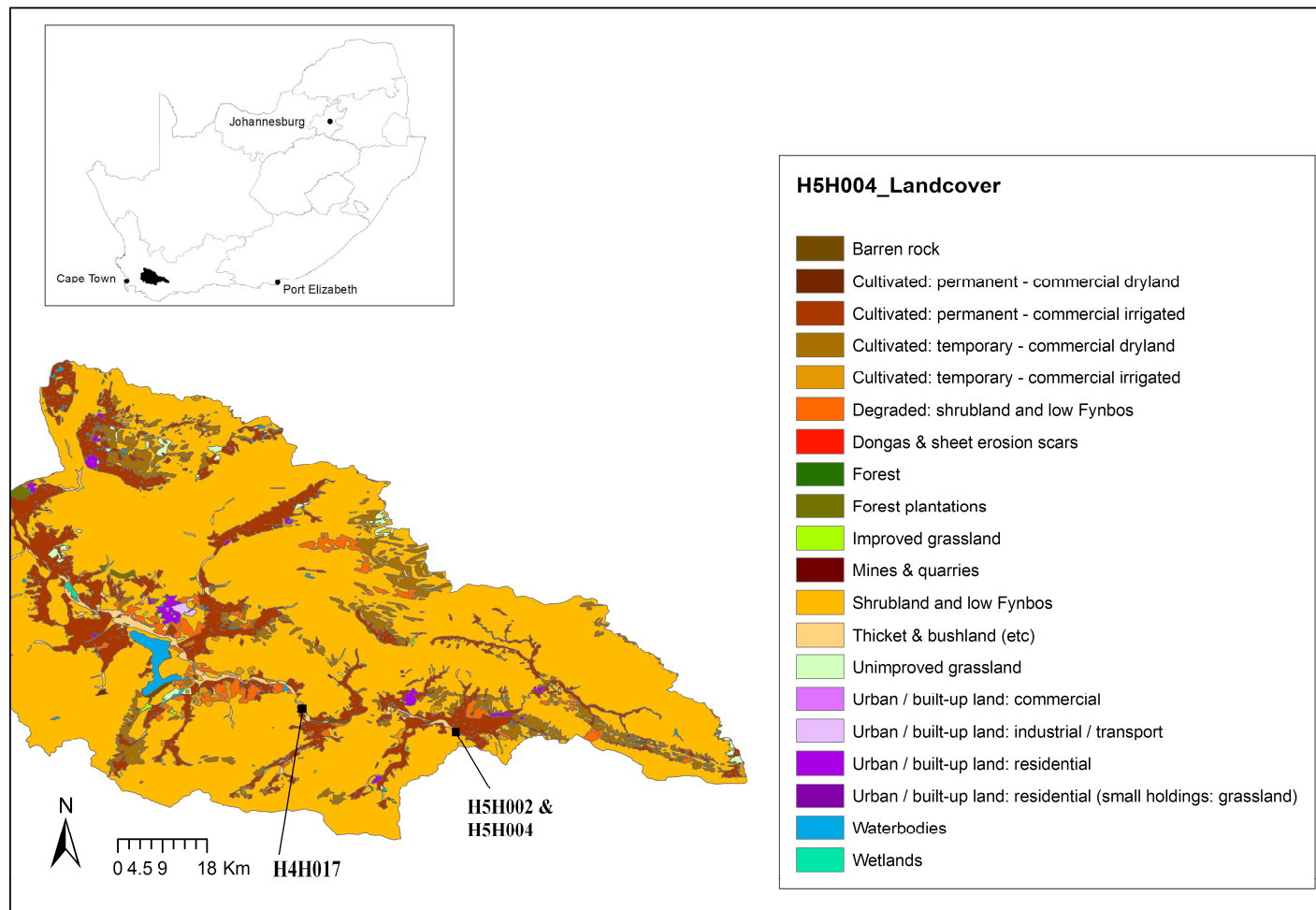


Figure 6.4: Diagram showing the location of the Breede River catchment within South Africa, and the dominant land cover types within the catchment as well as the position of the water quality monitoring gauges.

6.3 Results

Table 6.1 shows the final salinity signatures used for the flow components in the calibrated water quality models for both rivers. These parameters specify the salinity signatures for surface water, interflow and ground water, throughout each study area. The model updates the salinity signature of interflow and ground water due to irrigation return flow, according to the proportion of irrigated land total land area within the study area.

Table 6.1: Salinity signatures used in a mass-balance water quality model

Modelled River	TDS Signatures (mg.L ⁻¹)		
	Surface Water	Interflow	Ground Water
Balfour	200	600	800
Breede	100	800	1500

6.3.1 Results of model applied to the Balfour River

According to the land cover map (Figure 6.3), there are no irrigated lands within the study area, only cultivated dryland, unimproved grassland, thicket and bushland and forest. There are some permanent irrigated lands downstream of the study area, where the Balfour River joins the Kat River, but this irrigation would have had no effect on the study area. Therefore, the area of irrigated land affecting the modelled reach is assumed to be negligible. However, the model was tested for sensitivity, by setting the irrigation area to 0 km², 0.5 km² and 1 km² in three separate model runs. Analysis of the results of running the water quality model for the Balfour River show that the simulated EC signature reasonably tracks the temporal trends and the range of measured salinity data. The modelled results of flow for no irrigation, irrigation of 0.5 km² and irrigation of 1 km², show very little variance from the observed flow (Figure 6.5). The modelled results of salinity with no irrigation are very similar to the observed salinity (Figure 6.6). The modelled results of salinity with irrigation however show an increase in salinity with irrigation (Figure 6.6).

6.3.2 Results of model applied to the Breede River

The hydrological model was roughly calibrated to match the observed flows at H4H017, taking into account the releases from Brandvlei Dam. Figure 6.7 show that the model roughly simulates the flow at H4H017. The results of the water quality model are shown in Figure 6.9. While the modelled results are in the same range as the observed TDS measures at H4H017, the simulated estimates do not accurately mirror the seasonal changes in observed TDS. This research however aims to simulate the changes in TDS downstream of H4H017, and only a rough calibration of the model for the river upstream of H4H017 was attempted. Therefore, these results were regarded as being sufficient.

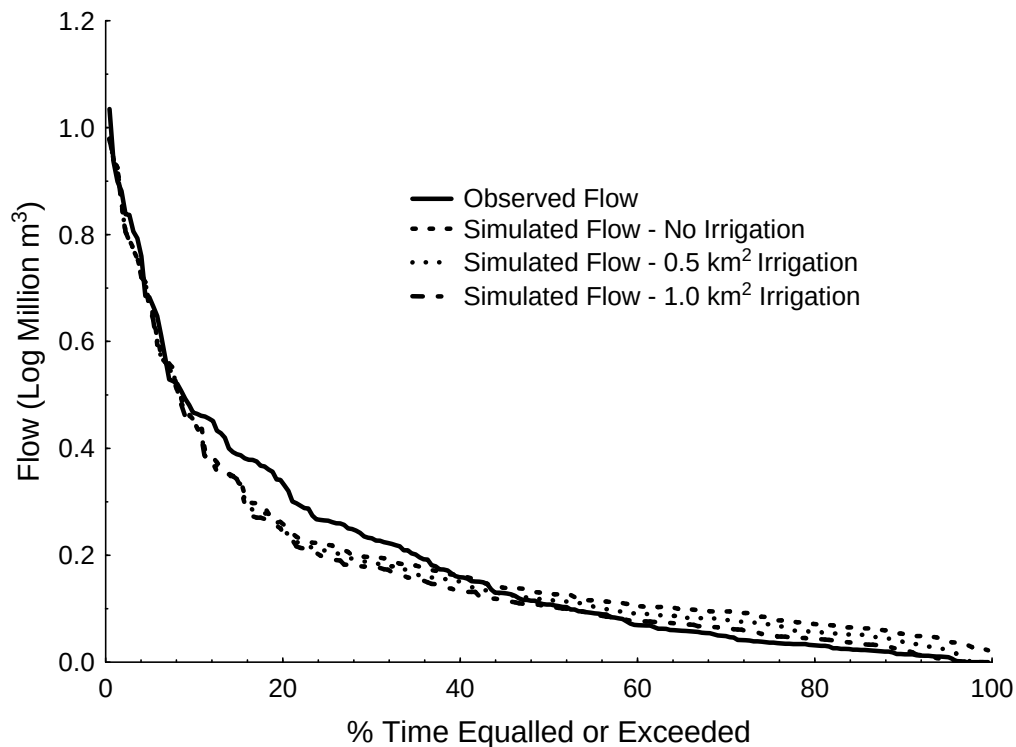


Figure 6.5: Flow duration curve for the Balfour River, showing observed flow, and modelled flow using scenarios of no irrigation, 0.5 km² irrigation and 1 km² irrigation.

It is important to realize that the model provides mean monthly simulations of TDS

concentrations, while observed measures of TDS are not averaged in any way. So the comparisons of observed TDS versus simulated, as seen in Figure 6.9, must be made considering that the simulated TDS results will not vary with the same range over time as the observed TDS results.

The hydrological model was set up without a pool storage component, as the Breede River is a permanently flowing river. Figure 6.8 shows the results of the model simulated flow for the downstream site H4H005 compared to the observed flows at this site, as a flow duration curve.

The results of the water quality model for the downstream site H5H004, are shown in Figure 6.10. The model was set to simulate irrigation return flow for an irrigation area of 30 km². The simulated mean monthly estimates of TDS seem to track the seasonal changes of the observed daily TDS values fairly well. A plot of the average monthly observed TDS values (Figure 6.10) shows that the model estimations are in addition within the same range as observed TDS values.

The seasonal salinity distribution for the upstream and downstream sections of the Breede River are shown in Figure 6.11. Figure 6.11 shows that the seasonal salinity trend is changed dramatically from upstream to downstream. Firstly, the salinity ranges downstream (Figure 6.11b) are much higher than that of upstream (Figure 6.11a). Secondly, the upstream observed seasonal salinity seems to have two peaks at about April and October, with TDS minimums occurring in July and December (Figure 6.11a). This is in contrast to the downstream seasonal TDS pattern, where there is a strong Summer TDS peak and a Winter TDS minimum (Figure 6.11b). Figure 6.11a shows that the model results roughly mirror the TDS trend for the upstream site, although the model seems to miss the July TDS minimum. The model simulated the downstream seasonal TDS signature fairly accurately (Figure 6.11b).

The total salt load introduced into the study area of the Breede River from 1980 to 1990 due to irrigation return flow was calculated using the principles of mass balance. Surface

water inflow, interflow and ground water contributions to salt load into the study area were calculated using the model outputs of the flow contributions from the contributing quaternary catchments and the TDS signatures of each component. Abstraction of flow and salt load from the river was in addition taken into account, and the final values of the irrigation return flow salt load were calculated taking into account the model generated flow and salt load into the study area, and the model generated flow and salt load leaving the study area. Table 6.2 lists the monthly averaged TDS signatures of the flow components, as well as the final salt load entering the study area due to irrigation return flow. TDS signatures of the flow components for the calibrated model are shown in Table 6.1. A study of DWA borehole data (DWA, 2010) available for the drainage region H40, showed that ground water salinity in the region varies dramatically, with a mean TDS of about 1000 mg.L^{-1} ($n = 78$, minimum = 20.15 mg.L^{-1} , maximum = 5220 mg.L^{-1}). Therefore, the ground water signature of the calibrated model of 1500 mg.L^{-1} is within the range of measured ground water salinities and close to the mean of observed groundwater salinities for the region.

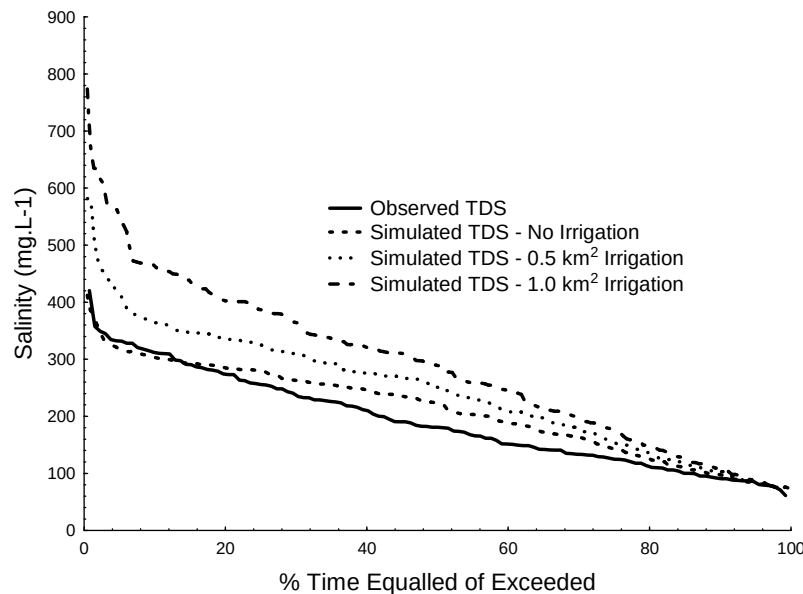


Figure 6.6: Duration curve for the Balfour River, showing observed and modelled TDS using scenarios of no irrigation, 0.5 km^2 irrigation and 1 km^2 irrigation.

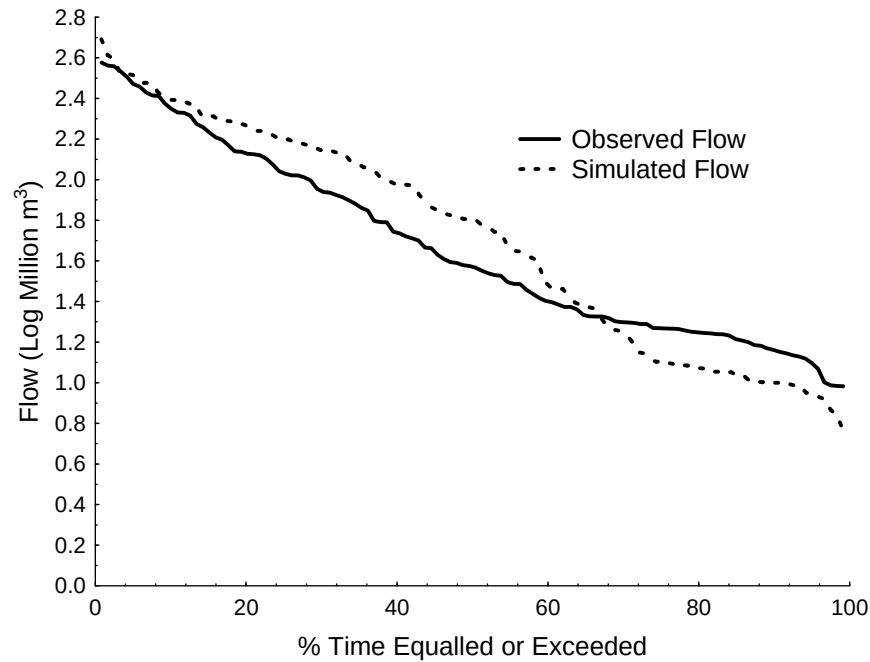


Figure 6.7: Flow duration curve for the Breede River for the upstream site H4H017 showing observed and modelled flow.

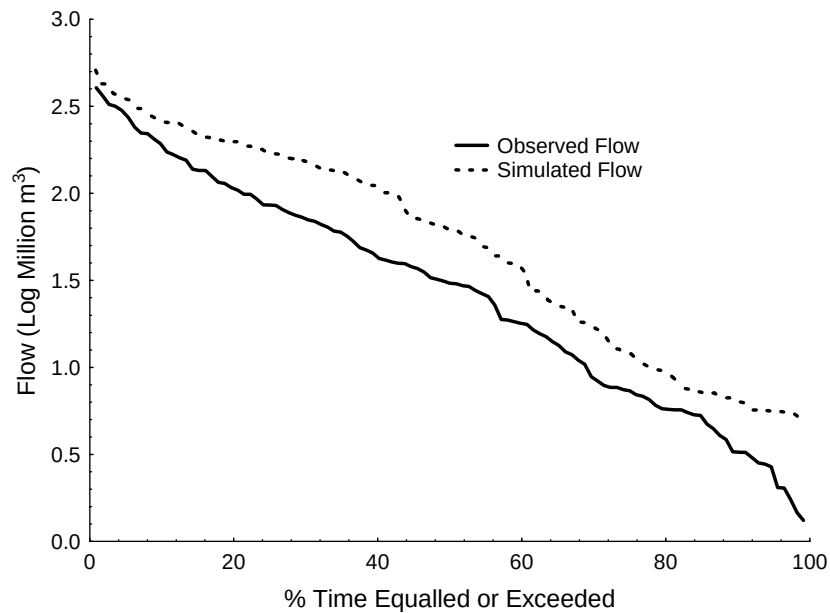


Figure 6.8: Flow duration curve for the Breede River for the downstream site H5H005 showing observed and modelled flow.

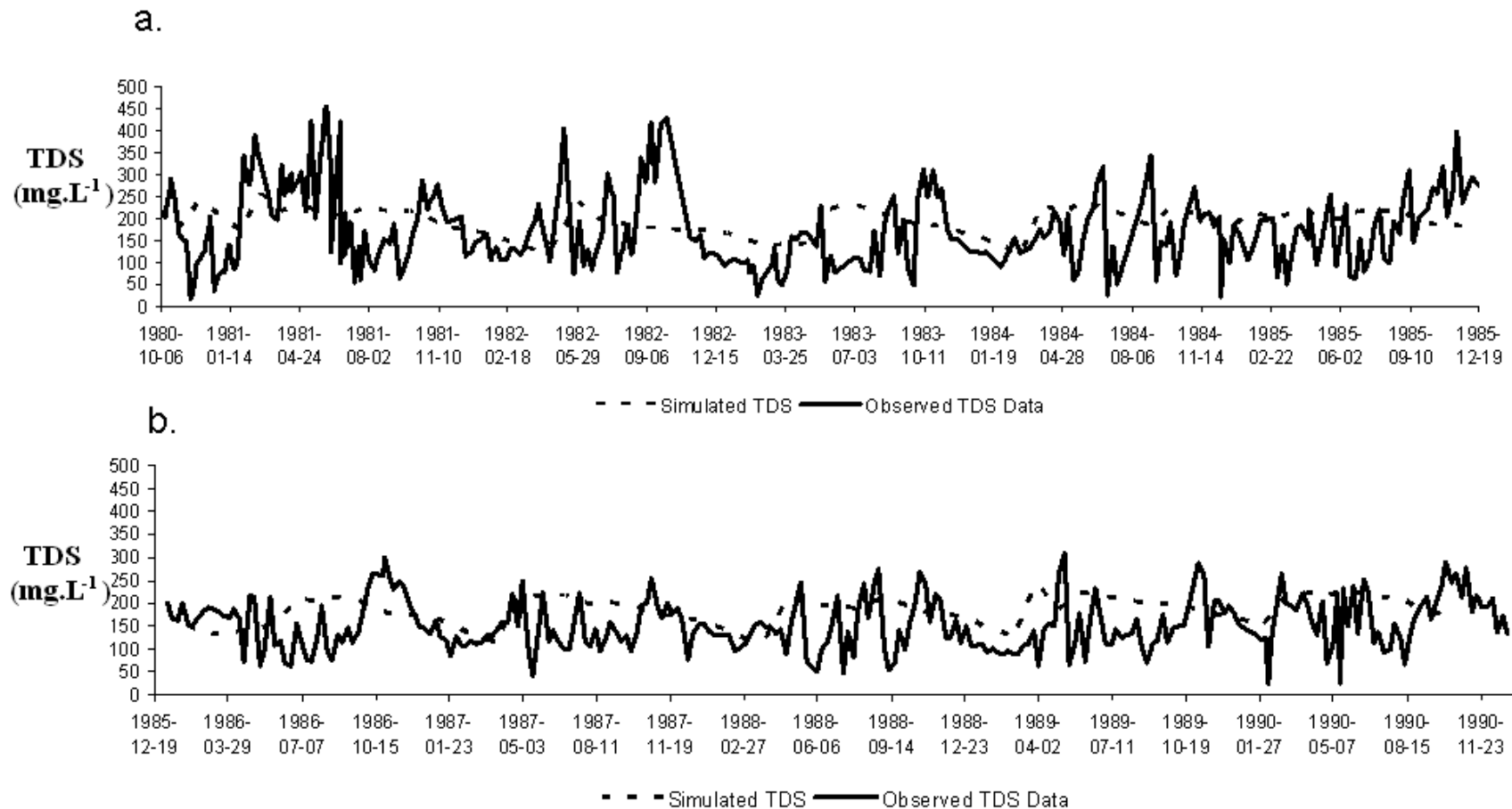


Figure 6.9: Graph showing observed TDS over time at the site H4H017 and the model monthly mean TDS simulations. Graph a – 1980 to 1985. Graph b – 1986 to 1990.

6.4 Discussion

This model is consistent with the overall aim of this thesis, namely to investigate the relationship between flow and water quality. The Pitman Model, which acts to simulate the hydrology of the investigated river reaches, simulates flow from upstream, flow from tributaries, and groundwater, interflow and surface flow from the catchment into the investigated reach. In-stream flow from upstream, tributaries and reservoir releases, may act to dilute agricultural return flow. The Pitman Model also simulates the groundwater, interflow and surface water flow components that the water quality model uses to estimate the exchange of salts between the channel bed and the soil of the banks surrounding the channel as well as the saline agricultural return flow coming into the investigated reach.

The results of applying the mass-balance water quality model to the Balfour River showed that the model is sensitive to the extensions made to simulate irrigation return flow. The model gave simulated salinity data for no irrigation that is close to, but slightly higher than the observed salinity. Incorporating irrigation return flow into the model by setting irrigated land area of the catchment to 0.5 and 1.0 km², raised the simulated salinity to above that of the observed data.

Further work was needed on validating whether the salinity signatures generated by the model for irrigation return flow are realistic. The model needed to be applied to a river system known to have a high salinity, so as to ascertain the relative effect of irrigation return flow on the salinity of the river water, and this is why the model was in addition applied to the Breede River within a region of intense irrigation.

To accurately model the flow and TDS signature within the study area of the Breede River between the monitoring points H4H017 and H5H004, the model had to be roughly calibrated to simulate the flow from upstream, and to estimate the general range of the TDS signature from upstream. It is possible that a detailed application of the model to the total catchment could have resulted in a better upstream calibration of the model.

However, it was felt that the amount of effort and time required to accurately calibrate the upstream site was too high for the purposes of this chapter. There is in addition a paucity of data with which to accurately calibrate the model for the upstream site. Importantly, it appears a lot of irrigation takes place above the study area (Figure 6.4), but the purpose of the study was to concentrate on the effect of irrigation within the study area on the TDS signature of the Breede River.

Figure 6.7 shows that the amount of flow from upstream flowing into the study area was relatively well estimated by the model. Figure 6.9 shows that while the model estimations of TDS concentrations upstream of the study area did not accurately mirror the time series patterns of observed TDS, the model estimations were, in general, within the same range as the observed values, and were reasonably representative of the seasonal distribution (Figure 6.11a). Importantly, it appears that salinization of the Breede River due to irrigation return flows only becomes a major factor within the middle reaches of the river i.e. within the study area. The TDS upstream of the study area appears to remain fairly low, but shows a significant increase within the study area, which can be attributed to saline irrigation return flow (Flugel and Kienzle, 1989; Kirchner *et al.*, 1997). The seasonal pattern of salinization in addition becomes much stronger in the studied region, with salinity showing a strong peak in summer and minimum in winter (Figure 6.11b).

The model estimated the flow within the study area of the Breede River fairly well (Figure 6.8) and so takes into account flow from upstream, freshening releases from Brandvlei Dam, contributions of surface water, interflow and groundwater from surrounding quaternary catchments, abstraction from the river, and saline irrigation return flow.

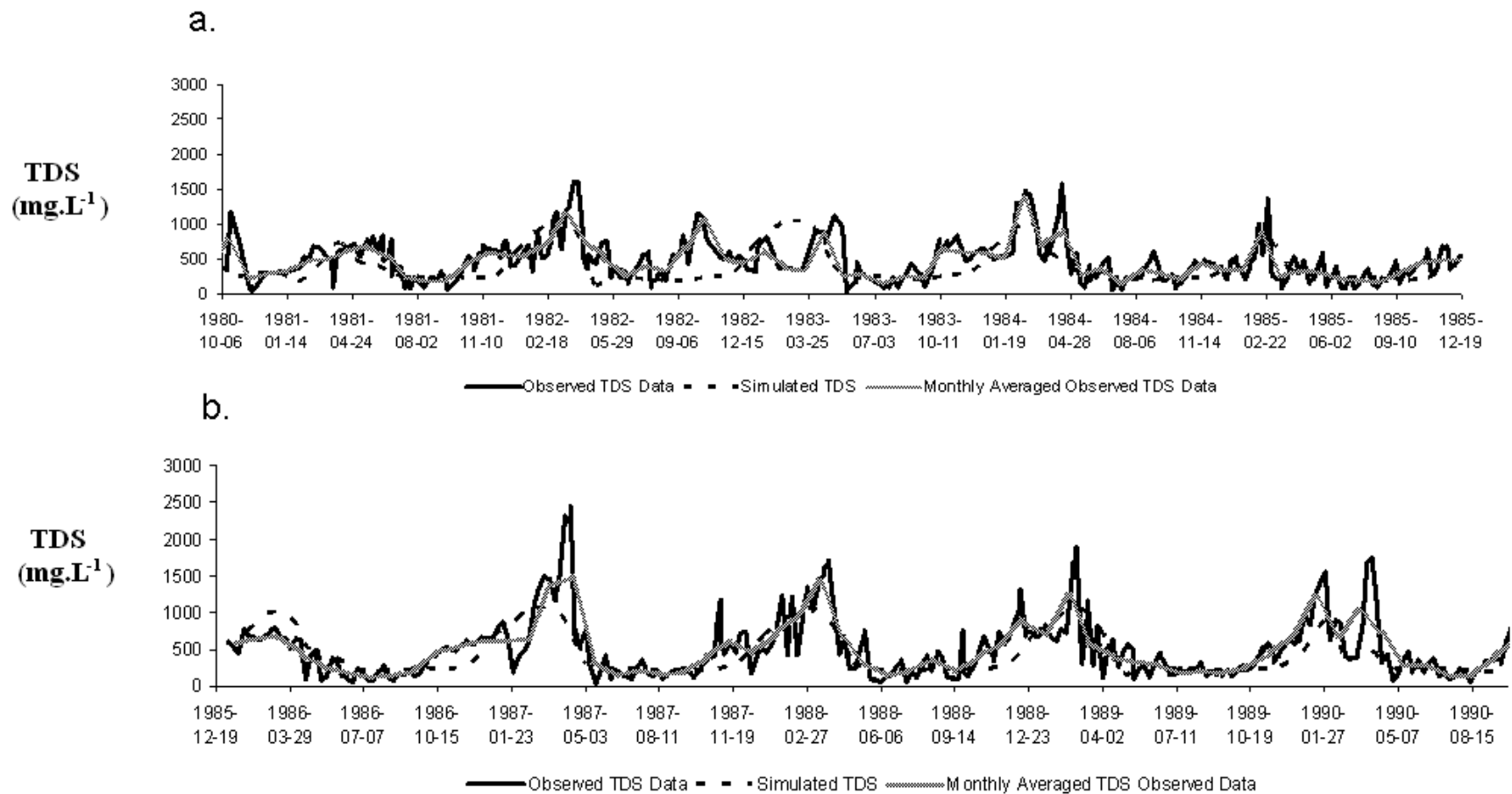
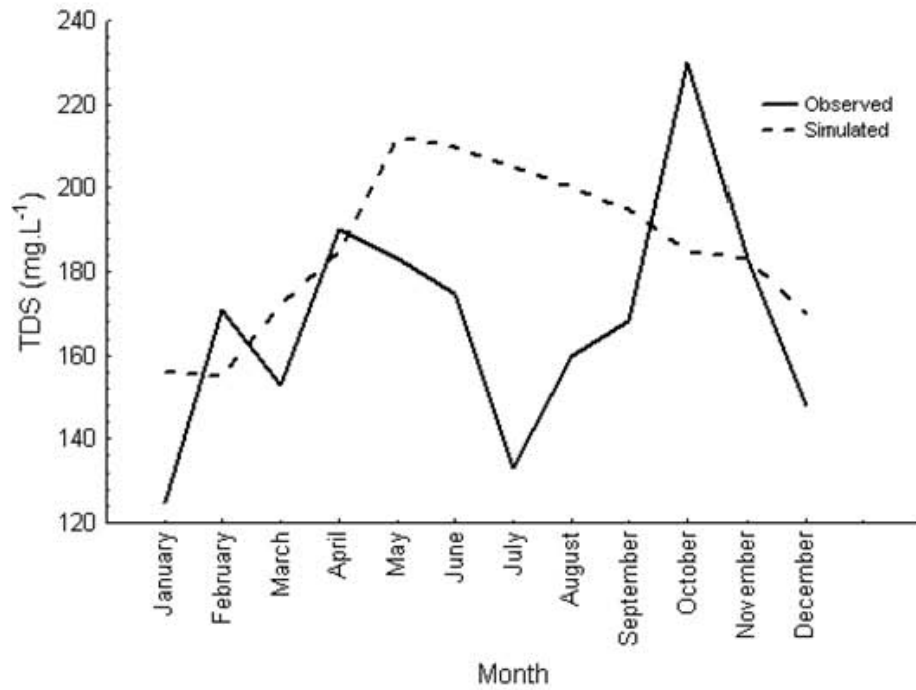


Figure 6.10: Graph showing observed TDS over time at the sites H5H002 and H5H004 and the model monthly mean TDS simulations. Graph a – 1980 to 1985. Graph b – 1986 to 1990.

a.



b.

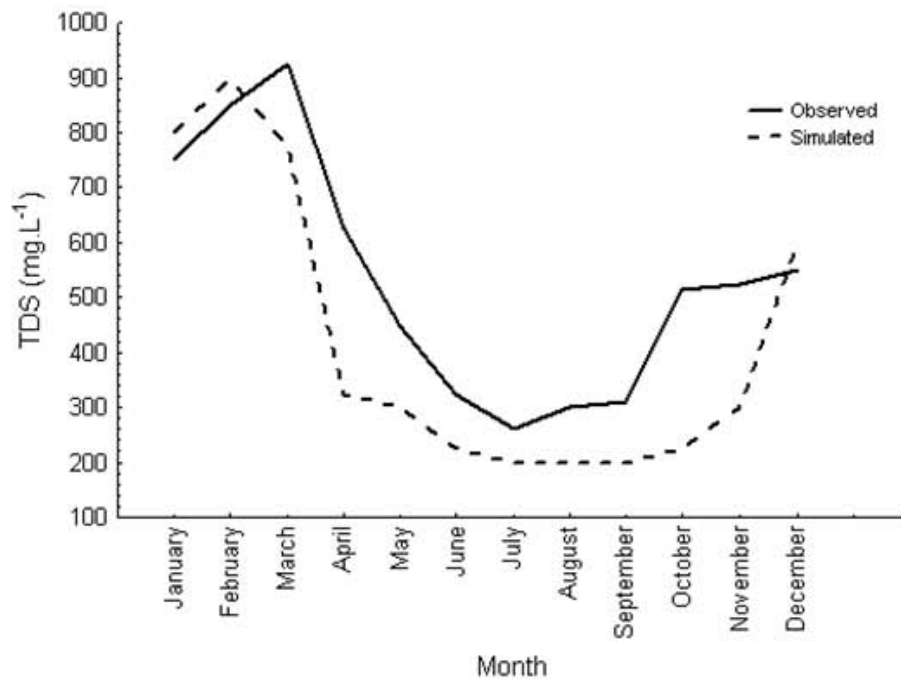


Figure 6.11: Observed and model estimated seasonal distribution of TDS for the studied section of the Breede River. a – Upstream TDS; b- Downstream TDS.

Table 6.2: Monthly averaged Flow and TDS signatures entering and leaving the Breede River between the DWA monitoring points H4H017 and H5004 as well as the monthly averaged salt load introduced by irrigation return flow as estimated by a mass-balance model between the years 1980 – 1990.

Month	Inflow Q (10 ⁶ m ³)	Inflow TDS (mg.L ⁻¹)	Outflow Q (10 ⁶ m ³)	Outflow TDS (mg.L ⁻¹)	Total change in salt load (kg)	Irrigation salt load (kg)	% salt load introduced by irrigation
January	39.37	156.17	41.70	801.84	27287.46	26467.97	97.00
February	24.93	154.68	23.28	892.75	16924.60	15911.69	94.02
March	16.83	171.29	14.74	770.47	8474.99	8075.43	95.29
April	51.66	184.28	69.06	323.67	12833.42	10364.88	80.76
May	115.14	212.18	124.24	291.98	11846.14	9029.16	76.22
June	160.64	210.04	166.96	231.30	4877.05	3416.30	70.05
July	204.43	204.39	211.71	216.65	4082.63	2460.83	60.28
August	207.31	199.31	217.70	212.27	4892.29	2957.18	60.45
September	161.46	194.24	167.74	218.65	5312.60	3606.39	67.88
October	92.56	185.05	96.50	234.31	5484.67	4223.93	77.01
November	48.61	182.48	49.46	306.90	6309.24	5262.87	83.42
December	21.26	170.98	18.97	587.74	7516.69	6875.79	91.47

The model estimations of the TDS signature within the study area in addition seem to accurately reflect the seasonal TDS signature as well as the range of observed TDS concentrations (Figure 6.10). Table 6.2 shows that the majority of salt load introduced into the middle reaches of the Breede River occur during the summer irrigation months from October to May, which is inverse to the rainfall in the area which increases flow within the river, which from Table 6.2 can be seen to occur from May to September. The model results shown in Table 6.2 indicate that the majority of salt introduced to the middle Breede River during summer is due to irrigation return flow. This is in agreement with the conclusions arrived at by Kirchner *et al.* (1997) that the salinization of the middle Breede River is due to irrigation return flow.

The results of this study indicate that the extensions of the Hughes (2008) water quality model to account for irrigation return flow, do allow the model to fairly accurately

estimate salinity in rivers affected by saline irrigation return flow. The model was designed to estimate changes in salinity within ephemeral rivers or perennial rivers, and it does appear that the model can be set to simulate changes in salinity within permanently flowing rivers such as the Breede River.

While there are statistical methods of quantifying fit of model simulated results to observed flow and water quality data, it was felt that a visual assessment of the fit within a duration curve gave a sufficiently good indication of the accuracy of the model.

Generally, there is not much published work on models that can predict the effect of agricultural land on salinity. Herold and le Roux (2004) report on a model framework software called WQ2000, which incorporates a monthly time-step hydro-salinity model. Herold and le Roux (2004) report that the model has a salt washoff sub-model that simulates the accumulation of salt within a catchment, and the release of salt during runoff events, as well as via interflow and groundwater flow. The hydro-salinity model in addition, includes a sub-model which simulates the accumulation of salt within irrigated lands and return flow. The irrigation sub-model is more complicated than the model outlined in this chapter (Chapter 6), and its functionality includes simulating the effect of multiple crops, additional return flow during wet periods and addition of salts via fertilizer (Herold and le Roux, 2004). The model outlined in this chapter (Chapter 6) is simpler, yet the initial applications of this model indicate that it can accurately simulate the effect of saline irrigation return flow on in-stream salinity. Due to its apparent complexity, the model given by Herold and le Roux (2004), is likely to be more difficult to set up and run, and would most likely require more data. Therefore, the model described in this chapter could be useful as a simpler model to manage salinity in rivers by indicating what effect irrigated lands would have on in-stream salinity. The model application to the middle Breede River, demonstrates that there are river reaches that are negatively affected by specific process and water quality variables. In this case, the Breede River is being salinized by irrigation return flow, and control of salinization may be a far more important management issue than eutrophication for example. This model is limited in its simulation capacity to estimating natural salinity processes, as well as

salinization due to irrigation return flow. However, its simplicity and narrow range of simulated processes, results in the model requiring much less data than a complex model framework. This research in addition demonstrates that the model is entirely suitable for estimating salinity in the middle Breede River. Therefore, there are situations where simple models are entirely appropriate, and in fact, preferable to more complex models.

A simple model, that simulates a few key processes, may be more appropriate than complex models for implementing Integrated Water Resource Management (IWRM) policies. As has been mentioned above, this model would require less monitoring data, and is relatively simple to calibrate and run, compared to a complex model. Yet, the model does seem to be able to give an accurate simulation of in-stream salinity for the limited number of applications that were investigated. A further issue for research to extend this model would be to incorporate other sources of salinity such as point sources. The model also requires further development to incorporate some measure of uncertainty into the simulated results.

This chapter (Chapter 6) partly addresses Aim 2, as the Mass – Balance Salinity Model is a relatively simple model, yet, can provide a realistic representation of the relationship between flow and salinity, in regions where the most important inputs of salinity into a river are derived from the surrounding geology, and from irrigation return flow.

Chapter 7: A simple nutrient model to predict nitrification reaction coefficients using historical monitoring data

7.1 Introduction

Deteriorating quality of surface water resources is a major concern in many countries and in South Africa in particular. A major water quality problem is that of eutrophication, caused by an increased input of nutrients into freshwater resources. The causes of these inputs include domestic and industrial effluent release into rivers (Walmsley *et al.*, 1999), as well as various diffuse source inputs from land utilized for urban and agricultural use (Hughes and van Ginkel, 1994). Eutrophication of water resources has resulted in various ecological and social problems, such as reduced quality of water resources for domestic and industrial use, increases in periphyton growth, surface algal scum, growth of floating macrophyte invasives and low light and low oxygen conditions in freshwater systems (van Wyke and van Wilgen, 2002; Withers and Jarvie, 2008).

Eutrophication is a major water quality management concern, and water quality models can play an important role in managing nutrient levels within freshwater systems. A water quality model is a tool that is used to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data (Rouch *et al.*, 1998), and models find their use in the rehabilitation of degraded aquatic ecosystems, management of systems under development, and the maintenance of aquatic ecosystems to remain within target water quality conditions (Beck, 1987).

Various models are able to simulate the fate of nutrients within water resources. Chapter 8 showed how QUAL2K, an established in-stream model, could estimate the fate of nutrients as they move downstream. There are other water quality models that can predict the fate of nutrients as they move downstream such as MIKEII (DHI, 1992), ADAPT

(Chung *et al.*, 1992) and WASP5 (Ambrose *et al.*, 1993). These models require certain reaction coefficients to be set so as to accurately simulate the processes responsible for nutrient fate. Usually, these coefficient values are set during the calibration process, where coefficient values are adjusted until observed data are adequately represented by model simulations. However, most models are unsuitable for use in the South African context as there is a lack of observed water quality data with which to accurately calibrate models.

The Department of Water Affairs (DWA) has collected daily historical flow data for rivers in South Africa. However, water quality data collected by DWA is sparse with gaps of up to multiple years between measures for some water quality monitoring points. The range of water quality constituents routinely measured by DWA is in addition limited, especially in terms of nutrient constituents. A model such as QUAL2K requires many water quality constituents measured at a temporal frequency of as frequent as hourly for a modelled section of a stream, which makes it virtually impossible to obtain sensible model estimations from the QUAL2K model using solely DWA historical water quality data. This is why dedicated data collection for a modelling exercise using QUAL2K was performed in Chapter 8. However, it is in the interest of Integrated Water Resources Management (IWRM) to develop models that can utilize the available DWA historical monitoring data to the full extent possible. It may not be feasible, from a cost or time perspective, to collect dedicated field observational data to apply more complex models such as QUAL2K for the management of water resources in South Africa.

In regards to the modelling of eutrophication, the DWA historical monitoring data cannot facilitate the accurate simulation of the uptake of nutrients due to primary production. This is due to chlorophyll-a concentrations not being well represented within the DWA data. However, compared to other water quality constituents, nitrogen species are relatively well represented within the data. As has been mentioned previously in this thesis, nitrogen is a nutrient and is assimilated by flora such as algae, phytoplankton and

macrophytes within water resources. Nitrogen is a non-conservative chemical constituent within water resources, as nitrogen can change chemical form. These chemical forms are particulate and dissolved organic forms as well as the inorganic forms of nitrate, nitrite and ammonium (Khalili and Weyhenmeyer, 2009). The nitrogen species undergo a cycle in water, where nitrogen existing as organic nitrogen is ammonified to ammonium (Chapra, 1997). Ammonium is in turn nitrified to become nitrite, and nitrite is nitrified to become nitrate (Chapra, 1997). This process is well illustrated by Figure 2.1 in Chapter 2. It may be possible to utilize the DWA historical monitoring data to model the processes of ammonification and nitrification. Reaction coefficient values obtained from such a model could be used to calibrate a more complex model such as QUAL2K, so as to more accurately simulate processes that are not possible using solely the DWA data.

The research presented in this chapter outlines a simple mechanistic nutrient model designed to use sparse historical nutrient data, such as that collected by DWA, to predict the fate of nutrients as they move downstream from a designated upstream point. The model is limited to predicting the fate of organic nitrogen, ammonium nitrogen, nitrate and nitrite, due to chemical change. The chemical change modelled is restricted to the decomposition process, and does not consider sediment processes or uptake due to primary production.

This chapter partly addresses Aim 2, in that this research determined whether a relatively simple model can reasonably accurately predict reaction coefficients involved in nitrification and ammonification. Since a major argument for a construction of this model, was to create a model that can utilize the DWA historical monitoring data, this chapter also addresses Aim 4.

7.2 Model description and data

7.2.1 Model description

The model aims to simulate the process of ammonification and nitrification. Ammonification is the transformation of organic nitrogen to ammonia (Chapra, 1997), and is simulated in the model using a first order reaction. Nitrification is the oxidation of ammonia to nitrite and nitrite to nitrate (Chapra, 1997) and is simulated in the model using first order reactions. The process requires three reaction coefficients and can be represented as a series of first order reactions (Chapra, 1997):

$$dN_0 / dt = k_{oa}N_0 \quad (\text{Equation 7.1})$$

$$dN_a / dt = k_{oa}N_0 - k_{ai}N_a \quad (\text{Equation 7.2})$$

$$dN_i / dt = k_{ai}N_a - k_{in}N_i \quad (\text{Equation 7.3})$$

$$dN_n / dt = k_{in}N_i \quad (\text{Equation 7.4})$$

where

N_0 = organic nitrogen, N_a = ammonium nitrogen, N_i = nitrite nitrogen, N_n = nitrate nitrogen and k_{oa} , k_{ai} and k_{in} are reaction coefficients involved in nitrification. Chapra (1997) describes techniques to solve these equations analytically, which have been used in the model.

$$N_0 = N_{00}e^{-k_{oa}t} \quad (\text{Equation 7.5})$$

$$N_a = N_{00}e^{-k_{oi}t} + ((k_{oa}N_{00})/(k_{ai} - k_{oa})) (e^{-k_{oa}t} - e^{-k_{ai}t}) \quad (\text{Equation 7.6})$$

$$N_i = ((k_{ai}N_{oO})/(k_{in} - k_{ai})) (e^{-k_{ait}} - e^{-k_{int}}) + (k_{ai}k_{oa}N_{oO}/(k_{ai} - k_{oa})) \\ (((e^{-k_{oat}} - e^{-k_{int}})/(k_{in} - k_{oa})) - ((e^{-k_{ait}} - e^{-k_{int}})/(k_{in} - k_{ai}))) \quad (\text{Equation 7.7})$$

$$N_n = N_{o0} + N_{a0} - N_{o0}e^{-k_{oat}} - N_{a0}e^{-k_{ait}} - (((k_{oa}N_{oO})/(k_{ai} - k_{oa})) (e^{-k_{oat}} - e^{-k_{ait}})) - \\ ((k_{ai}N_{oO})/(k_{in} - k_{ai}))(e^{-k_{ait}} - e^{-k_{int}}) - ((k_{ai}k_{oa}N_{oO}/(k_{ai} - k_{oa})) \\ (((e^{-k_{oat}} - e^{-k_{int}})/(k_{in} - k_{oa})) - ((e^{-k_{ait}} - e^{-k_{int}})/(k_{in} - k_{ai})))) \quad (\text{Equation 7.8})$$

Where N_{o0} is the initial organic nitrogen concentration in mg.L^{-1} , N_{a0} is the initial ammonium nitrogen concentration in mg.L^{-1} and t is the reaction time in days.

Besides the reaction rates, the analytical equations all require a reaction time to be solved, which is linked to flow as flow pushes water downstream and drives the residence time of water in the modelled system. In addition, the estimation of flow in the system depends on the hydraulic channel characterization used in the model.

The model is implemented in Delphi using a daily time step. Inputs to the model are upstream daily flows and associated organic nitrogen and ammonium values where available. The model steps through the input, and for each daily flow that is greater than zero, a new data encapsulation object within the model, representing a package of water moving downstream, is created. The model calculates the flow velocity, Manning's Roughness and reach depth for each non-zero flow using a simple iterative method. This iterative method uses the Manning Equation (Chapra, 1997) to estimate average flow velocity given flow.

$$R = A_c / P \quad (\text{Equation 7.9})$$

$$U = (1/n) R^{2/3} S_e^{1/2} \quad (\text{Equation 7.10})$$

Where U is velocity in m.sec^{-1} , R is the channel's hydraulic radius in meters, P is wetted perimeter in meters, A_c is the channels cross-sectional area in m^2 , n is the Manning's Roughness coefficient, and S_e is the slope of the channel.

$$\text{Since } Q = A_c U \quad (\text{Equation 7.11})$$

$$Q = (1/n) A_c R^{2/3} S_e^{1/2} \quad (\text{Equation 7.12})$$

Q is flow in $\text{m}^3 \cdot \text{s}^{-1}$. Since the channel shape is assumed to have a trapezoid geometry, the cross sectional area and hydraulic radius can be expressed as a function of depth (Figure 7.1):

$$A_c = (B_0 + sd) d \quad (\text{Equation 7.13})$$

$$P = B_0 + 2d(s^2 + 1)^{1/2} \quad (\text{Equation 7.14})$$

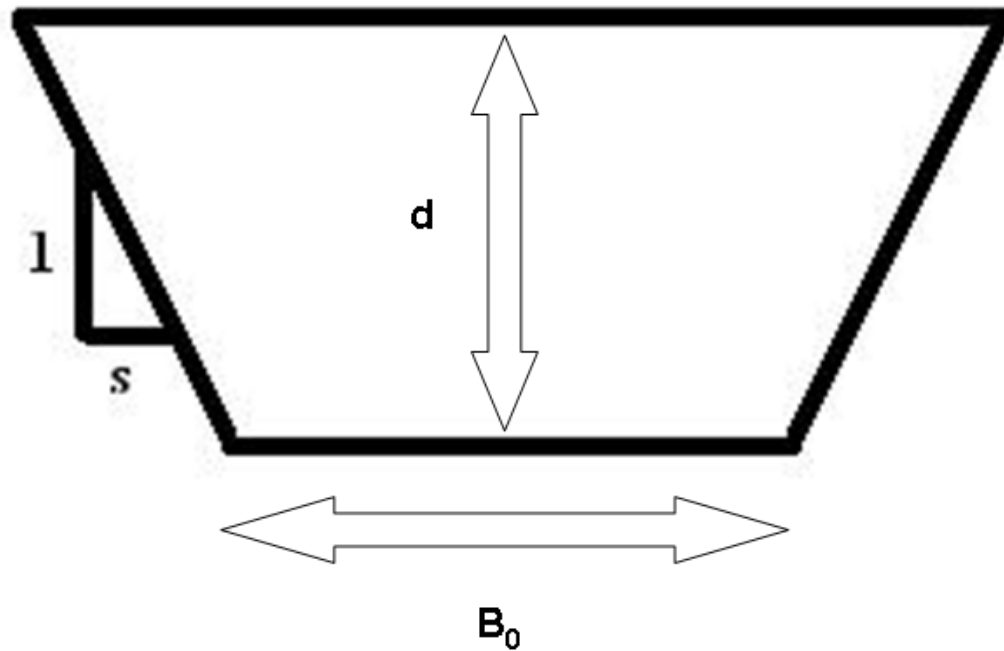


Figure 7.1: The Manning Equation is based on the assumption that a river channel cross sectional shape can be represented by a trapezoidal shape. B_0 represents the bottom width, d represents the depth and s represents the side slope (Chapra, 1997).

And substituting equation 7.13 and 7.14 into 7.12:

$$Q = (1/n) (((B_0 + sd) d)^{5/3} / (B_0 + 2d(s^2 + 1)^{1/2})^{2/3}) S_e^{1/2} \quad (\text{Equation 7.15})$$

Where B_0 is bottom width in meters, s is side slope and d is reach depth in meters. Values of B_0 , s and S_e are set by the user of the model. Equation 7.15 assumes that a river reach has achieved a steady state flow condition, and in addition assumes a trapezoidal channel shape.

The iterative method sets the reach depth d to a maximum reach depth set by the user of the model, and uses Equation 7.15 to calculate flow, which is compared to the actual observed flow, and if the calculated flow is greater than the observed flow, then the method decreases reach depth d by a very small amount (1 mm) with each iteration until the calculated flow is equal to the observed flow. However, with each iteration, the Manning's Roughness coefficient n , and the channel slope S_e are updated to reflect the new reach depth d , as the values of n and S_e are assumed to be dependant on d . The value of n and S_e are updated with a function that mirrors the outcomes of an 'S' shaped graph, where reach depth d would be read as the value of the 'x' axis, and the value on the 'y' axis would be used to update the Manning's Roughness coefficient n , and the channel slope S_e . Once the iterative method obtains a model estimated flow that is equal to the observed flow, the cross sectional area Ac (m^2) is calculated using the estimated value of reach depth d that was calculated through gradual iterative diminishment.

$$Ac = d (B_0 + (sd)) \quad (\text{Equation 7.16})$$

Velocity U ($m.s^{-1}$) is then calculated

$$U = Q / Ac \quad (\text{Equation 7.17})$$

The velocity is used to calculate the distance travelled by the water flowing in the stream in one day, and the following attributes of the packages of water (from now on referred to as RiverPackages) are updated:

1. Package length = the distance travelled by the water in the stream in one day.
2. Start position = 0.
3. End position = the distance travelled by the water in the stream in one day.

If the model finds associated nitrogen data with the flow data, the following attributes in the new RiverPackage are updated, depending on which nitrogen data are recorded:

1. Organic nitrogen.
2. Ammonium nitrogen.

Each time a new RiverPackage data encapsulation object is added to the list, the list of previously added RiverPackages is stepped through (except for the one just added) and the start position and end position of each is updated with the distance travelled by flow on that day. While stepping through the list of RiverPackages, if it is found that the current RiverPackage has nutrient data, then the organic nitrogen, ammonium nitrogen, nitrite nitrogen and nitrate nitrogen attributes are updated by calling the relevant functions that calculate the effect of nitrification and ammonification for one day of residence time. Importantly, even if there were no flow on that particular day, the nitrogen attributes are still updated as the nitrogen species are still undergoing reactions under zero flow. While stepping through the list of RiverPackages, the attributes of the river package found to be positioned at an area of interest (area of reach with a monitoring point with calibration data) are written to an output file. The results can then be matched with available observed data from a monitoring point downstream, and the reaction coefficients involved in nitrification can be adjusted (calibrated) until there is a reasonable fit between the model estimated nitrogen values and the observed nitrogen values. Once acceptable calibration has been achieved, the calibrated model can be

applied to an independent confirmation data set.

Point and diffuse contributions of nutrients in the river reaches investigated in this research would most likely make successful calibration of the model impossible unless they were taken into account. Therefore, the historical DWA monitoring data of the upstream and downstream gauging stations were analyzed for point and diffuse signatures, using the model outlined in Chapter 4, hereafter referred to as the Mechanistic/Statistical Nutrient Model. The Mechanistic/Statistical Nutrient Model estimates point source signatures defined by four parameters:

$$Q_{pmax}, Q_{pmin}, C_{pmax}, C_{pmin}$$

where Q_{pmax} is the maximum point source inflow in $m^3.sec^{-1}$, Q_{pmin} is the minimum point source inflow in $m^3.sec^{-1}$, C_{pmax} is the maximum point source nutrient concentration in $mg.L^{-1}$, and C_{pmin} is the minimum point source nutrient concentration in $mg.L^{-1}$. The Mechanistic/Statistical Nutrient Model in addition provides a diffuse signature which is defined by two parameters A and B, which would define the signature in a power relationship using the following equation:

$$C_{diff} = AQ^B \quad (\text{Equation 7.18})$$

Where C_{diff} is the concentration of nutrients in a river due to diffuse signatures in $mg.L^{-1}$.

The Mechanistic/Statistical Nutrient Model estimation of nutrient inputs to the downstream site will include all accumulated inputs from upstream, whereas an estimation of the inputs between the upstream site and downstream site is required in the present model. Therefore, the estimation of point and diffuse inputs for both the upstream and downstream site was obtained using the Mechanistic/Statistical Nutrient Model. Thereafter, the concentrations in the estimated point and diffuse signatures were converted to a load for each site, and the upstream site load was subtracted from the

downstream site load. The loads were converted back to concentrations, and the point and diffuse signatures for the stretch of modelled river between the upstream and downstream site was calculated using the Mechanistic/Statistical Nutrient Model.

Taking account of the diffuse and point source influences on the modelled data will result in two values for each modelled output, as the point source signature is defined by a maximum and minimum possible point source inflow and nutrient concentration. Therefore, the modelled output of this research (Chapter 7) is defined by a minimum and maximum nutrient concentration, which can then be compared to the observed nutrient concentration at the target downstream site:

$$C_{\text{minsim}} = C_{\text{sim}} + ((Q_{\text{pmin}}C_{\text{pmin}})/Q) + (AQ^B) \quad (\text{Equation 7.19})$$

$$C_{\text{maxsim}} = C_{\text{sim}} + ((Q_{\text{pmax}}C_{\text{pmax}})/Q) + (AQ^B) \quad (\text{Equation 7.20})$$

Where C_{sim} is the output of the nutrient model outlined in this chapter (Chapter 7) in mg.L^{-1} , which only takes account of nitrification and ammonification, Q is the recorded flow at the target downstream site in $\text{m}^3.\text{sec}^{-1}$, C_{minsim} and C_{maxsim} is the minimum and maximum output of the model respectively when point and diffuse source influences on the target downstream monitoring point are taken into account.

Because the point source signature tends to be highly variable at low flows and less variable at higher flows as point source signatures become diluted by natural flow (see Chapter 4), the recorded observed data taken at higher flows are more valuable for calibrating this model as there is less uncertainty. The model output is compared to observed data and nitrification reaction coefficients are manipulated until the best visual fit between the model output and the observed data is obtained.

7.2.2 Model data

The model depends heavily on the availability of organic nitrogen values in historical monitoring data, to be able to predict the value of ammonium and nitrate nitrogen further downstream. Therefore, DWA monitoring sites were investigated for the following attributes when selecting data sets for this research:

1. The modelled river reach had to have two DWA monitoring sites which were not too far away from each other, so as to minimize the impacts of processes not simulated in the model such as uptake of nutrients by flora, and incoming tributaries into the main river channel.
2. The upstream DWA monitoring station would require a continuous flow record, as well as a good water quality record including values of organic nitrogen and ammonia.
3. The downstream DWA monitoring station would require a continuous flow record and a good water quality monitoring record that coincides with the dates of the measures taken at the upstream DWA monitoring point taking into account the residence time of water from the upstream site to the downstream site.
4. Where possible, sites were selected where there were no obvious signs of agriculture or settlements so as to minimize the effect of point or diffuse sources.

Although DWA historical data does not contain measures of organic nitrogen, some data sets contain values of dissolved Kjeldahl nitrogen. Organic nitrogen can be estimated from the values of Kjeldahl nitrogen:

$$[\text{NH}_3\text{-N}] = 10^{(\text{pH} - 9.25)} * [\text{NH}_4^+\text{-N}] \quad (\text{Equation 7.21})$$

$$[\text{N}_{\text{organic}}] = [\text{N}_{\text{Kjeldahl}}] - ([\text{NH}_3\text{-N}] + [\text{NH}_4^+\text{-N}]) \quad (\text{Equation 7.22})$$

Where $[\text{NH}_3\text{-N}]$ is the concentration of ammonia nitrogen, pH is the measured acidity in the river, $[\text{NH}_4^+\text{-N}]$ is the measured concentration of ammonium ion nitrogen, $[\text{N}_{\text{Kjeldahl}}]$ is the measured concentration of dissolved Kjeldahl nitrogen, and $[\text{N}_{\text{organic}}]$ is the calculated concentration of dissolved organic nitrogen.

Suitable data were found for three rivers, namely the Buffalo River, the Crocodile River, and the Orange River, and the attributes of the data are shown in Table 7.1. Figures 7.2 – 7.4 show the land cover attributes of the river reaches modelled in this research. The land cover map of the Buffalo River catchment in the vicinity of the modelled area (Figure 7.2 c) shows that the land cover is dominated by thicket and bushland and unimproved grassland, with a small percentage of cultivated temporary subsistence dryland and some informal settlements. Although there would most likely be some diffuse inputs of nutrients coming into the river in this part of the catchment, one would not expect diffuse impacts to be large. The reach of the river between the DWA monitoring points R2R001

Table 7.1. Attributes of DWA monitoring point data used in a simple nutrient model

River Name	DWA monitoring points			Calibration Data Set		Confirmation Data Set	
	Upstream	Downstream	Distance	From	To	From	To
Buffalo	R2R001	R2H027	23 km	17-May-94	15-Mar-06	NA	NA
Crocodile	X2H017	X2H016	57 km	03-May-94	09-Jul-96	04-Mar-03	04-Dec-07
Orange	DH8004	DH8008	40 km	15-Aug-93	14-Jun-97	24-Jul-97	11-Jul-99

NA - Not Applicable

and R2H027 was chosen. R2R001 measures the outflow and water quality from Laing Dam on the Buffalo River and R2H027 measures flow and water quality approximately 23 km downstream. Due to the paucity of water quality data for these monitoring points, the data were used only to calibrate a nutrient model for the Buffalo River, and no attempt at confirmation was made.

Data from the monitoring points X2H017 and X2H016, approximately 57 km

downstream, were selected from the Crocodile River. The land cover map of the Crocodile River in the vicinity of the modelled area (Figure 7.3 c) shows land cover dominated by forest, and irrigated cultivated land. One could expect significant inputs of nitrogen into the modelled section due to land cover in the modelled area. There is, in addition, a tributary that joins the main stem of the Crocodile River before X2H016. The land cover, as well as the fact that a tributary joins the main stem within the studied area would in most likelihood confound the modelled results. However, since there are very few DWA monitoring sites that measure Kjeldahl nitrogen, it was decided to continue modelling this section of the Crocodile River. Even if land cover in this section of the Crocodile River does cause modelling results to be inaccurate, it will serve to illustrate the limitations of the model.

For the Orange River, data from the monitoring points DH8004 and DH8008, approximately 40 km downstream, were selected. The land cover map of the Orange River in the vicinity of the modelled area (Figure 7.4 c) shows land cover dominated by shrubland, with very little or no evident land cover associated with anthropogenic activities. Unfortunately, only land cover from the South African side of the catchment could be illustrated, as land cover information for the Namibian side is not available. However, it is not likely to be drastically different from the South African side. Google Earth images however, show a strip of cultivated land adjacent to the river reach in some parts of the investigated catchment. There may be diffuse sources of nutrients associated with these cultivated lands, but it is not likely to be extremely large.

Where possible, data sets from chosen DWA monitoring sites were divided into independent calibration and confirmation data sets. It was found that there were very few direct comparisons available between modelled results and measured data for the same date at the monitoring point downstream, so modelled results were compared to measured results that were taken within 1 week (7 days) with the assumption that water quality would not change much within that time period.

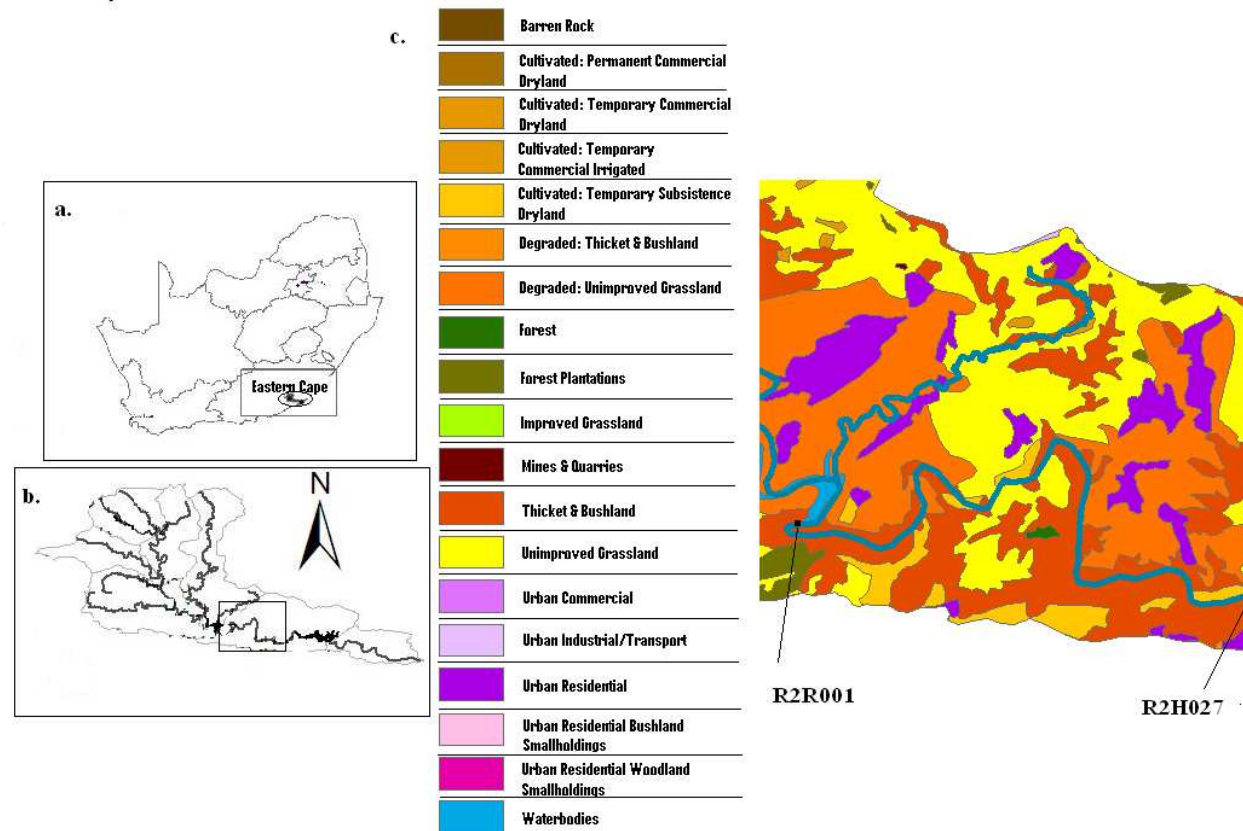


Figure 7.2: a - Position of the Buffalo River catchment within South Africa. b - The catchment of the Buffalo River which lies within the Eastern Cape. c - The land cover categories occurring in the catchment of the Buffalo River in the vicinity of the DWA monitoring points R2R001 and R2H027.

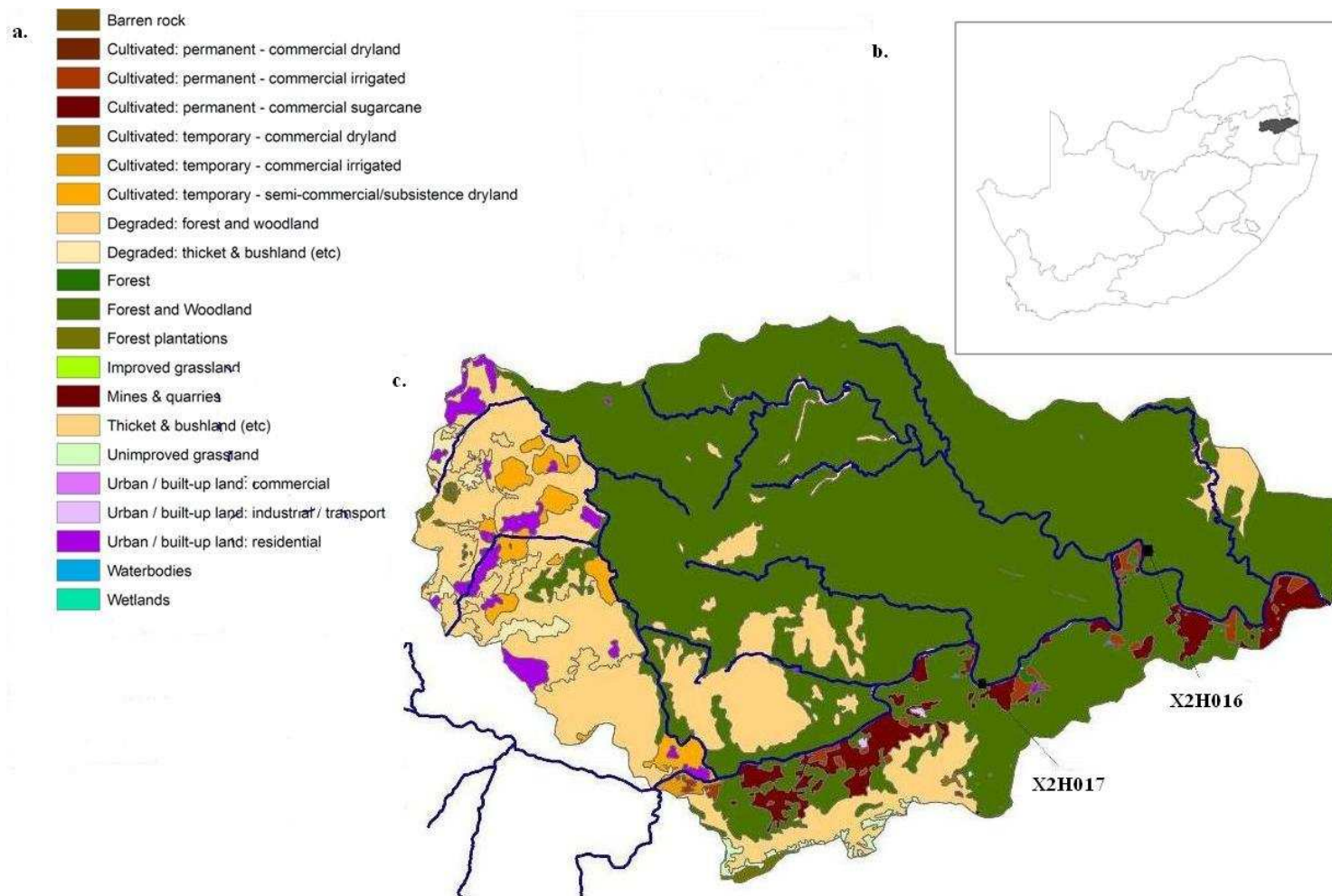


Figure 7.3: a. Relevant land cover categories. b. Position of the Crocodile River catchment within South Africa. c. Land cover of the immediate catchment surrounding the monitoring points X2H017 and X2H016 on the Crocodile River.

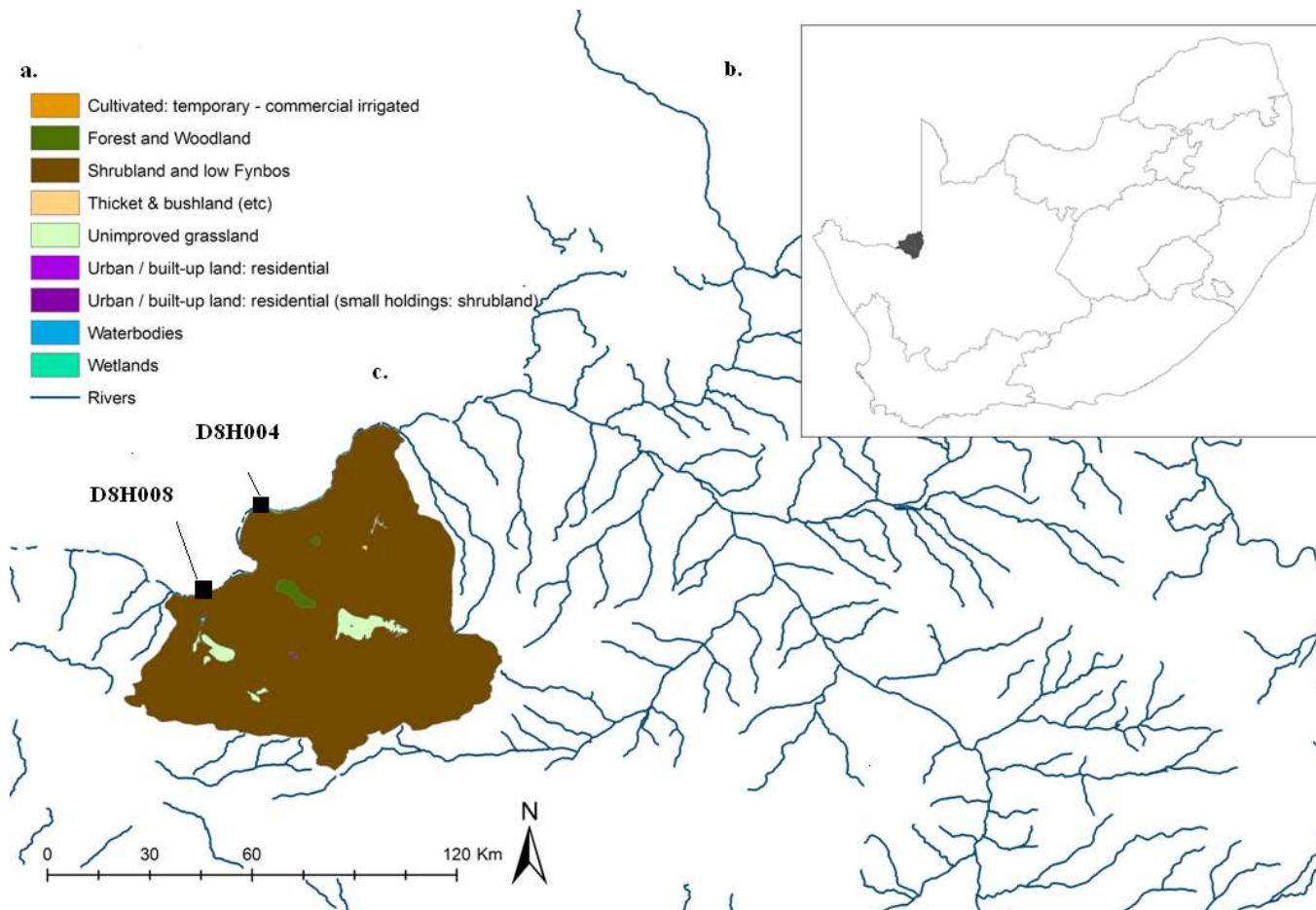


Figure 7.4: a. Relevant land cover categories. b. Position of the modelled segment of the Orange River within South Africa. c. Land cover of the immediate catchment surrounding the monitoring points D8H008 and D8H004 on the Orange River.

This assumption is dependent on the season and the likelihood of high flows between the sample dates. Within the calibration process, simulated maximum and minimum nutrient concentrations, and observed nutrient concentrations were plotted against flow, with reaction coefficients adjusted until a visual assessment determined that an optimal number of observed nutrient concentrations were lying between the minimum and maximum simulated concentrations.

7.3 Results

7.3.1 Model applied to the Buffalo River

Historical water quality data for the upstream site R2R001 and the downstream site R2H027 showed no strong diffuse signatures for NH_4^+ -N (Figure 7.5 a and b). While the upstream site R2R001 shows a diffuse signature for nitrite plus nitrate (Figure 7.5d), the downstream site R2H027 (Figure 7.5 e) shows no diffuse signature for nitrite plus nitrate.

The calculated point and diffuse signatures for the reach between R2R001 and R2H027 are shown in Figure 7.5 c and f, while Table 7.2 lists the values of the parameters characterizing the point and diffuse signatures.

Even with the adjustment to compare model estimated values with measured values taken within 7 days of the same date, only 6 comparisons were possible in total. The reaction coefficients for nitrification were adjusted within the model until the observed results fitted within the model estimated maximum and minimum results (Figure 7.6). The final values for the reaction coefficients chosen were as follow:

$$k_{oa} = 0.70; k_{ai} = 10.00 \text{ and } k_{in} = 6.0.$$

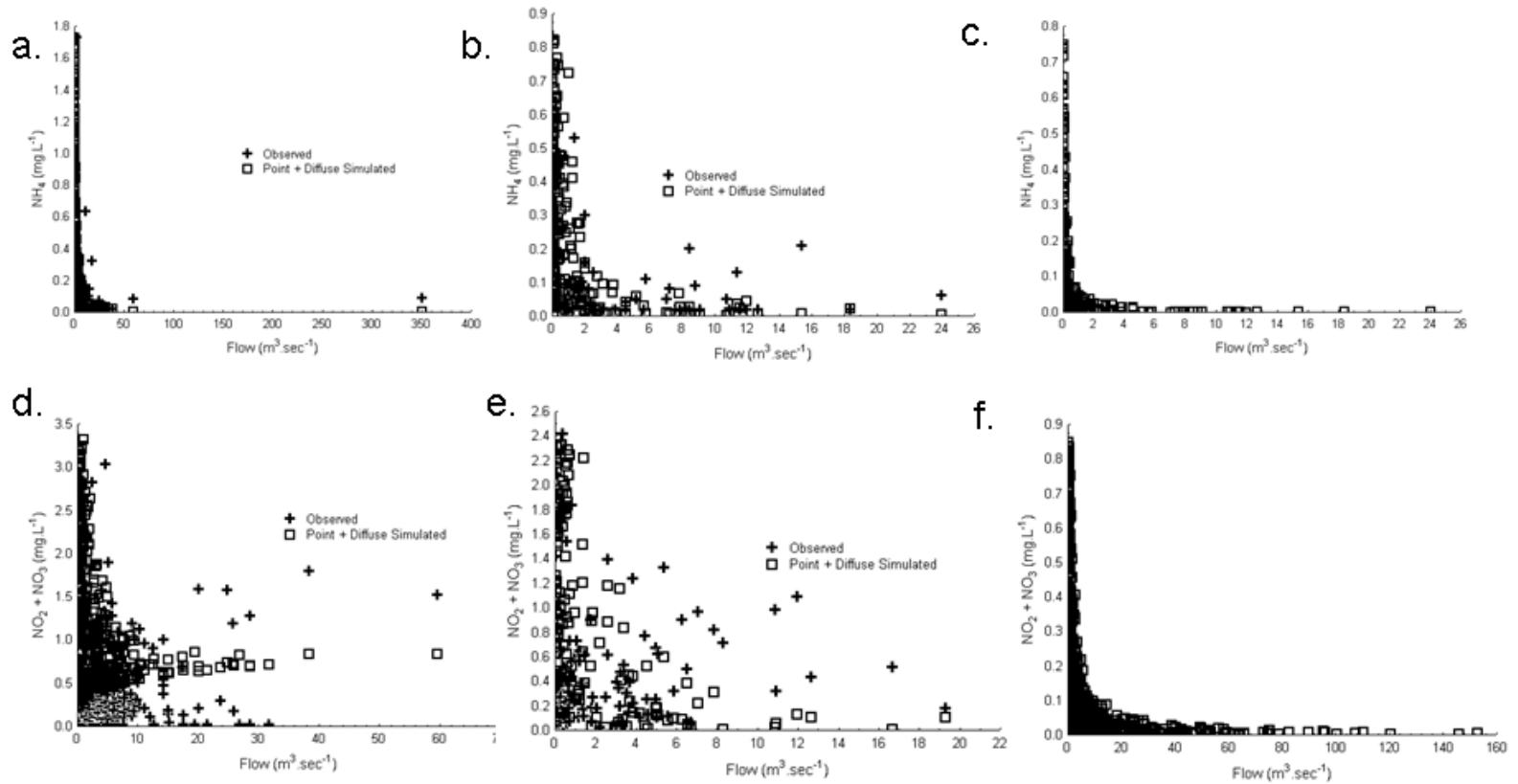


Figure 7.5: Results of the Point - Diffuse Model applied to DWA historical data for the investigated section of the Buffalo River. a and d – R2R001; b and e – R2H027; c and f – model estimated point and diffuse signatures for the reach between R2R001 and R2H027

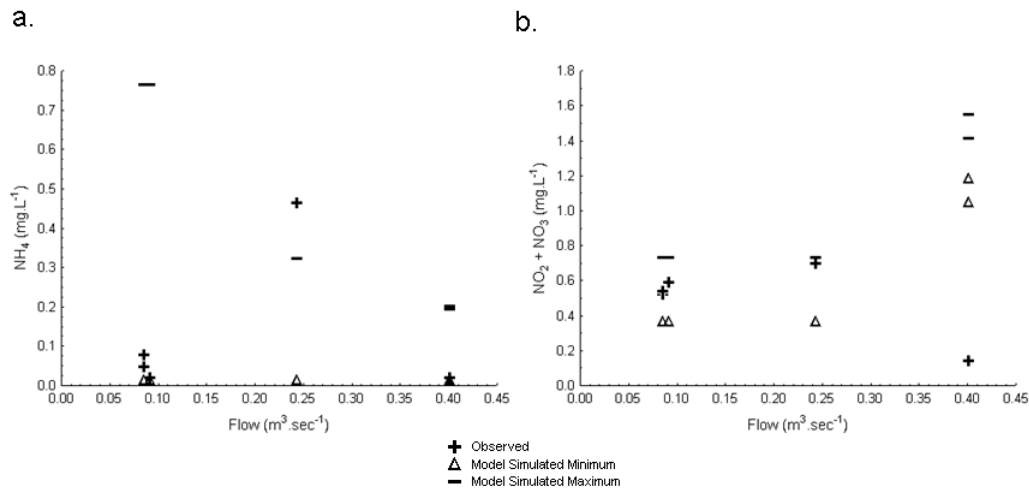


Figure 7.6: Results of the calibration process for the Buffalo River. Flow on the x- axis represents the recorded flow at R2H027. a- observed and model estimated results for ammonium; b- observed and model estimated results for nitrite plus nitrate.

There were not enough observed organic nitrogen (Kjeldahl nitrogen) values within the DWA data to accurately calibrate the model estimated organic nitrogen results. Since DWA gives measured values for nitrite plus nitrate, the model estimated results of nitrite and nitrate were added to compare to measured data. The calibration process showed that the model was very sensitive to k_{oa} and k_{ai} , while the value of k_{in} does not really effect modelled results as the model compares nitrite plus nitrate to measured values.

Unfortunately, only comparisons between model estimated and observed values were possible at relatively low flows, which resulted in a large numerical difference between the maximum and minimum model estimated nutrient values. Even though the observed results fell between the maximum and minimum model estimated results, the lack of observed nutrient measures at high flows only allowed a rough calibration of the model to

take place.

7.3.3 Model applied to the Crocodile River

The Mechanistic/Statistical Nutrient Model applied to the upstream site X2H017 and the downstream site X2H016 both showed a diffuse signature for organic nitrogen (Figure 7.7), however the downstream site diffuse signature (Figure 7.7b) was lower than that of the upstream site signature (Figure 7.7a) and consequently, the characterization of the point and diffuse signatures for the reach between X2H017 and X2H016 included no diffuse signature (Figure 7.7c, Table 7.2). Neither the upstream site nor the downstream site showed evidence of a diffuse ammonium signature (Figure 7.7 d and e), and consequently, no diffuse signature of ammonium was determined for the characterization of the reach between the X2H017 and X2H016. Both the upstream and downstream sites showed a diffuse signature for nitrite plus nitrate (Figure 7.7 g and h), however, since the downstream site (Figure 7.7h) showed a weaker diffuse signature, the characterization of the signatures of the reach between X2H017 and X2H016 included no diffuse signature (Figure 7.7i, Table 7.2).

The DWA monitoring point X2H016 does have some measured values of Kjeldahl nitrogen, so an assessment of the model in terms of organic nitrogen estimation could be performed. A total of 167 comparisons between model estimated values and measured values were possible for all the model estimated nutrients, namely organic nitrogen, ammonium and nitrite plus nitrate. The following parameter values used in the calibration resulted in a good fit for the Crocodile River (Figure 7.8 to 7.10):

$$k_{oa} = 0.01; k_{ai} = 8.00 \text{ and } k_{in} = 6.00.$$

While there was a high numerical difference between maximum and minimum model estimated nutrient concentrations at low flows, observed nutrient concentrations generally

fell between the model estimated maximum and minimum model estimated values. The observed nutrient concentrations were in addition close the model estimated maximum and minimum model estimated values at higher flows, indicating that the reaction coefficients chosen were fairly accurate.

The calibrated model was applied to the confirmation data set. Here 187 comparisons between model estimated results and observed values were possible (Figure 7.11). Unfortunately, all comparisons with observed results were at fairly low flows, resulting in a large numerical difference between the model estimated maximum and minimum values. Therefore, while the calibration process indicated that the chosen reaction coefficients are appropriate to fit the data, the model could not be entirely confirmed because of a lack of data at high flows.

7.3.2 Model applied to the Orange River

Figure 7.12 shows the results of the Mechanistic/Statistical Nutrient Model applied to the DWA historical observed data for the upstream site D8H004 and the downstream site D8H008 while Table 7.2 lists the values of the parameters characterizing the signatures. There was some evidence of a diffuse signature for organic nitrogen for both the upstream and downstream sites (Figure 7.12 a and b), however the downstream site diffuse signature was weaker than the upstream diffuse signature, and subsequently the characterization of the reach between D8H004 and D8H008 included no diffuse signature of organic nitrogen (Figure 7.12c).

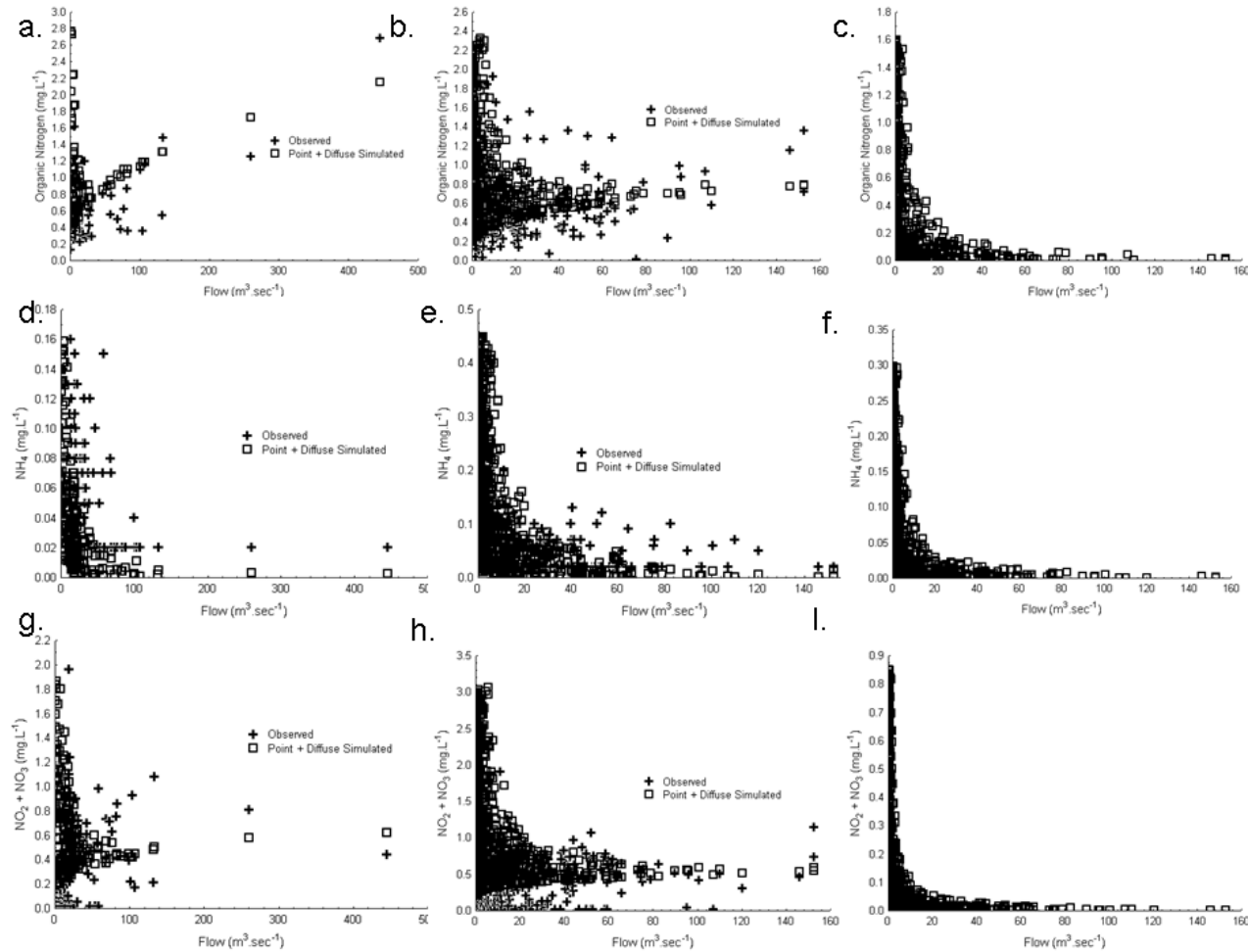


Figure 7.7: Results of the Point - Diffuse Model applied to DWA data for the investigated section of the Crocodile River. a, d and g – X2H017; b, e and h – X2H016; c, f and i – model estimated point and diffuse signatures for the reach between X2H017 and X2H016.

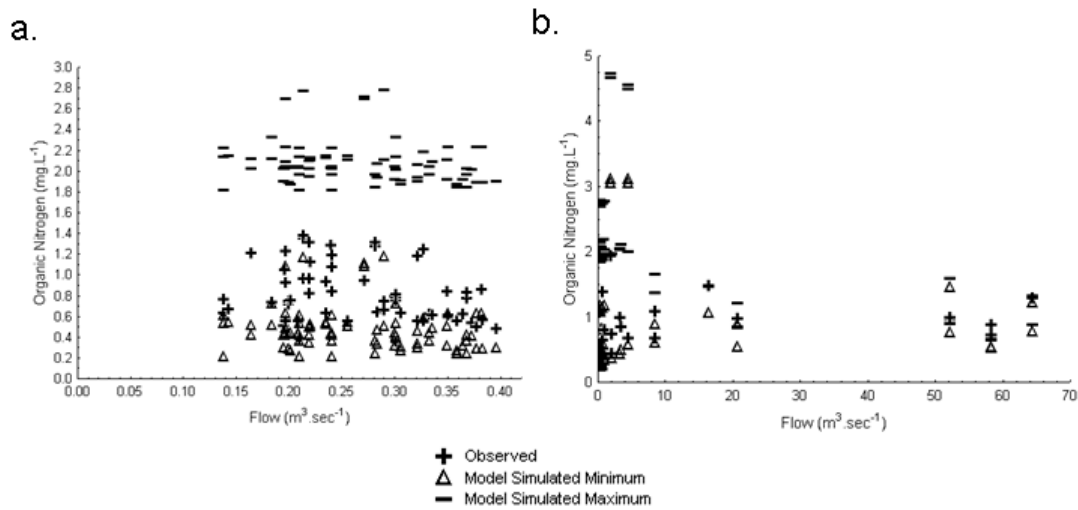


Figure 7.8: Results of the calibration process for the Crocodile River for Organic Nitrogen. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for observed flow up to 0.4 m³.sec⁻¹; b- model estimated results for observed flow greater than 0.4 m³.sec⁻¹.

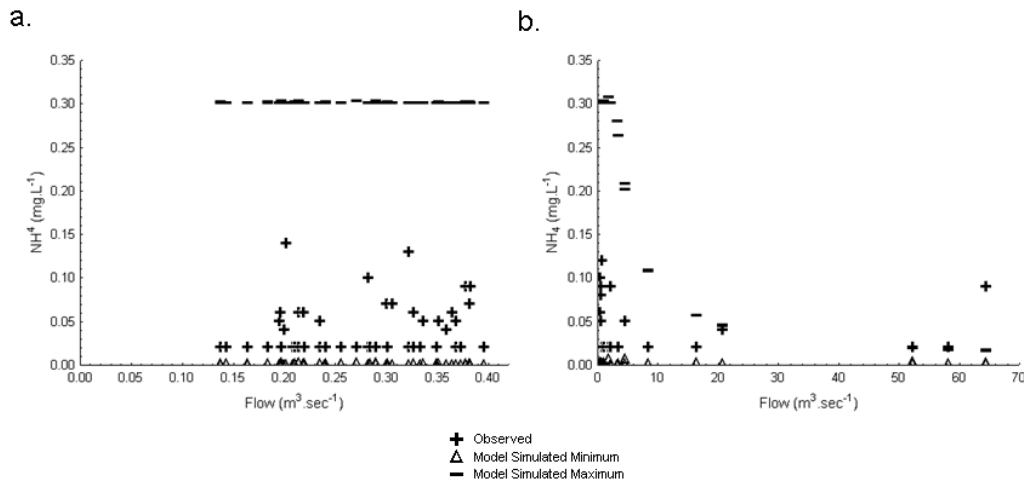


Figure 7.9: Results of the calibration process for the Crocodile River for ammonium. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for ammonium for observed flow up to 0.4 m³.sec⁻¹; b- model estimated results for ammonium for observed flow greater than 0.4 m³.sec⁻¹.

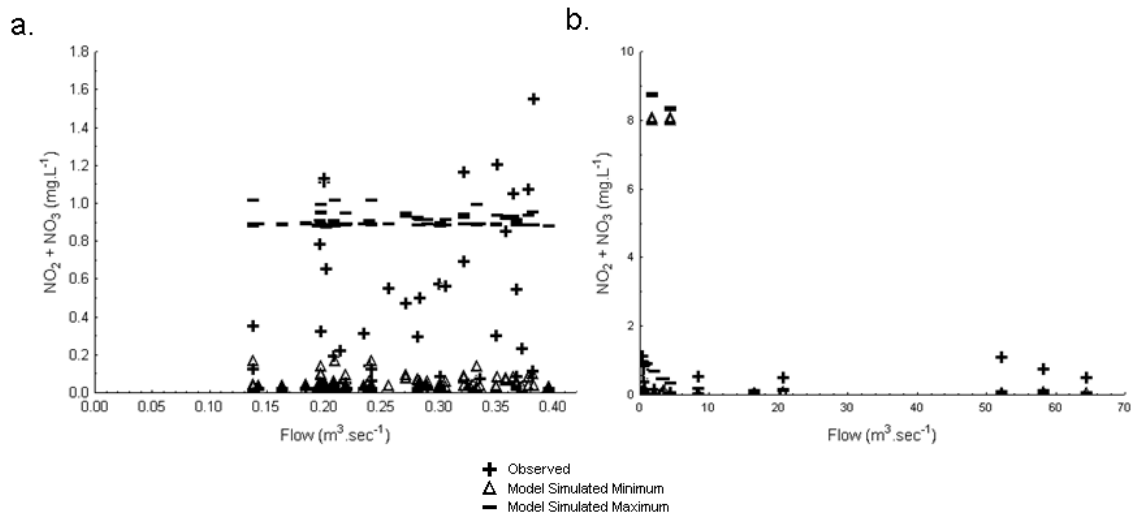


Figure 7.10: Results of the calibration process for the Crocodile River for nitrite plus nitrate. Flow on the x- axis represents the recorded flow at X2H016. a- model estimated results for nitrite plus nitrate for observed flow up to $0.4 \text{ m}^3.\text{sec}^{-1}$; b- model estimated results for nitrite plus nitrate for observed flow greater than $0.4 \text{ m}^3.\text{sec}^{-1}$.

There was a no diffuse signature for ammonium for the upstream site (Figure 7.12d), while the downstream site had a weak diffuse signature (Figure 7.12e), therefore, the characterization of the reach between D8H004 and D8H008 included a weak diffuse signature (Figure 7.12f, Table 7.2). While both the downstream and upstream site had a diffuse signature for nitrite plus nitrate (Figure 7.12 g and h), the downstream site D8H008 had a stronger diffuse signature and therefore, the characterization of the reach between D8H004 and D8H008 for nitrite plus nitrate included a diffuse signature (Figure 7.12 i, Table 7.2).

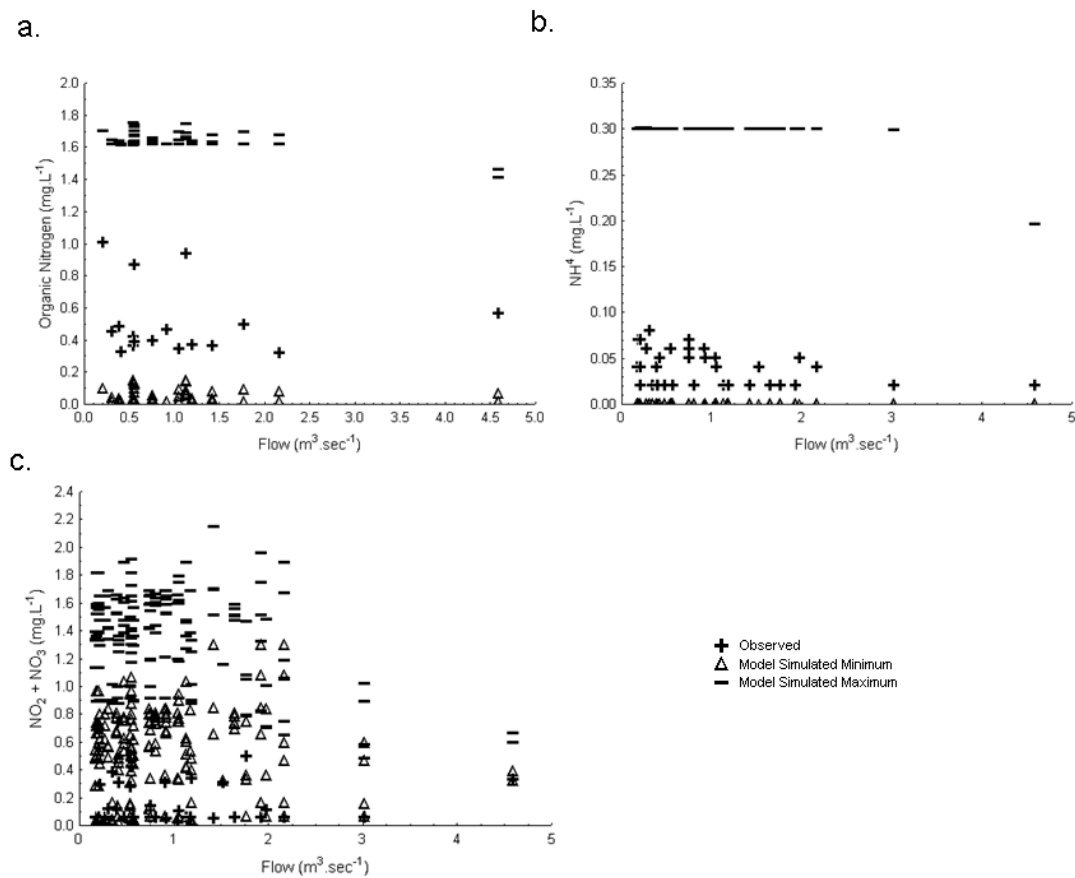


Figure 7.11: Results of the confirmation process for the Crocodile River. Flow on the x-axis represents the recorded flow at X2H016. a- observed and model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.

Since the DWA monitoring site data for D8H008 contained no measured values of Kjeldahl nitrogen within the model calibration or verification data sets, no assessment of the model in terms of organic nitrogen estimation could be done. However, approximately 140 comparisons were possible for calibrating the model in terms of both model estimated ammonium and nitrite plus nitrate. The parameter values chosen for the Crocodile River were found to be appropriate for the Orange River:

$k_{oa} = 0.01$; $k_{ai} = 8.00$ and $k_{in} = 6.00$.

Figure 7.13 shows the results of the calibration process. Observed ammonium values were relatively low in the downstream site, and a high k_{ai} was chosen to bring model estimated ammonium values down to measured levels. The estimated model data generally showed the same pattern as the observed data, indicating that some degree of successful calibration of the model had taken place.

The model with the calibrated nitrification reaction coefficients was applied to the confirmation data set. 193 comparisons between model estimated and observed values were possible. Figure 7.14 shows the results of the confirmation process. Generally, model fit was similar to that obtained in the calibration process indicating that some degree of successful calibration had occurred.

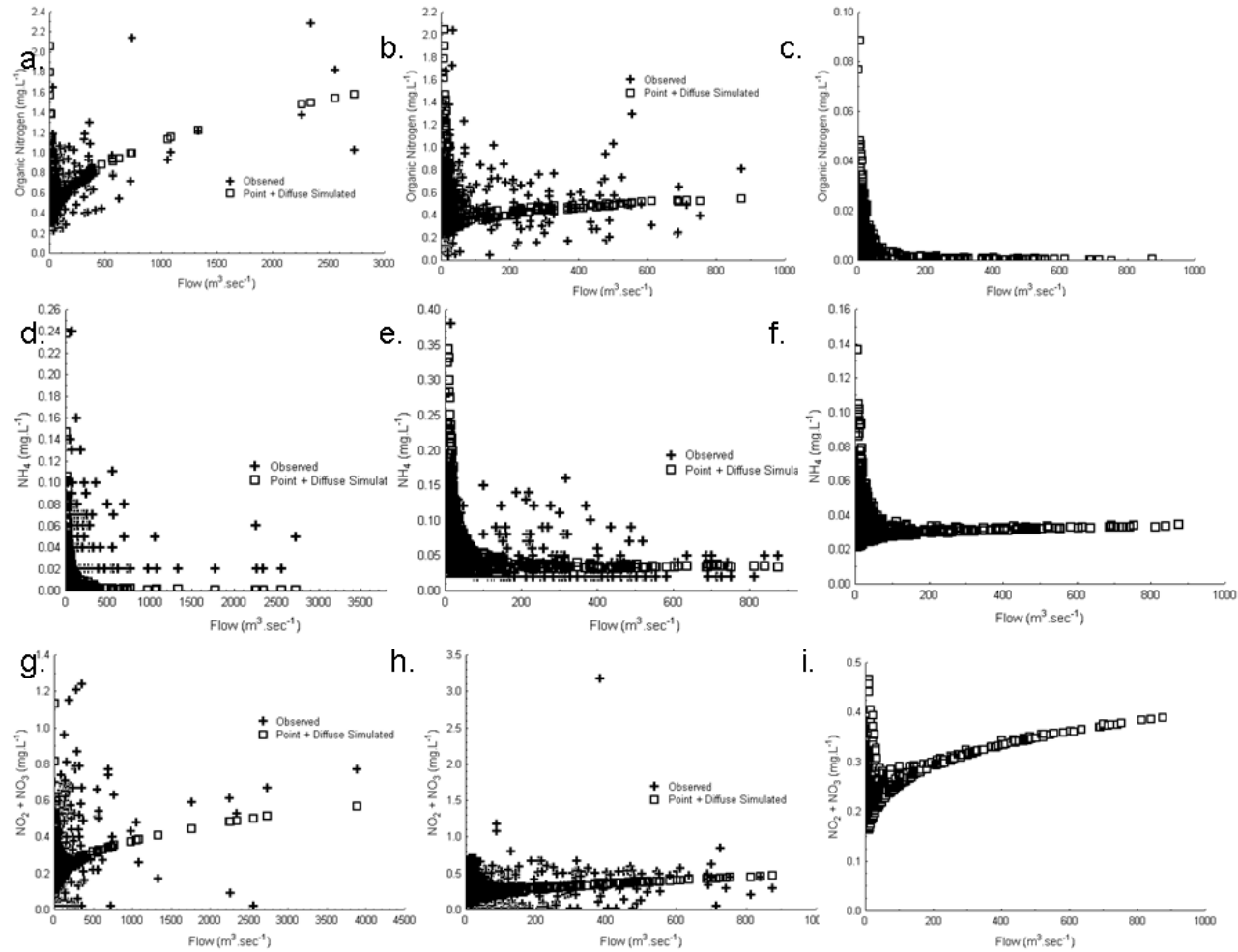


Figure 7.12: Results of the Point - Diffuse Model applied to DWA data for the investigated section of the Orange River. a, d and g – D8H004; b, e and h – D8H008; c, f and i – model estimated point and diffuse signatures for the reach between D8H004 and D8H008.

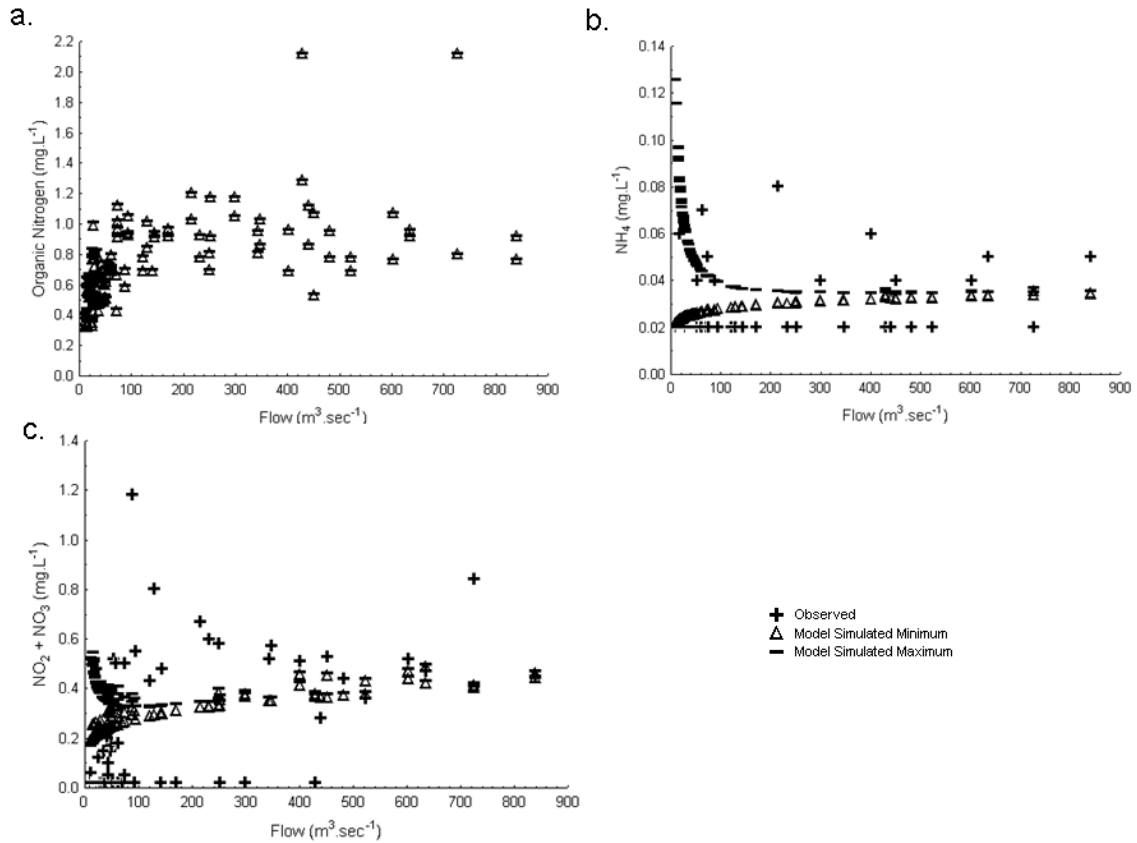


Figure 7.13: Results of the calibration process for the Orange River. Flow on the x- axis represents the recorded flow at D8H008. a- model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.

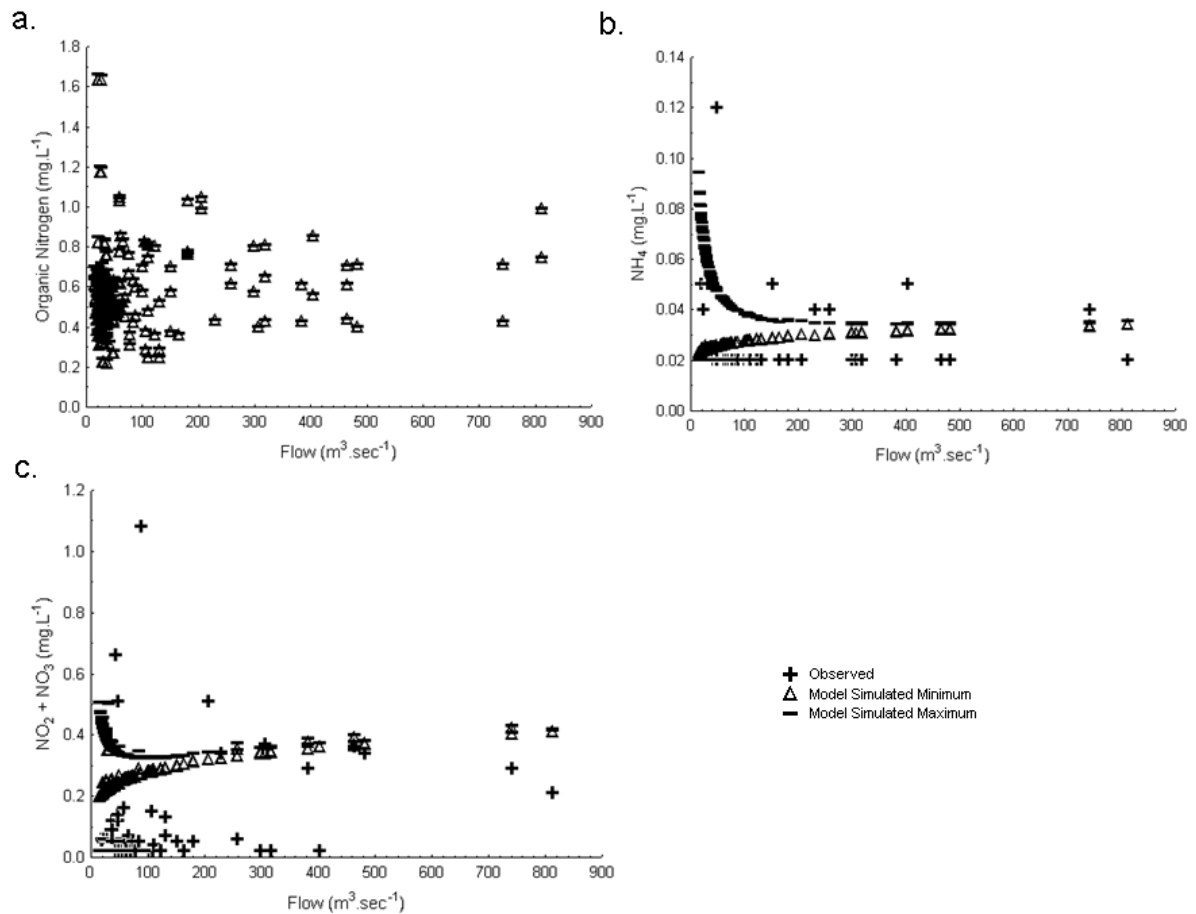


Figure 7.14: Results of the confirmation process for the Orange River. Flow on the x-axis represents the recorded flow at D8H008. a- model estimated results for organic nitrogen; b- observed and model estimated results for ammonium; c- observed and model estimated results for nitrite plus nitrate.

Figure 7.15 shows how the modelled processes of ammonification led to a decrease in concentration of nutrients with increased residence time. The values shown in Figure 7.15 are taken from the Crocodile River calibration model, and model estimated values with residence time show the results of ammonification and nitrification without considering diffuse or point source inputs. Figure 7.15 illustrates that the model is adjusting initial

nutrient values measured upstream, by simulating the nutrient cycle process, so that initial values of organic nitrogen and ammonium measured upstream decrease with travel time as they move downstream.

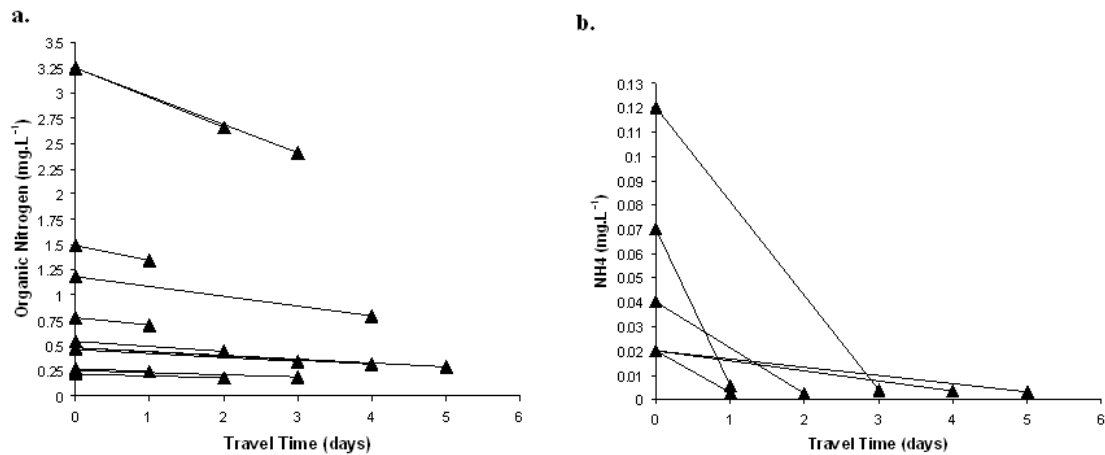


Figure 7.15: Examples taken from the Crocodile River calibration model showing how ammonification and nitrification leads to a decrease in model estimated organic nitrogen and ammonium respectively with residence time from the upstream site.

Table 7.3 is a summary of parameter values obtained in calibration of the models applied to all three rivers investigated.

Table 7.2: Parameters characterizing point and diffuse inputs in the studied regions as estimated by the Mechanistic/Statistical Nutrient Model.

River	Site	Nutrient	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
Buffalo	R2R001	NH_4^+-N	1.000	0.001	1.730	0.000	0.000	0.000
Buffalo	R2H027	NH_4^+-N	1.000	0.002	0.830	0.020	0.000	0.000
Buffalo	Modelled reach	NH_4^+-N	0.100	0.002	0.750	0.000	0.000	0.000
Buffalo	R2R001	$NO_2^- -N + NO_3^- -N$	2.000	0.001	3.027	0.000	0.291	0.256
Buffalo	R2H027	$NO_2^- -N + NO_3^- -N$	3.200	0.010	2.410	0.020	0.000	0.000
Buffalo	Modelled reach	$NO_2^- -N + NO_3^- -N$	2.500	0.010	0.360	0.000	0.000	0.000
Crocodile	X2H017	Organic Nitrogen	5.000	0.596	2.680	0.120	0.152	0.435
Crocodile	X2H016	Organic Nitrogen	7.000	0.105	2.070	0.017	0.184	0.285
Crocodile	Modelled reach	Organic Nitrogen	4.000	0.105	1.600	0.000	0.000	0.000
Crocodile	X2H017	NH_4^+-N	10.000	0.600	0.160	0.020	0.184	0.285
Crocodile	X2H016	NH_4^+-N	7.000	0.105	0.450	0.020	0.184	0.285
Crocodile	Modelled reach	NH_4^+-N	3.000	0.105	0.300	0.000	0.000	0.000
Crocodile	X2H017	$NO_2^- -N + NO_3^- -N$	10.000	0.410	1.960	0.020	0.113	0.279
Crocodile	X2H016	$NO_2^- -N + NO_3^- -N$	7.000	0.105	2.820	0.020	0.210	0.177
Crocodile	Modelled reach	$NO_2^- -N + NO_3^- -N$	1.500	0.105	0.850	0.000	0.000	0.000
Orange	D8H004	Organic Nitrogen	10.000	1.000	2.280	0.220	0.098	0.351
Orange	D8H008	Organic Nitrogen	10.000	1.940	2.030	0.040	0.119	0.224
Orange	Modelled reach	Organic Nitrogen	6.000	2.000	0.100	0.000	0.000	0.000
Orange	D8H004	NH_4^+-N	10.000	1.000	0.240	0.020	0.098	0.351
Orange	D8H008	NH_4^+-N	10.000	1.940	0.380	0.020	0.017	0.104
Orange	Modelled reach	NH_4^+-N	9.000	1.940	0.120	0.000	0.017	0.100
Orange	D8H004	$NO_2^- -N + NO_3^- -N$	10.000	1.000	1.240	0.020	0.044	0.310
Orange	D8H008	$NO_2^- -N + NO_3^- -N$	15.000	1.940	0.600	0.020	0.034	0.383
Orange	Modelled reach	$NO_2^- -N + NO_3^- -N$	14.000	0.500	0.330	0.000	0.100	0.200

Table 7.3. Summary of values for calibrated parameters used in the nutrient model to simulate ammonification and nitrification processes.

River Name	k_{oa}	k_{ai}	k_{in}	Max depth(m)	Min slope	Max slope	Min n	Max n	Bottom width(m)
Buffalo	0.70	10.00	6.00	1	0.002	0.02	0.04	0.2	5
Orange	0.01	8.00	6.00	10	0.002	0.02	0.04	0.2	100
Crocodile	0.01	8.00	6.00	5	0.002	0.02	0.04	0.2	50

7.4 Discussion

The results of this research show that the model could be roughly calibrated to the data from the Buffalo River, although due to a lack of data, the calibration results are presented tentatively (Figure 7.6). Confirmation of the calibrated parameters was not possible due to the paucity of observed water quality data. In addition, because comparisons between model estimated and observed values could only be made at low flows, there was a large numerical difference between the higher and lower model estimations.

The Mechanistic/Statistical Nutrient Model did not pick up significant diffuse sources of organic nitrogen, ammonium and nitrite plus nitrate in the investigated reach of the Crocodile River, while point sources resulted in high variability of organic nitrogen, ammonium and nitrite plus nitrate at low flows (Figure 7.7). While the calibration process was fairly successful (Figures 7.8 – 7.10), the observed values for all three nutrients in the confirmation process were however taken at low flows, and the model estimates all had a large numerical difference between the minimum and maximum model estimated values (Figure 7.11). The observed values generally fell between the minimum and maximum model estimated values for organic nitrogen, ammonium and nitrite plus

nitrate in the confirmation process.

The application of the Mechanistic/Statistical Nutrient Model to the Orange River so as to determine the point and diffuse signatures may not be entirely appropriate, as the Orange River is a comparatively large system where many other processes may confuse the results. However, the point and diffuse signatures in these data were nevertheless estimated, and showed that there is diffuse input of ammonium and nitrite plus nitrate within the studied section of the river (Figure 7.12). The model could be successfully calibrated to ammonium and nitrite plus nitrate (Figure 7.13), while the confirmation model in addition fitted the data fairly well (Figure 7.14). The same reaction coefficients chosen for the Crocodile River resulted in a fairly good model fit in the calibration process for the Orange River. There were no observed organic nitrogen values against which the model estimated values could be gauged. The fit of the model for the confirmation process indicated that the reaction coefficients chosen in the calibration process were fairly appropriate.

As was stated earlier in this chapter, sites on investigated river reaches were chosen to not be too far from each other, so as to minimize the input of nutrients into the studied region due to point and diffuse sources, as well as tributaries, and also to minimize the effect of primary production on nutrient concentrations. However, this is also disadvantageous to the model, as only relatively low flows would allow residence time of water within the studied region to be greater than a day. This is why the model often only could make comparisons between simulated nutrient concentrations and observed nutrient concentrations at low flows. The low flow comparisons between simulated and observed nutrient values were sub-optimal as there is usually a large disparity between the maximum and minimum simulated nutrient values because of the nature of the simulated point source signature in the Mechanistic/Statistical Nutrient Model. Possibly, future research could use the same model to investigate nutrient fate between gauging stations that are further apart.

The nitrification and ammonification rate coefficients calculated in this study compare well to those calculated in other studies using other water quality models such as QUAL2E. Bowie *et al.* (1985), in a review of rates used in water quality modeling, list previously used k_{oa} values to be in the range of 0.001 to 0.14, while previously used k_{ai} values are in the range of 0.003 to 3.00 and previously used k_{in} values are in the range of 0.09 to 10.0. The k_{ai} values used in this research (Chapter 7) ranged from 8 to 10.00. This is higher than is listed in the range given by Bowie *et al.* (1985), but compares well with the values chosen in the calibration of QUAL2K applied to the Buffalo and the Bloukrans, where the k_{ai} values chosen were 7 and 5 respectively (see Chapter 8). Study of historical DWA monitoring data, the research done in this chapter (Chapter 7), as well as the field data collected for the Buffalo and the Bloukrans listed in Chapter 8, shows that generally, ammonium has a very low residence time in the water column within South African rivers. Therefore, the high values of k_{ai} chosen for the modelling exercises are appropriate. The Simple Nutrient Model used in this chapter (Chapter 7) is sensitive to the k_{oa} and k_{ai} reaction coefficients, but not to k_{in} , as model estimated values of nitrite and nitrate are added to compare to measured results. This is why values of 6.0 were used for k_{in} in all model runs investigated, and this value is rather arbitrary in this respect, but within the range of values used in other research. If observed values of both nitrite and nitrate were available, then the model could theoretically be sensitive to the k_{in} reaction coefficient. It must be mentioned that the application, and confirmation of the model shown here (Chapter 7), is limited by lack of historical observed data. However, the model demonstrates that it is possible to use existing DWA water quality and flow data to obtain an indication of nutrient fate due to nitrification. The model may in addition be useful in obtaining an idea of the reaction coefficient values to use in a more comprehensive model such as QUAL2K. Malan and Day (2002a) attempted to apply QUAL2E to South African data, but got very poor results from the model for most water quality constituents investigated, especially when confirming/validating the model, which they partly attributed to a lack of calibration data with which to accurately calibrate the

model. The main motivation for the development of model presented here (Chapter 7), was to derive a model that could predict nutrient fate, using DWA historical monitoring data in the most optimal way possible. This is in the interest of water resource management, as usually resources are not available to collect dedicated observed data of high temporal and spatial frequency that comprehensive models such as QUAL2K require. The implementation of Integrated Water Resources Management (IWRM) policies is held back by the lack of data, both observed and simulated, to represent processes occurring within water resources (Biswas, 2008). This model is an initial method of deriving information on nutrient fate where there is a paucity of observed data, and may provide accurate estimations of rate coefficients involved in nutrient fate, for use in more comprehensive models. I am not aware of any other model that can use sparse historical monitoring data to simulate nitrification in the same way that the Simple Nutrient Model does.

This research demonstrates that DWA data that contain measures of Kjeldahl nitrogen are useful for water quality modelling. Unfortunately, there are very few DWA monitoring points that include measures of Kjeldahl nitrogen in their historical water quality data. Therefore, DWA should be encouraged to include values of Kjeldahl nitrogen into their monitoring regime of river water quality where possible.

This chapter addresses Aim 2, and proves, as with many of the previous chapters, that relatively simple models can reasonably accurately represent limited but important processes within rivers that affect water quality. Since this model uses solely DWA historical monitoring data, this model addresses Aim 4 and re-inforces the idea that this type of data, although limited, can be of great use in modelling the relationship between flow and water quality.

Chapter 8: Application of QUAL2K to the Buffalo River and Bloukrans River

8.1 Introduction

Eutrophication of rivers due to domestic and industrial effluent release has become a major water quality problem in South Africa (Walmsley *et al.*, 1999). During low flow conditions, point sources from waste water treatment works (WWTWs) and other point sources of nutrients have a far greater impact on the water quality of rivers than diffuse sources. An in-stream nutrient model can be used to estimate the effect of point source effluent release on downstream water quality, provided that point sources can be indentified and the quality of the effluent adequately monitored. It has generally been found that water quality models struggle to simulate the effect of diffuse sources on downstream water quality as data such as temporal frequency of diffuse input, and loading from diffuse inputs, are lacking.

Flow controls the residence time of nutrients within a river, and natural flow in addition acts to dilute pollutants within a river. In-stream models that predict the fate of nutrients, taking into account the effect of flow therefore, explicitly model the link between flow and water quality. An example of a model that does this is QUAL2E/QUAL2K.

QUAL2E has been used worldwide (Shanahan *et al.*, 1998), and with some success in South Africa (Venter *et al.*, 1997; Malan and Day, 2002a) to estimate the transport and fate of nutrients and water quality variables. QUAL2E has been used in at least one modelling study within South Africa by consultants, where the report on the results is not freely available. QUAL2E is an in-stream model that operates at a time step of less than 1 day as the model simulates diurnal water quality kinetics (Wimberly and Coleman, 2005). QUAL2E assumes a steady state flow, and represents a river as a 1- dimensional channel

(Pelletier *et al.*, 2006) and requires model parameters to be calibrated so as to obtain the best fit between estimated and observed data. QUAL2K is a modernized version of QUAL2E which includes all the functionality of QUAL2E, but in addition simulates bottom algae, and the fluxes of nutrients and oxygen between the sediment and water column (Pelletier *et al.*, 2006). QUAL2K is implemented in Excel and programmed in Visual Basic (Pelletier *et al.*, 2006).

QUAL2E and QUAL2K are in-stream water quality models designed specifically to simulate water quality in rivers and streams. While QUAL2E has been widely used, a search of the literature reveals that very few studies have utilized QUAL2K to simulate water quality in rivers. Fan *et al.* (2009) used QUAL2K in combination with another model to simulate BOD in a river in Taiwan. The lack of studies in the literature that have applied QUAL2K to rivers could be due to the fact that QUAL2K is a fairly new model, and either studies utilizing the model have not been published yet, or there is some reluctance to move away from more established models such as QUAL2E.

The aim of this research is to determine whether QUAL2K can accurately simulate the effect of point nutrient sources on downstream river water quality. Water quality and flow data from point sources and upstream in-river monitoring points are used to predict downstream in-river water quality in a section of the Buffalo River, Eastern Cape, South Africa, near the city of East London. In addition, QUAL2K was applied to the Bloukrans Stream as it leaves the city of Grahamstown in the Eastern Cape, South Africa. For this exercise, the model was used to predict the fate of nutrients and DO along the modelled river reaches.

Since the QUAL2K model is relatively complex, this chapter does not attempt to address Aim 2. However, this chapter can indicate whether accurate simulations of in-stream – nutrient concentrations can be obtained if diffuse inputs of nutrients are ignored, and in what kind of situations this can be done. Therefore, this chapter attempts to address Aim 3.

8.2 Sites, Data and Model

8.2.1 Sites

In this study, sections of the Buffalo River, and the Bloukrans River were chosen for water quality modelling. The catchments of both the Buffalo River, and the Bloukrans River occur in the Eastern Cape province of South Africa (Figure 8.1).



Figure 8.1: Map showing South Africa, with the Bloukrans River catchment outlined near Port Elizabeth, and the Buffalo River catchment outlined near East London.

8.2.1.1 The Buffalo River

The Buffalo River is situated in the Eastern Cape, South Africa (Figure 8.2). O’Keeffe *et*

al. (1996) have given a good description of the river and geology of the catchment. The Buffalo River is a relatively short river of about 125 km, starting from its source in the Amatola Mountains and then flowing south east through King Williams Town and entering the sea at East London. Rainfall in the Buffalo catchment ranges from 1500 mm.y⁻¹ in the upper catchment, to 500 mm.y⁻¹ in the middle reaches to about 700 mm.y⁻¹ at the coastal zone (DWA, 1986; O’Keeffe *et al.*, 1996). Most of the rainfall occurs in summer (O’Keeffe *et al.*, 1996), although the catchment of the middle and lower reaches occur in a year- round rainfall region DWA (1986). Marine sediment occurs within the catchment which accounts for about 65% of the salt in the river while soils within the catchment are either grey sandy loam or red and black clays (O’Keeffe *et al.*, 1996). While the river in the upper catchment at the source flows permanently, often the river is reduced to a trickle after Rooikrans Dam (Figure 8.2). The upper reaches below Rooikrans Dam support intensive agriculture and livestock farming while the middle reaches of the river flow through King Williams Town, in which intense industrial activities take place and dense urban development occurs (O’Keeffe *et al.*, 1996). Effluent return flow through this stretch increases the flow substantially. The river enters Laing Dam just after this stretch, often leading to the dam being very eutrophic and saline. Although further pollution occurs in the lower reaches, such as effluent return flow in the Mdantsane region, areas of ecological importance in addition occur downstream in the lower reaches, such as coastal forest and the estuary (O’Keeffe *et al.*, 1996).

This research studied the middle reaches of the Buffalo River, through King Williams Town (Table 8.1). This research restricted the study area to this stretch of the Buffalo River for the following reasons:

1. The stretch of river studied occurs between two Department of Water Affairs (DWA) flow and water quality monitoring points. When deciding on a stretch of river to model, the availability of some historical flow and water quality data made this stretch of the river an attractive choice.

2. There is usually some flow in this stretch of the river, from the upstream site which is reduced to a trickle in low flow, to the downstream sites where flow becomes progressively stronger because of sewage return flow.
3. This stretch of the river is dominated by 3 identified and well known point sources, and all 3 point sources are accessible for field measures.
4. The Buffalo River after the last site studied flows into the Laing Dam. QUAL2K is an in – stream water quality model for rivers and streams, and an addition of an impoundment to the studied river stretch would have complicated the modelling exercise.
5. The stretch of the Buffalo River studied is short enough so that day length sampling field trips are sufficient to sample all the sites.

The water quality of the upstream site is relatively clean compared to the downstream sites, but the water quality of the Buffalo River running into King William's Town is still impacted by activities upstream such as informal settlements and livestock. The QUAL2K model takes account of the headwater site water quality (in this case site1) and the water quality downstream is simulated with the model taking into account point source impacts.

Three sites on this section of the Buffalo River, as well as three identified point sources were chosen for flow and water quality measures (Figure 8.2). From upstream to downstream, the first site (site 1) chosen was the Department of Water Affairs (DWA) flow gauging weir R2H005, upstream on the outskirts of King William's Town. Approximately 3.5 km downstream, water samples of final effluent were taken from the King William's Town waste water treatment works (WWTW) (site2).

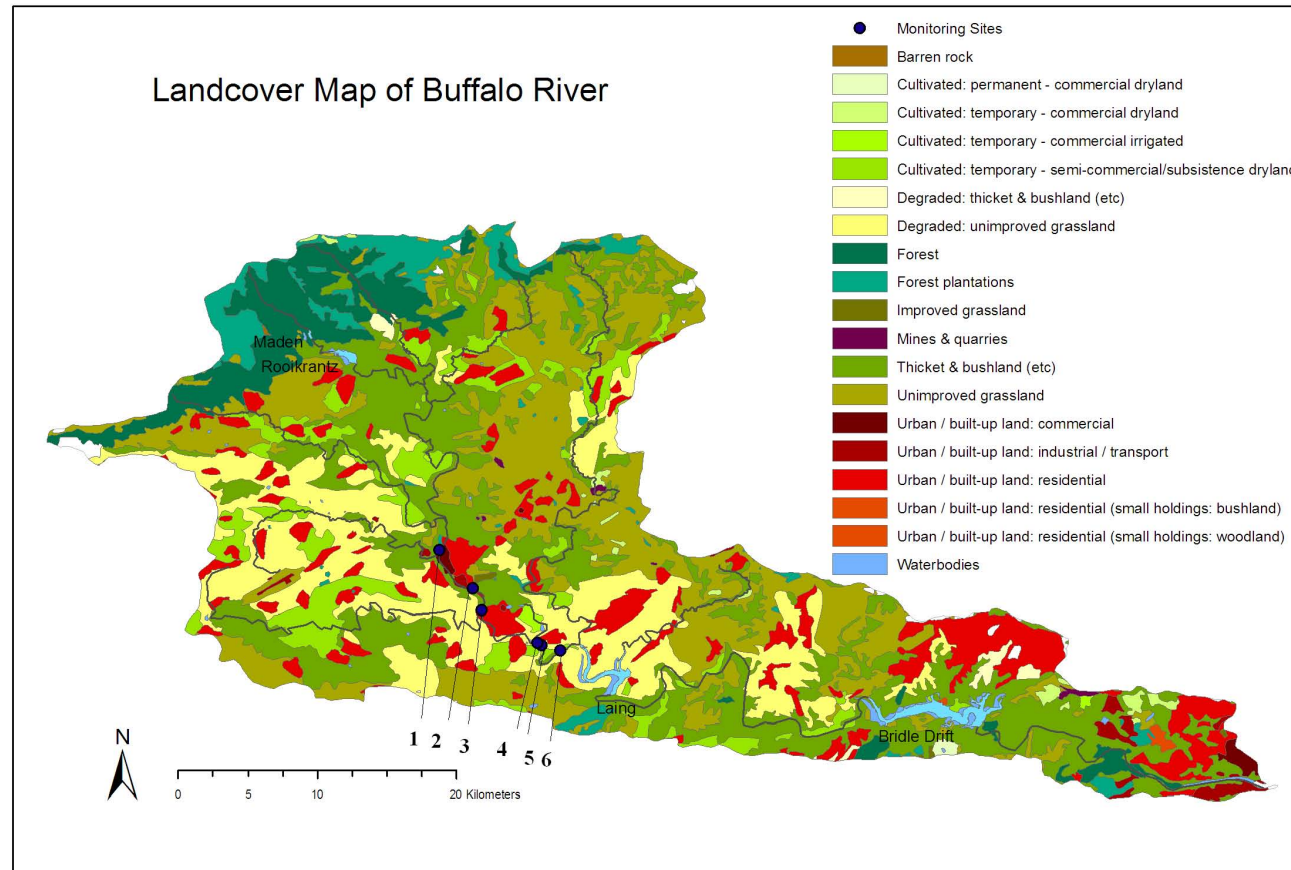


Figure 8.2: Buffalo River catchment, showing sites investigated as well as predominant land cover

Table 8.1: Sites chosen on the middle Buffalo River for water quality modelling

Site	Description	Location
Site 1	DWA gauging weir R2H005 above King Williams Town	32°52'31.45"S; 27°22'57.82"E
Site 2	King Williams Town Waste water treatment works (WWTW)	32°54'04.45"S; 27°24'06.97"E
Site 3	Buffalo River below King Williams Town WWTW	32°54'51.60"S; 27°24'34.80"E
Site 4	Tributary from textile factory	32°54'06.60"S; 27°24'45.00"E
Site 5	Zwelitsha WWTW	32°54'12.60"S; 27°24'55.20"E
Site 6	DWA gauging weir R2H010: Above Laing Dam	32°54'24.60"S; 27°24'39.00"E

River samples (site 3) were taken approximately 5.5 km downstream of site 1. Samples of textile effluent flowing from the Mlakalaka tributary into the Buffalo River (site 4), as well as final effluent samples from the Zwelitsha WWTW (site 5) were taken at approximately 11 km downstream of site 1. Finally, river samples were taken from the DWA gauging weir site R2H010 (site 6) approximately 15 km downstream of site 1, just before the inflow into Laing Dam. The land cover map (Figure 8.2) shows the studied section of the Buffalo River catchment to be dominated by urban residential and industrial land, with some cultivated land and some degraded thicket and bushland. The dominance of urban residential and industrial land would most likely result in point source influences dominating water quality in this section of the Buffalo River during low flow conditions. Nutrients from the surrounding catchment soil surface would however most likely be washed into the river during a rainfall event, but all sampling was taken during low flow conditions.

Three field trips lasting 1 day each were undertaken in 2009, where water quality grab samples and measures of flow were taken once at each site. The first field trip was undertaken on the 26th August 2009, where there had been little or no rain for several weeks, and the river was in low flow with measured flow being approximately 0.026 m³.sec⁻¹ at site 1 upstream of King Williams Town (see Table 8.3). The second field trip was undertaken on 18th November 2009, where there had been a small amount of rain in

the preceding week (6 mm), and while there was no noticeable run off, natural flow at site 1 was slightly stronger than during the first field trip ($0.085 \text{ m}^3.\text{sec}^{-1}$ see Table 8.3). A third field trip was undertaken on the 10th December, where conditions were much like that of the preceding field trip, with very little natural flow ($0.076 \text{ m}^3.\text{sec}^{-1}$ see Table 8.3).

8.2.1.2 The Bloukrans River

The Bloukrans River (Figure 8.3) is a tributary of the Kowie River in the Eastern Cape, near Grahamstown. The River runs through the residential areas of Grahamstown, where land cover such as informal settlements, and livestock grazing have an effect on water quality. The catchment of the Bloukrans lies within a strip of the Bokkeveld Series which consists of shale and sandstone (Heydorn and Grindley, 1982). Mean annual rainfall in the region is $600 - 800 \text{ mm.y}^{-1}$, with the area receiving year-round rainfall (DWA, 1986). Mean annual evaporation in the region is $1400 - 1600 \text{ mm.y}^{-1}$ (DWA, 1986). As the River leaves Grahamstown, effluent from the Grahamstown WWTW is continually released into the River, which substantially increases the flow. The River runs through a small area of intense dairy farming and irrigated agriculture on the outskirts of Grahamstown (Figure 8.3). The predominant land cover further downstream is natural bushland (Figure 8.3). Approximately 40 km downstream, the River enters a pool within the Blaauwkrans Nature Reserve. This pool is of ecological and social importance, as it is a habitat for the rare and highly endangered East Cape Rocky *Sandelia bainsii* and the pool is in addition used for religious and spiritual ceremonies by the local people (pers comm Dr Jim Cambray).

Five sites were chosen on the Bloukrans River for sampling, as well as the final effluent released from the Grahamstown WWTW (see Figure 8.3 and Table 8.2). Site 1 is situated on the outskirts of Grahamstown, just before the WWTW. Approximately 500 meters downstream of site 1, samples of the WWTW effluent were taken at site 2. Site 3 occurs 1 km downstream of site 1, just after the sewage effluent enters the river. Site 4 occurs approximately 6 km downstream of site 1. Site 5 occurs approximately 12 km downstream of site 1. The last site just before the stream enters the pool at the

Blaauwkrantz Nature Reserve, occurs approximately 40 km downstream of site 1. As with the field trips to the Buffalo River, three field trips were undertaken to the Bloukrans River, lasting 1 day each where single grab samples and estimations of flow were undertaken at each site.

The first field trip was undertaken on the 5th November 2009. Relatively heavy rains had occurred approximately 10 days before (44 mm). It was hard to determine whether any runoff from the surrounding land into the river was still occurring on this day, as much of the River is inaccessible from the access road, and the River is surrounded by thick riverine vegetation in many parts. The flow at site 1 was still relatively low ($0.047 \text{ m}^3 \cdot \text{sec}^{-1}$ see Table 8.5). The second field trip was undertaken on the 11th November 2009. No significant rain events had occurred between this field trip and the first and flow at site 1 was still fairly low ($0.043 \text{ m}^3 \cdot \text{sec}^{-1}$ see Table 8.5).

Table 8.2: Sites chosen on the Bloukrans River for water quality modelling

Site	Description	Location
Site 1	Outskirts of Grahamstown	33°18'52.20"S 26°33'10.20"E
Site 2	Inflow from Grahamstown Waste water treatment works (WWTW)	33°18'56.73"S 26°33'31.33"E
Site 3	Bloukrans River just below Grahamstown WWTW	33°19'05.01"S 26°34'06.30"E
Site 4	Bloukrans River approximately 6 km downstream of site 1	33°19'25.50"S 26°35'59.20"E
Site 5	Bloukrans River approximately 12 km downstream of site 1	33°19'40.10"S 26°38'35.00"E
Site 6	Bloukrans River just before inflow into the pool at the Blaauwkrantz Nature Reserve approximately 40 km downstream of site 1	33°23'26.10"S 26°42'24.40"E
Site 7	Mountain Drive site	33°19'32.60"S 26°31'44.93"E

A third field trip was undertaken on the 10th December 2009. No rain had occurred in the weeks proceeding this field trip, and natural flow at site 1 remained similar to the previous sampling event at a fairly constant ($0.043 \text{ m}^3 \cdot \text{sec}^{-1}$ see Table 8.5).

8.2.2. Data

Physical variables such as electrical conductivity (EC), temperature and pH were measured for input into the model, although the aim of the research was not to explicitly simulate these variables within the model, but to use them as supporting information within the model for the simulation of nutrient fate and DO. Measures of EC using a Cyberscan 200 meter, dissolved oxygen (DO) using a Cyberscan DO 300 meter, pH using a Cyberscan pH300 meter, temperature using a mercury-in-glass thermometer and turbidity using a Orbeco-Hellige 966 meter were measured on site. Depth and velocity measures were performed on site (DWA, 2009), after which a model outlined in DWA (2009) was used to estimate flow.

A ruler of approximately 1.4 m long, 10 cm wide and 1 cm in thickness was used to take depth measures in transects across the rivers where flow measures were required. With each depth measure, a measure of distance across the channel was noted. In addition, the difference in depth between the surface of the ruler facing the flow, and the opposite surface of the ruler was noted. This information was entered into a model given by DWA (2009) to calculate velocity and flow for the transect.

Samples for nutrient analysis were collected in plastic 0.5 L sample bottles collected facing upstream so that disturbed sediment would flow away from the bottles. Samples for CBOD₅ analysis were collected separately in 1 L glass bottles that had been autoclaved beforehand to ensure sterility. All sample bottles were filled to the rim with no headspace, and transported to the laboratory stored in a cooler box with ice. Samples were stored in a fridge at 4 °C and chemical analysis was undertaken within 5 days. Zuma (2009) found that nutrient concentrations of samples collected and preserved in this way did not change significantly provided chemical analysis is performed within 1 week of collection. The CBOD₅ analysis procedure was started within 24 hours of collecting the sample, as recommended by APHA (1992). CBOD₅ analysis was performed for the Bloukrans River but not for the Buffalo River.

Chemical analysis for nitrites was done according to the protocol of APHA *et al.* (1971) method number 354.1 using a Biotek microplate reader at 540 nm. Analysis for nitrates was performed according to the method of Velghe and Claeys (1983) using a Shimadzu mini 1240 spectrophotometer at 388 nm.

BOD₅ was measured according the standard method 5210 B (APHA, 1992). Spectroquant® phosphate and ammonium concentration test kits were used according to the manufacturer's instructions using a Shimadzu mini 1240 spectrophotometer at 660 nm.

8.2.3 QUAL2K modelling procedure

The QUAL2K model user interface (data input, model result output and graphs) are implemented in Microsoft Excel. There is an executable file that is run in the background, which executes algorithms for first order reactions that estimate the fate of nutrients for example. In between the executable file, and the Excel user interface, a layer of procedures written in Visual Basic handles input data, and in addition develops model output data into output graphs within the Excel user interface. The Excel file has worksheets for inputting the time zone, headwater quality and flow, main stem tributaries, reaction rates, weather and altitude and point and diffuse source information. The headwater input section is where users enter the quality of the most upstream section of the river stretch that is to be modelled, in this case site 1. The headwater input section has input boxes for various chemical variables, such as temperature, conductivity, inorganic solids, DO, slow CBOD, fast CBOD, organic nitrogen, ammonium nitrogen, nitrate nitrogen, organic phosphorus, phosphate, phytoplankton, internal nitrogen, internal phosphorus, detritus and alkalinity.

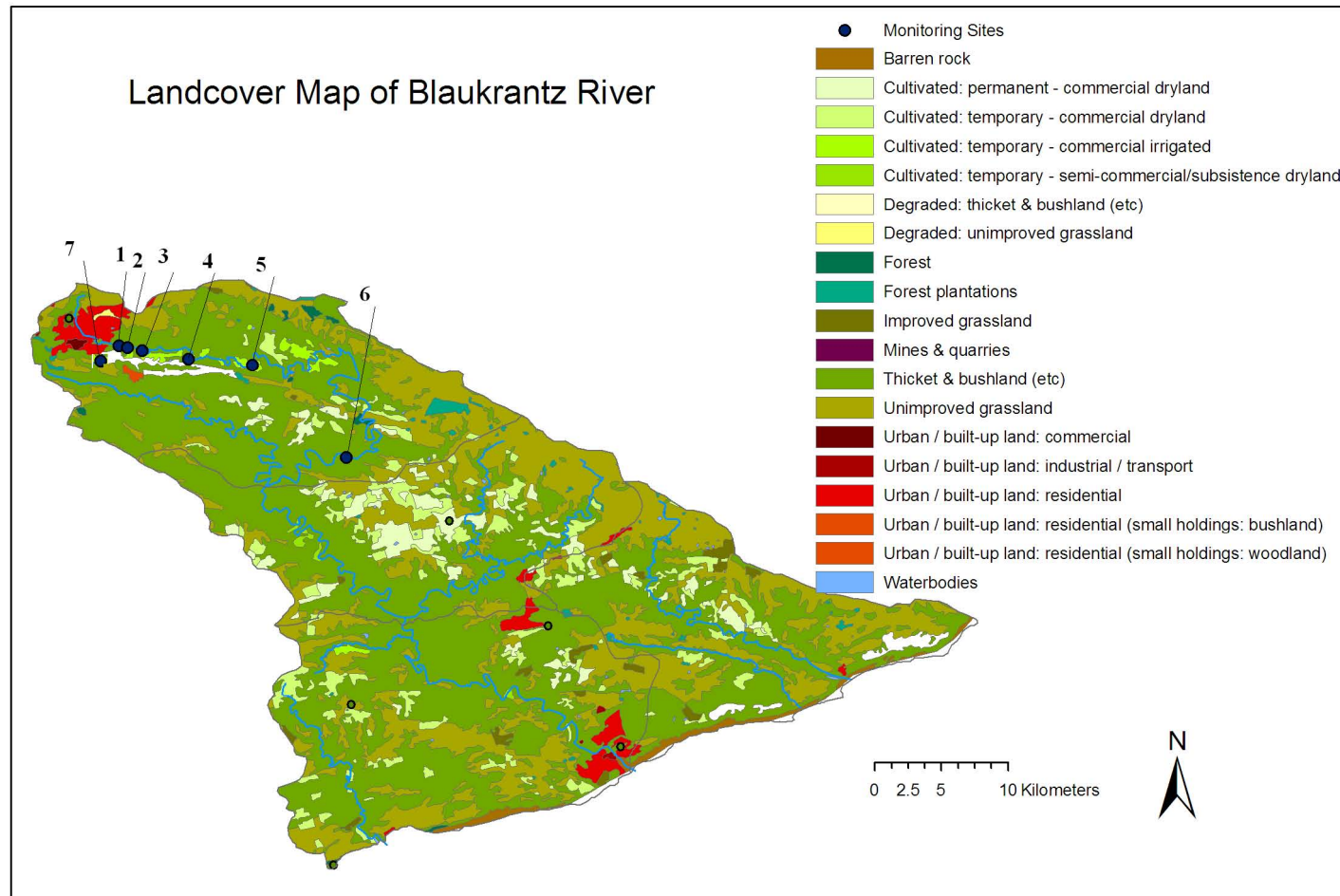


Figure 8.3: Bloukrans River catchment showing sites investigated as well as predominant land cover.

In addition, values can be added at hourly intervals from 12 am to 11 pm. Only values for available measured parameters were inputted into the model. Part of the aim of this research was to investigate whether QUAL2K could give sensible results with the restricted number of measured chemical data available.

The model has an input page for entering downstream chemical information, which allows the same input of chemical variables as was allowed in the headwater input page. Here, chemical values that were measured at site 6 were entered into the model. A page for entering reach information allows the user to divide the modelled river reach into segments, and to give each segment a label. In this investigation, the modelled reach was divided into 1 km segments. This page in addition allows the user to enter some hydrological information for each segment. QUAL2K can calculate flow through rating curves or the Manning formula. In this research, information was entered so that the Manning formula was used by default by the model. This information included values for channel slope, Manning n , bottom width and side slope. The model allows rate coefficients to be entered either by river reach segment, or as a global value for the entire modelled reach, and allows users to enter rate coefficients such as reaeration, fast and slow CBOD oxidation rate, organic nitrogen and organic phosphorus hydrolysis rate, ammonium nitrification rate, nitrate denitrification rate and various phytoplankton and benthic algae parameters such as maximum growth rate, respiration rate, excretion rate, death rate and settling velocity. Reaction coefficients that were relevant for the actual chemical constituents measured in the field were changed in the calibration process, while default coefficients were used for constituents that were not measured. The model in addition includes input sections where the user can enter hourly climate variable values such as air temperature, dew point temperature, wind speed and cloud cover. Important for the model simulation, the model includes a section for entering point sources and diffuse sources respectively, where the user can enter values such as the location of the point or diffuse source on the modelled reach, the effluent inflow rate, temperature, conductivity, DO, CBOD fast and slow, organic nitrogen and phosphorus, nitrate nitrogen, phosphate, internal nitrogen and phosphorus and alkalinity. The model has output sections where graphs display the value of simulated variables on the y axis, and

the distance downstream from the headwater site on the x axis.

One data set from each river was used as a calibration data set. Parameters within the model relevant to the measured data were adjusted until the model gave estimations of water quality parameters that were close to the observed parameters. Historical DWA data were not actively used in either the calibration or confirmation process in this research. Once a calibrated model for each river was obtained, new model runs were attempted with the two confirmation data sets, keeping the parameter values unchanged from those determined in the calibration model. If the model still estimated observed values from the confirmation data sets to a reasonable degree, then one can assume the model is adequately calibrated. Once a model is adequately calibrated, the model can be applied to the river reach it is calibrated for to investigate management scenarios, or to predict future water quality. This research aims only to investigate whether QUAL2K can be adequately calibrated and confirmed with the limited field data that was measured, and does not attempt to investigate management scenarios or make management recommendations.

Once the model is calibrated, the model needs to be confirmed to ensure that parameter values chosen are actually correct. Therefore, independent field data sets need to be measured. The conditions when these field data are measured, and the number of data sets measured for confirmation are important. Chapra (2003) recommends confirmation of a model on three different levels:

1. Confirmation of a model where the confirmation data conditions, i.e. flow and diffuse and point loadings, are very similar to the data used in the calibration of the model.
2. Confirmation of a model where the confirmation data involves wetter conditions or more natural flow than the data used to calibrate the model.
3. Confirmation of the model where the confirmation data contains significantly different loadings from point and diffuse sources than the data use to calibrate the model.

The most useful data sets for calibration of models may be at extreme or unusual conditions, where effects such as point sources and diffuse sources would have a major

impact on water quality (Shanahan *et al.*, 1998). Therefore, data sets were chosen for use in calibrating the models, where conditions were such that pollution sources would have a high impact i.e. low flow conditions in point source dominated reaches, or wet conditions in river reaches where diffuse sources would have an impact on water quality.

Initial parameter values for input into the model, representing rates of chemical change and other processes, were chosen from Bowie *et al.* (1985). Bowie *et al.* (1985) is a review paper listing values of rate constants used in previous published modelling exercises. These values are used as initial parameter values in the calibration process as they reflect realistic reaction coefficients obtained in other studies, and can be further refined to the calibration data set through the calibration process. The values listed in Bowie *et al.* (1985) are listed as values at 20°C. Besides listing parameter values, Bowie *et al.* (1985) in addition lists values of Θ for each parameter, which is used in an equation to adjust a parameter value according to the water temperature.

$$k_T = k_{20}\Theta^{T-20} \quad (\text{Equation 8.1})$$

Where k_T = rate constant at temperature T and k_{20} = rate constant at 20°C

The average values of rate constants and Θ for each rate constant were used as initial parameter values within QUAL2K, and are listed in Table 8.4. Parameter values were adjusted if necessary to obtain a good fit to observed data. The confirmation process, where the reaction coefficient values determined through the calibration process are used in the model applied to independent measured data, determine whether the reaction coefficient values chosen are accurate. Table 8.4 usefully shows the average, min and max values for various reaction coefficients that can be found in the literature, as well as the average value of Θ for the respective reaction coefficients that is found in the literature (Bowie *et al.*, 1985). As is mentioned previously, the averages were used in the models by default, and then adjusted during the calibration process. Table 8.4 in addition shows the final values for the reaction coefficients for the models calibrated to both the studied river reaches. This will usefully allow the reader of this thesis to compare the values of the final reaction coefficients chosen between the two studied river reaches, and

with the maximum, minimum and average values of these coefficients found in the literature, and thereby give the reader a sense of how realistic the values of the coefficients used in the modelling exercise are.

QUAL2K provides a simple measure of uncertainty by simulating maximum and minimum water quality estimations in addition to the mean simulation. A large part of QUAL2K's estimation of minimum and maximum water quality estimations is driven by the variability of the water quality of the effluents of the identified point sources. The model allows for the input of a mean water quality value, as well as the range/2 for a particular point source. Since single grab samples of point source effluents were done for each field trip, it was not possible to obtain an estimation of the range of water quality from point source effluents within a day. However, an attempt at obtaining an estimation of minimum and maximum water quality estimations from the model was made by finding the range of water quality from identified point sources from all three sampling days. This range was used in each model run to facilitate the estimation of minimum and maximum water quality predictions.

For modelling purposes, the river reaches investigated were divided into 1km segments, and elevation upstream and downstream of each segment was entered into the model. The elevation data were obtained from 1:50000 maps. The model in addition requires that each segment be divided into 1 or more sub-segments for modelling purposes. A sub-segment number of 1 per segment was chosen. Flow estimations at all in-river sites were performed during the field work, however the QUAL2K model only allows a flow value to be input for the headwater site, and the model calculates for the modelled reach internally. Point and diffuse sources of flow as well as abstraction of water can however be specified in the model. While the model can calculate hydraulics through a weir calculation, rating curves or the Manning equation, the model was set up so that the Manning equation would be used as it is the simplest method to set up in the model. Bottom width for each segment was measured in the field as part of the field flow measures, and the bottom width measures were entered into the model. A Manning Roughness value of 0.1 was chosen as being appropriate for low flows in both systems

(Pers Comm, Professor D. Hughes) as the effect of resistance to flow as water flows over the stream bed will increase with lower flows. Initial values chosen within the model for channel slope and side slope were 0.0002 and 2.0 respectively, which could change with the calibration process. Air temperature, dew point temperature and wind speed data for each data set were entered into the model. These data were obtained from <http://WWTW.wunderground.com>.

8.3 Results

8.3.1 The Buffalo River system

8.3.1.1 Field Data

Water quality measures and flow onsite, as well as the measurements of nutrient concentrations are listed in Table 8.3.

Site 1 above King Williams Town is characterized by fairly high DO, which drops somewhat by site 3 due to the WWTW at site two, but seems to recover fully by site 6 just before Laing Dam despite the introduction of low DO effluent at Site 4 (Textile stream) and Site 5 (Zwelitsha WWTW final effluent). Nitrate and nitrite levels are low at site 1, but the introduction of high nitrate and nitrite levels from the King Williams Town WWTW leads to elevated nitrogen levels at site 3. The Zwelitsha WWTW in addition introduces high concentrations of nitrates and nitrites. Site 6 however does seem to show some recovery in nitrogen levels as compared to site 3. Ammonium levels at site 1 are low, and the effluent from the King Williams Town WWTW does not show any ammonium. Site three does show elevated levels of ammonium. This could be due to the conversion of organic nitrogen introduced from the King Williams Town WWTW to ammonium through the process of ammonification (Chapra, 1997). The textile stream and the Zwelitsha WWTW in addition introduce large amounts of ammonium to the river, but ammonium levels at site 6 are relatively low considering the inputs upstream, indicating

that ammonium does not have a long residence time in the river. Phosphate levels at site 1 are undetectable, however high inputs of phosphate at the King Williams Town WWTW, the textile stream and the Zwelitsha WWTW led to elevated levels in stream. However the sharp drop in phosphates by site 6, despite high input from point sources indicates that phosphates are being removed from the water column fairly rapidly.

Natural flow at site 1 was fairly low during all three sampling trips, although there was slightly more natural flow in October and November. Flow from the King Williams Town WWTW increased the flow substantially, as did the effluent from the Zwelitsha WWTW. On average, effluent flow across the three field trips contributed around 85 % of the flow through this stretch. Flow from the textile stream was negligible during all three field trips, and it is doubtful that the effluent from the textile stream had any significant influence on the water quality downstream. For some water quality parameters, the three identified point sources showed high temporal variation in concentrations. For example, the Zwelitsha WWTW DO ranged from 2.7 – 7 mg.L⁻¹, while nitrates in the King Williams Town WWTW and the Zwelitsha WWTW showed a high degree of temporal variability. Phosphates showed less temporal variability across the point sources. While water hyacinth started becoming profuse after site 6 at the start of Laing Dam, there were no evident water hyacinth along the modelled reach. The model would simulate the effect of riffles on reaeration in its internal simulation of flow as measured values of depth at the investigated sites were inputted into the model.

8.3.1.1 Model Results

The QUAL2K model accurately estimated measured flow, once point source inputs were added to the model (Figure 8.4). The steps in the graph indicate the dramatic effect on flow that point source inputs of effluent had from the two WWTWs.

Table 8.3: Values of water quality parameters measured in the Buffalo River. All water quality values measured are in mg.L^{-1} while flow is measured in $\text{m}^3.\text{sec}^{-1}$. Standard deviation is listed in brackets after average values where several replicates were measured.

Date	DO	NO_3^- -N	NO_2^- -N	NH_4^+ -N	PO_4^{3-} -P	Flow
Site 1-Instream above King Williams Town						
26-Aug-09	8.630	0.126	0.045	< 0.01	< 0.01	0.026
12-Oct-09	6.370	0.451	0.038	0.132 ($\pm$ 0.065)	< 0.01	0.085
18-Nov-09	7.550	1.416	0.006	< 0.01	< 0.01	0.076
Site 2 – King Williams Town WWTW final effluent						
26-Aug-09	4.610	3.269	0.511	< 0.01	3.774 ($\pm$ 0.126)	0.295
12-Oct-09	5.290	7.638	0.089	< 0.01	3.574 ($\pm$ 0.415)	0.295
18-Nov-09	5.540	10.606	0.169	0.060 ($\pm$ 0.063)	3.967 ($\pm$ 0.280)	0.094
Site 3-In stream below King Williams Town WWTW						
26-Aug-09	6.430	1.283	0.368	1.643 ($\pm$ 0.258)	0.836 ($\pm$ 0.072)	0.321
12-Oct-09	5.880	4.706	0.436	2.820 ($\pm$ 3.400)	1.288 ($\pm$ 0.054)	
18-Nov-09	7.310	3.526	0.075	0.008 ($\pm$ 0.026)	0.137 ($\pm$ 0.202)	0.170
Site 4 – Textile Stream Effluent						
26-Aug-09	4.770	< 0.5	0.569	0.439 ($\pm$ 0.146)	4.369 ($\pm$ 0.165)	0.006
12-Oct-09	5.150	< 0.5	0.161	0.528 ($\pm$ 0.105)	6.923 ($\pm$ 0.164)	0.010
18-Nov-09	0.360	< 0.5	0.140	0.528 ($\pm$ 0.217)	6.539 ($\pm$ 0.213)	0.004
Site 5 – Zwelitsha WWTW Final Effluent						
26-Aug-09	5.360	2.450	1.781	6.836 ($\pm$ 0.345)	5.371 ($\pm$ 0.185)	0.061
12-Oct-09	2.720	4.277	0.805	7.693 ($\pm$ 0.546)	6.280 ($\pm$ 0.031)	0.266
18-Nov-09	7.000	1.631	0.306	3.891 ($\pm$ 0.171)	5.083 ($\pm$ 0.015)	0.125
Site 6–In stream Before Laing Dam						
26-Aug-09	8.070	0.908	0.296	0.280 ($\pm$ 0.160)	3.071 ($\pm$ 0.386)	0.388
12-Oct-09	6.470	3.562	0.306	0.729 ($\pm$ 0.146)	1.744 ($\pm$ 0.219)	0.656
18-Nov-09	7.890	0.915	0.060	0.039 ($\pm$ 0.004)	0.333 ($\pm$ 0.086)	0.299

Site 6 is about 15 km downstream from site 1, which corresponds with the values on the x-axis. The data set collected on the 12th October was used as the calibration data set for water quality and flow estimations. The calibration processes successfully simulated the values of all measured nutrients and flow (Figure 8.5).

The reaction rates used are listed in Table 8.4. The data set collected on 26th August was

used as the first confirmation data set, while the data set collected on the 18th November was used as the second confirmation data set. The model estimated that oxygen would go through a dip coinciding with input from the King Williams Town WWTW, recovering slightly before going through another dip at the Zwelitsha WWTW and then recovering again. The first confirmation data set seems to confirm the calibration model. The second confirmation data set however is not as close to the model estimations in the middle sections of the modelled reach, although the estimated final DO value is not far from the observed value.

Model estimations of nitrate were generally accurate, although the high degree of temporal variability in nitrate released by both WWTWs, led to a wide range between the estimated maximum and minimum nitrate levels by the model. The model could not estimate the ammonium concentration at site three, probably because organic nitrogen was not measured, and it is possible that the King William's Town WWTW was releasing high concentrations of organic nitrogen that were being converted to ammonium due to the process of ammonification (Chapra, 1997) leading to high concentrations of ammonium at site 3.

The King Williams Town WWTW did not release any ammonium into the river over the three sampling dates which is why the model did not simulate ammonium at site 3 in the absence of organic nitrogen measurement. However, the model seemed to estimate the process of nitrification accurately from ammonium entering the river from the Zwelitsha WWTW, and concentrations of ammonium at site 6 were accurately estimated.

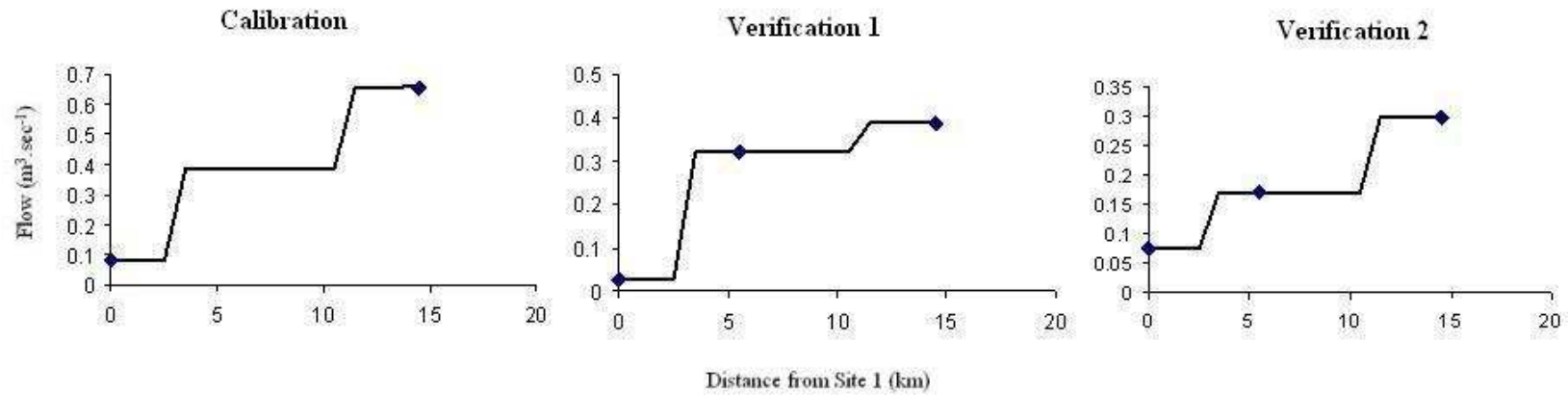


Figure 8.4: QUAL2K model flow estimations as compared to observed flow measures in the Buffalo River for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of flow were taken.

The model was calibrated against observed phosphate concentrations, but could not be confirmed against the two confirmation data sets. Model simulations of phosphate were very different to observed values.

8.3.2 The Bloukrans River system

8.3.2.1. Field Data

Water quality measures and flow onsite, as well as the measurements of nutrient concentrations are listed in Table 8.5. DO in the Bloukrans seems to dip around the Grahamstown WWTW and slowly increases along the studied section of reach. Nitrogen concentrations in the River are very high after the Grahamstown WWTW and nitrogen concentrations slowly decrease, but are still fairly high in the ecologically sensitive Blaauwkrantz Reserve pool.

Ammonium concentrations are high in the Grahamstown WWTW effluent, but concentrations decrease quickly downstream, indicating that ammonium does not have a long residence time in the system. Phosphate concentrations increase dramatically in the River because of the high concentrations in the WWTW effluent, and slowly decrease downstream. However, in the calibration data set, phosphate concentrations increase again between sites 5 and 6, indicating that there is some unknown source of phosphates between these two sites. In all three data sets, flow seems to increase marginally at site 4. In the first two data sets, flow increases substantially at site 5. These two data sets were collected in November, a few weeks after relatively substantial rainfall (44 mm over 2 days). No obvious sources of surface flow were found during an investigation of this area during this period. However, the River is particularly inaccessible in this area, and sources of water input to the River may have been missed. Possibilities responsible for the increased flow here include surface water flow, groundwater input, or return flow from the many agricultural activities that occur here.

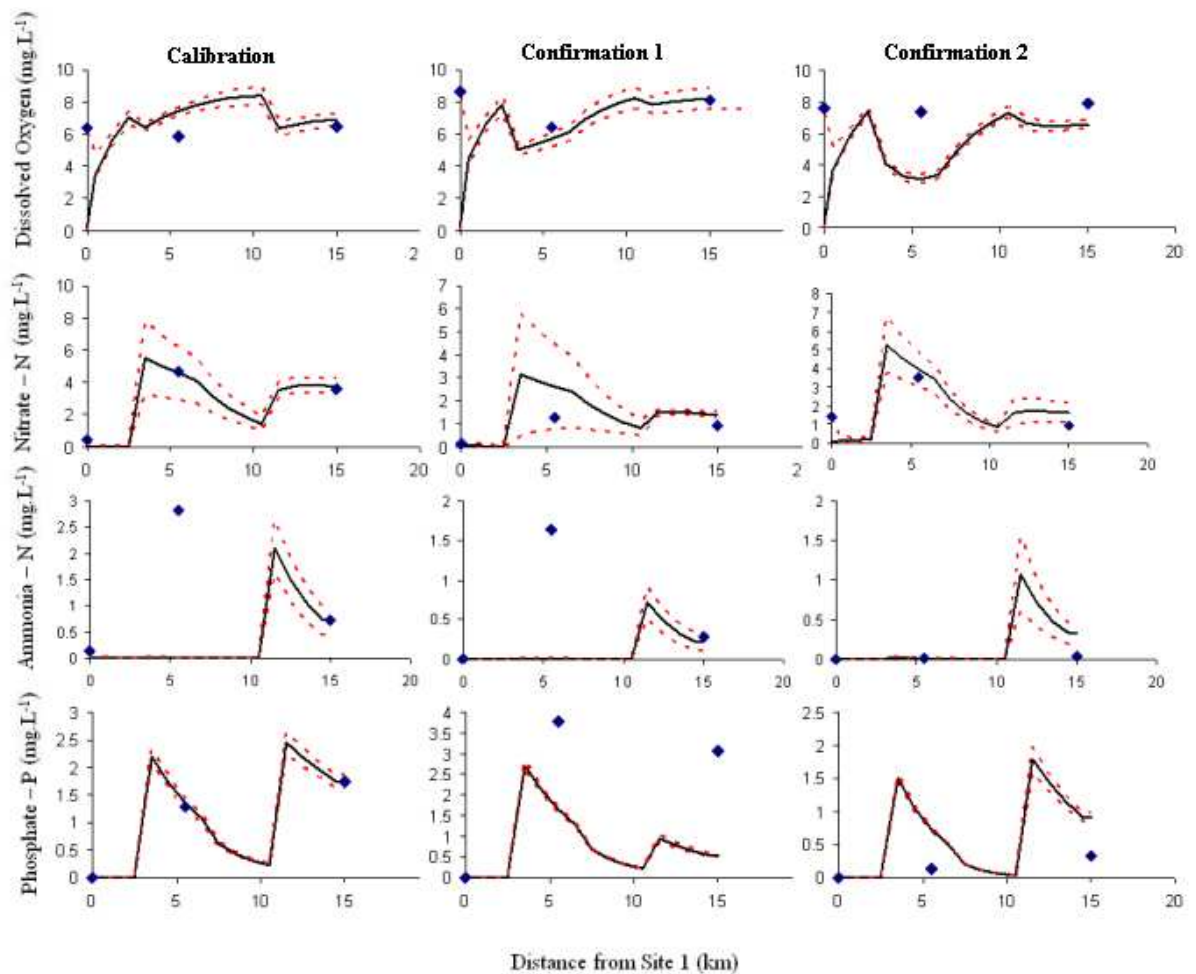


Figure 8.5: QUAL2K model estimations as compared to observed water quality measures in the Buffalo River for a range of water quality constituents and for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of water quality were taken. The dotted lines indicate measures of maximum and minimum simulated data.

It is possible that surface water runoff was flowing into the River. Since no sources of surface water could be found running into the Bloukrans River over this period, it was decided to investigate the quality of a known source of surface water in the same catchment, so that the measured water quality could be entered into the model. This would allow the model to simulate nutrient fate with the assumption that the extra flow in the river was due to surface water flow. If the addition of the extra water as surface water flow leads to inaccurate simulations, then other possibilities for the extra water, such as irrigation return flow, could be investigated. A known source of surface flow that flows relatively constantly was investigated on Mountain Drive, relatively close to the Bloukrans River. It can be expected that surface water on Mountain Drive and that entering the Bloukrans River share the same source as they are in close proximity (Figure 8.3). Table 8.5 shows the results of chemical analysis on the surface water identified at Mountain Drive. The results of chemical analysis show that this surface water is relatively pure.

8.3.2.2. Model Results

All three data sets showed an increase in flow at site 4, and the two data sets collected in November showed in addition an increase in flow at site 5 (Figure 8.6). The two data sets in November were collected within weeks of relatively heavy rain. No surface water flow was evident during any of the field work over this period, although this area of the River is particularly inaccessible in some parts. It was hypothesised that some sort of agricultural return flow is occurring in this area. The data set collected on the 5th November was used as the calibration data set. These were the data collected soonest after heavy rains, and are the most influenced by unknown sources of increased flow between site 3 and site 5.

Table 8.4: Rate constants used in QUAL2K to model water quality in the Buffalo River and the Bloukrans River. Default values listed are taken from Bowie *et al.* (1985). QUAL2K uses many more rate constants, but the default values in the program were used if not indicated here.

Rate Constant	Default Value				Buffalo River		Blaauwkrantz River	
	Average	Min	Max	Average Θ	Final Value	Θ	Final Value	Θ
CBOD _f Oxidation Rate (d ⁻¹)	0.51	0	4.24	1.047			0.001	1.047
Nitrification Rate (d ⁻¹)	0.384	0.01	3	1.07	7	1.07	5	1.07
Denitrification Rate (m.d ⁻¹)	0.16	0	1	1.05	0.16	1.05	0.16	1.05
Sediment Denitrification Transfer Coefficient (m.d ⁻¹)					0.5	1.05	0.5	1.05
Inorganic P Settling Velocity (m.d ⁻¹)					0.775 - 1.5 *		0	
Reaeration Coefficient (d ⁻¹)					4	1.02	0.04 - 5 *	1.024

* A range of rate constant values were used across different segments of the system

Table 8.5: Values of water quality parameters measured in the Bloukrans River. All water quality values measured are in mg.L^{-1} while flow is measured in $\text{m}^3.\text{sec}^{-1}$. Variance is listed in brackets after average values where several replicates were measured.

Date	DO	$\text{NO}_3^- - \text{N}$	$\text{NO}_2^- - \text{N}$	$\text{NH}_4^+ - \text{N}$	$\text{PO}_4^{3-} - \text{P}$	CBOD_f	Flow
Site 1 – Just before the Grahamstown WWTW							
05-Nov-09	4.700	1.345	0.915	1.997 (± 0.167)	0.446 (± 0.041)	10.729	0.047
11-Nov-09	6.710	3.705	0.879	3.065 (± 0.332)	0.543 (± 0.027)	11.780	0.043
10-Dec-09	6.620	3.633	0.300	0.904 (± 0.198)	0.335 (± 0.008)	4.020	0.043
Site 2- Grahamstown WWTW Final Effluent							
05-Nov-09	3.580	19.239	2.797	4.691 (± 1.114)	5.030 (± 0.234)	31.824	0.073
11-Nov-09	4.900	17.629	3.159	1.212 (± 0.218)	4.565 (± 0.257)	13.450	0.035
10-Dec-09	4.820	14.590	2.869	1.287 (± 0.058)	4.682 (± 0.201)	10.100	0.028
Site 3 – Just After the Grahamstown WWTW							
05-Nov-09	4.440	12.981	1.386	1.683 (± 0.807)	2.985 (± 0.392)	10.569	0.120
11-Nov-09	5.570	14.468	1.748	< 0.01	2.771 (± 0.031)	8.720	0.078
10-Dec-09	6.540	5.779	1.567	0.811 (± 0.048)	2.646 (± 0.041)	2.560	0.071
Site 4 - 6 km Downstream of Site 1							
05-Nov-09	5.850	11.965	0.299	0.534 (± 0.635)	2.494 (± 0.071)	9.049	0.575
11-Nov-09	6.200	9.963	0.118	< 0.01	2.851 (± 0.062)	3.080	0.107
10-Dec-09	7.870	3.097	0.226	0.116 (± 0.018)	2.351 (± 0.188)	2.860	0.195
Site 5 – 12 km Downstream of Site 1							
05-Nov-09	6.930	8.210	0.125	< 0.01	2.396 (± 1.165)	8.269	1.560
11-Nov-09	6.080	8.139	0.089	< 0.01	1.047 (± 0.027)	8.300	0.749
10-Dec-09	7.700	3.669	0.089	0.039 (± 0.010)	1.342 (± 0.117)	3.520	0.179
Site 6 – Blaauwkrantz Reserve pool 40 km Downstream of Site 1							
05-Nov-09	7.510	6.494	0.111	< 0.01	4.387 (± 0.821)	7.789	0.532
11-Nov-09	6.450	1.345	0.067	< 0.01	1.590 (± 0.049)	7.260	0.130
10-Dec-09	7.430	1.738	0.038	< 0.01	1.641 (± 0.076)	1.900	0.086
Site 7 – Surface Water on Mountain Drive							
17-Nov-09	6.76	< 0.5	0.01	< 0.01	< 0.01	-	-

To account for the increase in flow, diffuse sources were added to the model to correspond with the increases at these sites. However, adding the diffuse sources as uncontaminated water as determined from the chemical analysis of surface water runoff at Mountain Drive, resulted in simulated nitrate, phosphate and CBOD_5 concentrations

being much lower than what was observed in the field. Therefore, an assumption was made that the water entering the River between site 3 and site 5 must contain high levels of nutrients and some CBOD₅. The land cover of the catchment in the region around the sites where addition flow was detected, include fields of intensely irrigated grass for dairy cows. Therefore, one could expect some irrigation return flow, especially during periods of rainfall. The chemical signatures of the diffuse sources entered in the calibration model were manipulated until a reasonable fit between model output and observed results were obtained for nitrate and phosphate (see Table 8.6). The models constructed for the data collected on the 11th November and on the 10th December used a combination of the diffuse sources identified from the calibration model, depending on where increased flow was observed in the field data.

Table 8.6: Possible diffuse sources influencing the Bloukrans River as determined by calibrating the QUAL2K model to observed data

Approximate location	CBOD ₅ (mg.L ⁻¹)	Nitrate (mg.L ⁻¹)	Phosphate (mg.L ⁻¹)
Between sites 3 and 4	15	13	3.5
Between sites 3 and 4	0	0.5	1
Between site 4 and 5	5	4	2

Diffuse sources 1, 2 and 3 were used in the calibration model, with relative flows from the diffuse sources adjusted to reflect observed flows and to obtain a good fit between simulated and observed chemical signatures. Diffuse sources 2 and 3 were used in the model constructed for the data collected on the 11th November. Only diffuse source 2 was used to construct the model for the data collected on the 10th December.

All three data sets in addition show a reduction in flow between sites 5 and 6. A point source of extraction was added to each model between sites 5 and 6, with no influence on water quality, so that model flow simulations mirrored that of observed flow measures. Figure 8.6 shows the results of flow estimations compared to the measured flows. The model estimated flow can be seen to be very similar to the measured flow within the river.

Figure 8.7 shows the results of modelling water quality on the Bloukrans with QUAL2K. The model simulates an initial drop in DO after the Grahamstown WWTW, and then a relatively quick recovery in DO, which reflects the observed data fairly well in the calibration model run. DO levels in the confirmation data sets do not differ much along the stretch of modelled River compared to the calibration data set, and the model estimates of DO are fairly accurate. In the calibration model, the initial lag in DO coincides with a jump in CBOD₅. The model simulates an initial jump in CBOD₅ after which the CBOD₅ drops to a stable level relatively quickly, which is generally reflected by the observed data.

The model simulates nitrate data as spiking after the effluent input from the WWTW, after which nitrate concentrations decrease. The model generally reflects the pattern in the observed nitrate data. The model is able to simulate the fast drop in ammonium concentration after the initial spike from the WWTW, indicating that the nitrification rate is relatively high, or that plants are making use of ammonium in preference to nitrate. The model was not able to simulate the dynamics of phosphate in the system. Although a rough pattern that reflects the data was achieved, it was nowhere near the accuracy achieved with the other parameters. The reaction rates used in the models are listed in Table 8.4.

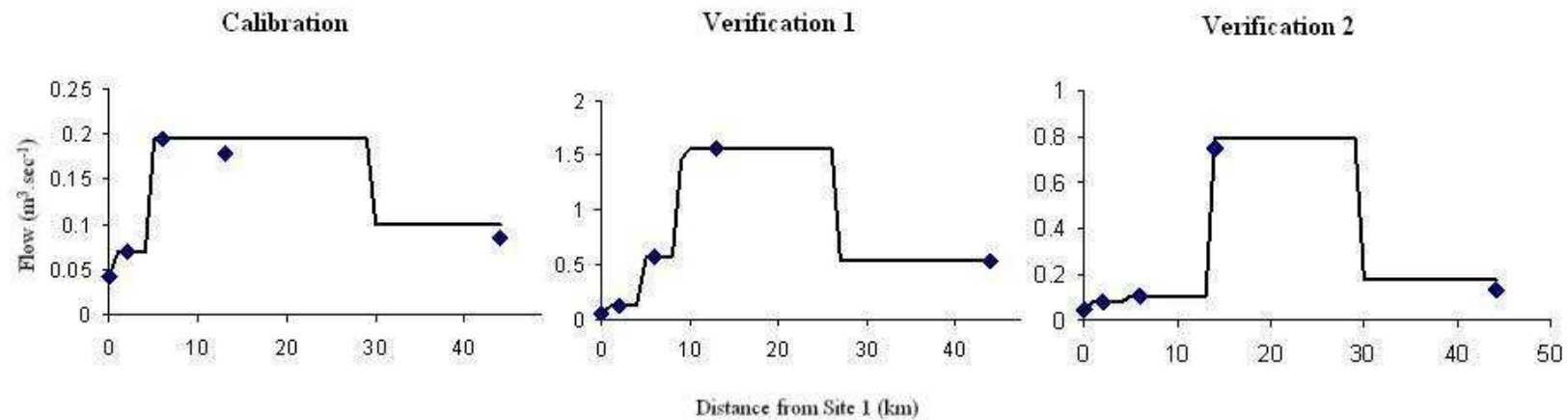


Figure 8.6: QUAL2K model flow estimations as compared to observed flow measures in the Bloukrans River for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of flow were taken.

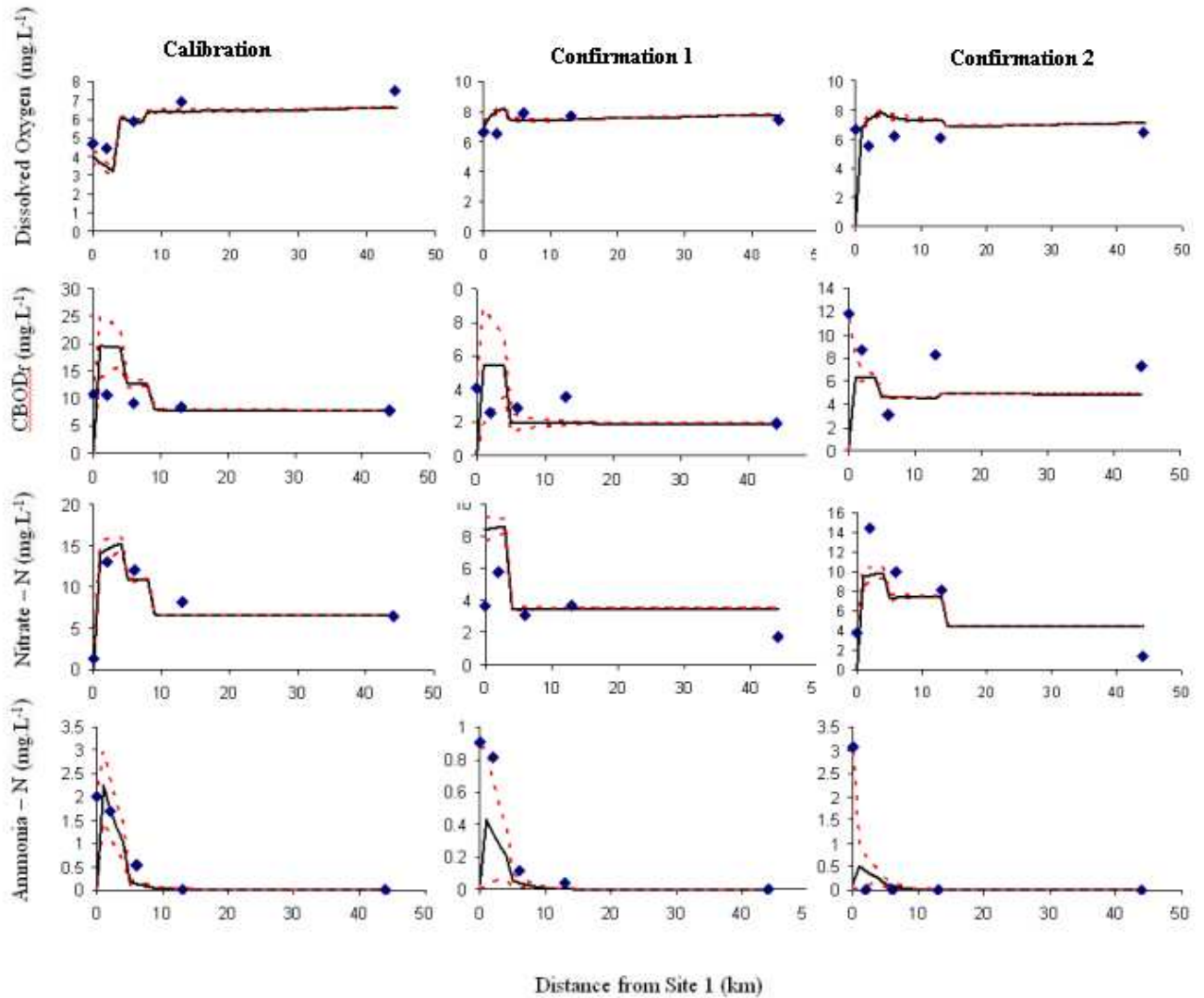


Figure 8.7: QUAL2K model estimations as compared to observed water quality measures in the Bloukrans River for a range of water quality constituents and for a calibration as well as two confirmation data sets. The points on the graph indicate where in-stream measures of water quality were taken. The dotted lines indicate measures of maximum and minimum simulated data.

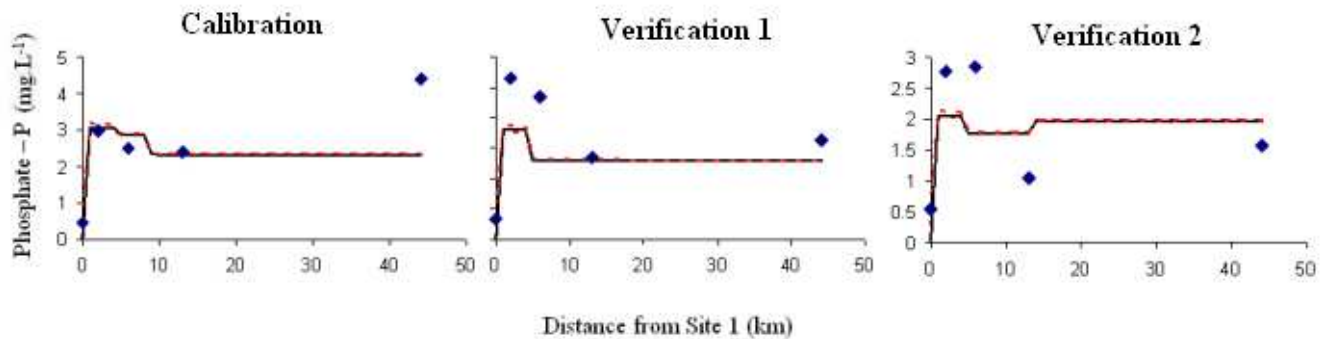


Figure 8.7 continued: QUAL2K model estimations as compared to observed water quality measures in the Bloukrans River for a range of water quality constituents and for a calibration as well as two confirmation data sets.

8.4 Discussion

8.4.1 Discussion of the Buffalo model results

All three field data sets were collected when there was very little natural flow in the Buffalo River through the section investigated. On average, effluent contributed about 85% of the flow in this section of the river on the dates field measures were taken. According to O’Keeffe *et al.* (1996), only heavy rainfall events in the Buffalo Catchment generate local runoff. Therefore, the claim that these data sets reflect a river stretch dominated by point source effluents is justified. The three data sets are different in that effluent loadings from the point sources identified varied over the three sampling dates with the King Williams Town WWTW releasing effluent ranging from 0.094 – 0.295 m³.sec⁻¹ and the Zwelitsha SWT releasing effluent in the range of 0.061 – 0.266 m³.sec⁻¹. This indicates that an assumption that WWTWs release constant rates of effluent would be incorrect, at least in the case of these two WWTWs. The textile stream had very little effluent flow and it is unlikely that this point source had any dramatic effect on the

Buffalo River water quality downstream. Water quality of the point sources identified varied dramatically for some parameters. Nitrate concentrations in the King Williams Town WWTW and the Zwelitsha WWTW varied dramatically over the three sampling dates, and DO varied greatly at the Zwelitsha WWTW over the three sampling dates.

QUAL2K appears to estimate DO fairly accurately, with the model closely matching the first confirmation data set. The model did not perform well on the second data set, although the final DO estimate at site 6 was close to that observed in the field. The model shows that the two WWTWs typically cause a dip in DO, after which DO levels start to recover. The calibration model required a reaeration rate of approximately 4 to obtain a fit to the observed data. Bowie *et al.* (1985), however, uses physical measures to approximate the reaeration rate. While the confirmation models indicate that a reaeration rate of 4 may be appropriate for at least 1 of the data sets, the practice of determining a rate in the calibration model and applying that value to confirmation models may not be appropriate for the reaeration rate in particular. The reaeration rate is a function of temperature, depth and velocity (Shanahan *et al.*, 1998) and confirmation data sets may well be different from the calibration data set in these respects so using the same reaeration rate for all three models may be invalid.

The model seems to simulate nitrates fairly well, with model estimates being fairly close to both confirmation data sets. Since the temporal variation of nitrate concentrations in the King Williams Town WWTW and Zwelitsha WWTW vary substantially, the model created a broad range between the minimum and maximum estimations of nitrate in the region influenced by the two WWTWs. The model typically shows a spike in nitrates after the King Williams Town WWTW, after which nitrate concentrations start to decline, but another smaller spike occurs in the region of the Zwelitsha WWTW.

The model estimations of ammonium clearly show that it was necessary to measure organic nitrogen in this study to fully estimate ammonium concentrations. Although no detectable amounts of ammonium were measured from the King Williams Town WWTW over all three collection dates, high concentrations of ammonium were found at in-river

site 3 just below the King Williams Town WWTW. This indicates that the most probable cause is that organic nitrogen released from the King Williams Town WWTW, is being converted to ammonium through the process of ammonification (Chapra, 1997). Since organic nitrogen was not measured in the study, ammonium dynamics in the middle of the studied reach section could not be accurately simulated. However, the model did simulate the nitrification of ammonium from the Zwelitsha WWTW down to site 6. The model fitted the confirmation data well from this point onwards at least. The model shows that ammonium is fairly rapidly removed from the system. This could either be as a consequence of a high rate of nitrification, or uptake from aquatic flora. The model was able to accurately simulate the high rate of ammonium loss by using a large nitrification coefficient (Table 8.4). The nitrification rate of 7 is higher than the maximum used in the literature as indicated by Bowie *et al.* (1985) of 3. Possible uptake by plants as well as a high nitrification rate could be influencing ammonium concentration in this system.

Model estimations of phosphate were not very good. Although the calibration model could be accurately fitted to the observed data, the model could not simulate the dynamics of phosphate in the two subsequent confirmation data sets. The two confirmation data sets are in addition very different from the calibration data set and each other in terms of observed phosphate concentrations. The underestimation of the model simulation in the first confirmation model run could indicate that there was perhaps some unknown source of phosphate in the river at that time, such as a once off pollution event. In addition, it is possible that the model is failing to take into account an important process that impacts on phosphate concentrations. The failure of the model to simulate the very low phosphate concentrations in the second confirmation data set in addition lends support to the theory that an important process is being missed or underrepresented. The process that is being missed in the model is not the influence of aquatic macrophytes such as water hyacinth, as none were evident in the modelled section of reach, as they tend to proliferate in slow flowing or static pools and impoundments. QUAL2K does simulate the effect of benthic algae, however, it is possible that the model did not simulate the extent of effect of benthic algae on nutrients sufficiently. Future research could investigate whether QUAL2K gives accurate simulations of benthic algae growth.

8.4.2 Discussion of the Bloukrans model results

Two of the three field collection trips were undertaken when there was obvious diffuse input of flow into the River. This is indicated by the jump in flow between sites 3 and 4 and 4 and 5, which was much more predominant in the two field collection dates soon after a heavy rainfall period (44 mm). The Grahamstown WWTW was an obvious identified point source on the system. The WWTW had a fairly consistent water quality signature across all three field sampling dates, with only ammonium and CBOD₅ being substantially higher on 5th November compared to the other two sampling dates. The amount of flow released by the WWTW did however vary from 0.061 to 0.266 m³.sec⁻¹ over the three sampling dates.

The influence of diffuse sources on the River made the model calibration process particularly difficult. The addition of three diffuse sources to the calibration model which are not confirmed by field measures, and combinations of these diffuse sources to the confirmation models, makes a claim of model confirmation very tentative to say the least. In this case, the data sets could not in all honesty be divided into a calibration data set and two confirmation data sets, as all data sets were needed to try and obtain some sort of idea of what processes are operating in the system. The model calibrated as it is, seems to indicate that there is input to the river of some water source of relatively pure water between sites 3 and 4 even during low flow. This could possibly be groundwater of some sort. The calibrated model in addition indicates that after the influence of heavy rain, there is a source of water input into the river of relatively high nutrient concentration between sites 3 and 4, and another source of high nutrient concentration water between sites 4 and 5 with the first source containing substantially more nutrients than the second.

However, the model calibrated as it is, did seem to estimate DO fairly well. Interestingly the re-aeration coefficient used is very low, ranging from 5 in the first two segments before the WWTW, to 0.04 for the rest of the segments downstream. This reaeration rate seems to estimate observed DO values fairly well for the two confirmation data sets. The

model in addition seems to generally simulate the pattern of CBOD₅, nitrates and ammonium fairly well. Interestingly, once again ammonium appears to be removed from the system fairly rapidly. Here a nitrification rate of 5 was used, which is in addition higher than the maximum listed in Bowie *et al.* (1985) of 3.

It was not possible to calibrate the model to the observed phosphate accurately, and the confirmation models did not simulate observed phosphate well. This could in part be due to the unknown source of phosphate between sites 5 and 6 as indicated in the calibration data set. Unknown diffuse sources of phosphate, settling of phosphate to the sediments, or movement of phosphate from the sediments to the water column could in addition be causing estimated phosphate results to be inaccurate.

8.4.3 Implications for modelling point sources versus diffuse sources with QUAL2K

This study shows that it is possible to adequately confirm QUAL2K in situations where diffuse sources do not influence water quality to any great effect. While it was possible to set up a QUAL2K model that explains all three observed data sets in the diffuse source dominated Bloukrans River catchment, confirmation that the model is correct is impossible without identifying and quantifying diffuse sources. This would be an extremely difficult process, as it is likely that the water quality signature from diffuse sources may vary substantially in space and time, and with varying rainfall event intensities. Azzellino *et al.* (2006) used QUAL2E to investigate point and diffuse sources on water quality in watersheds in Italy, where point and diffuse sources were stipulated indirectly by estimation from population equivalent specific emission factors for point sources and land use area-specific emission factors for diffuse sources. The researchers found that the technique worked badly for wet weather indicating that QUAL2E did not have enough information, or that the estimations for diffuse sources in terms of flow and nutrient concentrations were incorrect. This chapter addresses Aim 3, and research done with the model QUAL2K in this study indicates that in certain situations where point

sources dominate, and there are negligible inputs of nutrients from diffuse sources, the QUAL2K model can reasonably accurately simulate the effect of point sources on in-stream water quality. The application of the model to the Bloukrans however, shows that in situations where diffuse inputs are substantial, such is the case with the Bloukrans catchment, the model QUAL2K provides simulations of water quality that are highly uncertain, due to lack of data.

8.4.4. Potential use of QUAL2K in water quality and flow management

In cases during low flow where diffuse sources do not become a major factor, and in a river dominated by identified point sources that are monitored for quality of effluent, it may be possible to use QUAL2K successfully to manage point sources to control water quality downstream. The model can be used to predict in-stream water quality downstream of point sources, and hypothetical ‘what if’ scenarios can be investigated to determine what flow and pollutant concentrations from the point sources would improve the water quality situation downstream.

It has been shown in this study that QUAL2K does not seem to be able to estimate phosphate dynamics accurately. This could be due to various factors. There may be sources of phosphate in both the Buffalo and Bloukrans that were not identified in the study. The calibration data set in the Bloukrans for example, shows an elevated reading in phosphate at site 6 compared to site 5, which means somewhere between site 5 and 6, a source of phosphate that was not identified entered the river. This source is however not replicated in the two confirmation data sets. Diffuse sources of phosphate that were not identified could in addition be entering both the Buffalo and Bloukrans river, which will make the model estimations inaccurate. Another possibility that could be causing inaccuracies in the model is that the model could be inadequately simulating an important process in the system that would have an impact on phosphate concentration, such as bottom algae and phytoplankton uptake, sedimentation of phosphate, or movement of phosphate from the sediments to the water column. The data from the Buffalo River seems to show that phosphates are fairly quickly removed from the water column after

inputs from the WWTWs. This pattern was in addition observed by Rossouw and Quibell (1993) who used QUAL2E to simulate nutrient dynamics in the middle Vaal. Rossouw and Quibell (1993) concluded that many assumptions had to be made in simulating the high phosphate removal rate in the Vaal, and that further research was required to investigate whether phosphate loss was due to biotic uptake or sediment adsorption. This study, especially in regards to modelling diffuse sources, in addition made a lot of assumptions as to processes involved in influencing water quality, and sources of pollutants, that require further research.

The application of the QUAL2K model required dedicated field measures to be undertaken, as the available DWA historical monitoring data is inadequate to run a complex model such as QUAL2K, both in terms of the number of different water quality variables measured, and the frequency of measures. The model could be applicable to specific reaches that are highly impacted by point sources, where there are already programs in place that measure the load of nutrients being released from point sources. It is unlikely that QUAL2K could be routinely used in South Africa to manage water resources, because of the complexity of the model and the high data requirements. The investigation of QUAL2K, in addition demonstrates the potential suitability of catchment scale model frameworks such as BASINS (Wimberly and Coleman, 2005), for water resource management, since the water quality models used in these frameworks are often similar to QUAL2K in data requirements as they simulate the same processes. For example, BASINS uses QUAL2E as its water quality model (Tong and Chen, 2002). Therefore, the investigation into QUAL2K could provide an indication of the difficulties that would be experienced in applying BASINS to a catchment, and in addition how accurate such a model framework may be in simulating various in-stream water quality variables.

Chapter 9: Conclusions and Recommendations

9.1. Outcomes of the models investigated

Chapter 3 outlined simple statistical models to represent the relationship between flow and various water quality constituents using historical monitoring data from Department of Water Affairs (DWA) sites. Simple flow-concentration (Q-C) regression models (linear, logarithmic or power) were applied to flow and water quality data (Malan and Day, 2002a). The results showed that the Q-C model approaches to predicting water quality are limited. While relatively good R^2 values (in the range of 0 to 0.82, and 21 % of R^2 values > 0.5) were obtained for the linear regressions applied to flow versus salinity data, the model fits for flow versus nutrient data (phosphate or nitrite plus nitrate) were very poor (R^2 in the range of 0 to 0.42 for phosphate and 0 to 0.58 for nitrite plus nitrate). In addition, it was found that better model fits were obtained by regressing available water quality observations against daily flow data, in contrast to the method used by Malan and Day (2002a), who used monthly averaged flow and water quality measures in their Q-C regression models. At virtually all monitoring sites investigated, salinity showed an asymptotic decrease with increasing flow. The rate of decrease and shape of the regression curves in the regressions of salinity versus flow were, however, different between monitoring sites. The shape of the regression curves are probably a function of geological region and the complexity of hydrological (surface and subsurface) processes that contribute to streamflow. In contrast, the trend of phosphate and nitrite plus nitrate data with increasing flow was much less clear, with considerable scatter of points and no seemingly simple linear relationship with flow. It is probable that natural as well as anthropogenic factors in combination influence the concentration of nutrients in rivers, and the relationship of nutrient concentration with flow is consequently difficult to capture with relatively simple regression. This indicated that non-linear regression, and most likely some mechanistic model, would be more appropriate to explain the relationship between flow and nutrients. Also evident from this initial investigation of

historical flow and water quality monitoring data from DWA, is that there are very few water quality measures taken at high flows, which seriously limits the investigation of the relationship between water quality and high flow conditions.

Chapter 4 builds on a statistical model that assumes some mechanistic understanding of the relationship between phosphate and flow according to whether the sources of phosphate to a river are from point or diffuse sources. This mechanistic understanding is based on the work by Bowes *et al.* (2008). Bowes *et al.* (2008) found that the relationship between phosphate concentration and flow in their data depended on whether sources of phosphate originate from point or diffuse sources. Bowes *et al.* (2008) found that sites affected by point sources of phosphate showed an asymptotic decrease in phosphate with increasing flow, while sites affected primarily by diffuse sources of phosphate showed an increase in phosphate concentration with increased flow. In addition, they found that many sites had both point and diffuse phosphate influences, and developed a statistical model with two terms to model the trend, which is basically a non-linear regression model. However, the DWA data investigated in Chapter 4 had considerably more ‘noise’ than the data investigated by Bowes *et al.* (2008). The data analyzed by Bowes *et al.* (2008) showed less variance at low flows, presumably because point sources in the United Kingdom are better managed and consequently, effluent from point sources have a fairly constant flow and concentration. Much of the DWA data show definite point source influence at low flows, but the concentrations show a lot of scatter, with concentrations ranging from close to zero, to very high concentrations in some cases.

This indicates that point sources, such as waste water treatment works (WWTWs), in South Africa tend to release effluent that is highly variable in flow magnitude and nutrient concentration. This assertion is supported by WWTW effluent monitoring data (see Chapter 4), as well as data taken in the field for the Buffalo and Bloukrans River (see Chapter 8). These factors would have made the application of the model suggested by Bowes *et al.* (2008) to the DWA data impractical. Therefore, a model with both mechanistic and statistical elements was developed (see Chapter 4). The model developed

seemed to fit observed data fairly well. It is important to recognize that the model is probably only appropriate to streams and small rivers, as there would be additional processes that play dominant roles in larger systems that the model would not be able to simulate. For example, high flow periods common in larger rivers could re-introduce nutrients to the water column through scouring of the bottom sediments. In addition, the model developed can not be confirmed in the conventional way. This is due to the random method of simulating the point source influence, which means matching estimated concentrations with observed concentrations would be inappropriate, as the model tries to mirror the range and scatter (uncertainty) of the point source influence, rather than try and simulate individual observed measures. The model appears to be successful for nitrite plus nitrate in explaining the relationship of this nutrient with flow in addition to phosphate. For the case study gauging station investigated, effluent data collected by DWA, as well as point source data collected in the field, seemed to confirm the point source parameter values determined in the model. In addition, the land cover within the catchment of a case study gauging station showing a strong diffuse nutrient signature was investigated. The land cover of the case study catchment comprised of high percentages of land cover categories that one would associate with diffuse nutrient input, such as irrigated agricultural land. The two case studies investigated indicate that the model is based on sound mechanistic understanding of the processes affecting the relationship between nutrients and flow.

Chapter 5 presents models that relate land cover information to nutrients. These models relate the diffuse signatures estimated by the model developed in Chapter 4, to land cover and flow information. The models do not attempt to correlate point source influences with land cover, as the assumption was made that land cover would have a greater correlation with diffuse sources and that the effects of point source and diffuse source influences can be separated within historical data. Models were developed to represent all regions, and models were developed to represent specific regions, in an attempt to isolate natural related signatures from anthropogenic signatures, as one would expect natural signatures to be related to regions, while anthropogenic related signatures may be

expected to be similar across regions. The regions chosen were based on natural water quality regions proposed by Day *et al.* (1998). Models were also developed to represent just land cover influences from a 1 km riparian zone on each side of the river reach within a catchment. One would expect certain land cover categories to contribute to a natural background nutrient concentration in rivers, while other land cover categories indicating anthropological use of land, may be responsible of anthropological influence on in-stream nutrient concentrations. Principal Component Analysis (PCA) was used in these analyses to obtain an initial indication of which land cover types explained the variation in the diffuse source parameters. The PCA results indicated that the land cover categories that explained the variation of the diffuse signature parameters are land cover categories that one would intuitively associate with diffuse source influences, such as irrigated agricultural land and urban areas. The results of the PCA also indicated that in some regions, wetlands explain water quality variation, by actually lessening the effect on diffuse sources of the other land cover types found in the same catchment. This result is consistent with the understanding that wetlands can behave as nutrient ‘sinks’. The PCA analysis indicated that there may in addition be natural nutrient signatures in many regions, as land cover types such as undegraded bush and unimpacted grassland explain the variation in diffuse signatures in many regions. The models implemented in Excel using Solver in many cases did not use all the land cover types that PCA had indicated as explaining variation in diffuse signatures. This could be because some land cover categories have a much stronger influence on the diffuse signatures than others. For some regions, the Excel models obtained the best model fit to observed data by using only constants within the model equation, and did not incorporate land cover information at all. This could indicate that land cover information in these cases, was not strongly correlated to diffuse sources. This analysis suffered from various shortcomings, such as a lack of representative sites, especially when monitoring data were divided into regions. The analysis also suffered because DWA monitoring data have very few water quality observations at high flows, which precludes the adequate representation of the full range of the diffuse source signature within catchments. The regionalization scheme chosen in this analysis may not have been entirely optimal, and perhaps dividing the data into

smaller regions would have resulted in stronger models, but alternative regionalization schemes to use for South Africa that are based on water quality are lacking in the published literature. There are alternative regionalization schemes for South Africa, such as ecoregions (Kleynhans and Hill, 1999) or bioregions (Eekhout *et al.*, 1996). The bioregion regionalization scheme is based on the broad distributions of macroinvertebrates and fish, while the ecoregions regionalization scheme is based on physiography, climate, rainfall, geology and potential natural vegetation. The regionalization scheme as proposed by Day *et al.* (1998) is based on natural water quality for rivers, and was therefore deemed the most appropriate regionalization scheme for the Land Cover Model. The land cover information may also not be wholly appropriate for this type of study, however, these data were the only data easily available. More specific information may have been more appropriate for relating to diffuse nutrient signatures, for example population density in urban areas, and farm fertilization and irrigation information. Despite the uncertainties of the models, this research does provide useful models to relate land cover to diffuse signatures to obtain an idea of possible diffuse signatures when no water quality information is available.

Chapter 6 extended a model given by Hughes (2008). This model is a simple mass-balance water quality model that was designed to simulate salinity within ephemeral or perennial streams by simulating the salinity of flowing or static water within channel pools. The model accepts hydrological data from the monthly time step Pitman Model, which includes simulations of surface runoff, interflow runoff, ground water, upstream inflow, abstractions, pool volume and downstream flow volume. The water quality model accepts these flow components and calculates the change in salt storage by simulating the exchange of salts between the channel bed and the soil of the banks surrounding the channel. The water quality component of the model assumes that the different flow components have independent water quality signatures which are set as parameters. The water quality model simulates the salt mass-balance in the channel water and includes a channel bank storage component. In Chapter 6, the water quality model was extended to simulate the effect of saline agricultural return flow on river salinity. An initial sensitivity

analysis of the model was performed by applying the model to the Balfour River, which is a tributary of the Kat River in the Eastern Cape. The hydrological model estimated the observed flow fairly well, while the salinity simulation for a scenario of no irrigation return flow was a fairly accurate estimation of the observed salinity. The Balfour River site could not be used to fully test the model as there is only a limited amount of irrigation practiced within the catchment. The model was therefore also tested on the middle reaches of the Breede River in the Western Cape where there is intensive irrigation and where the observed impacts on water quality are extremely large (Flugel and Kienzle, 1989; Kirchner *et al.*, 1997).

Only a rough calibration of the model to match simulated flow and salinity data to observed data was attempted for the site upstream of the study area. This was deemed adequate, as the aim of the research was to simulate irrigation processes within the study area, and there were a paucity of data with which to calibrate the model for the upstream area. Even though only a rough calibration of the hydrological and water quality models was performed for the upstream site on the investigated reach of the Breede River, the hydrological and water quality model performed fairly well for estimating the flow and salinity within the study reach. The salinity estimations generally mirrored the seasonal variation as well as the numerical range of the observed salinity values. The observed salinity trends show a drastic change from the upstream site to the downstream site, with the downstream site showing a much larger salinity signature, and a much stronger seasonal signature with a pronounced summer peak and winter minimum. The model was able to simulate both the seasonal signature and the range in salinity signatures for the downstream site. The model indicates that the majority of the salt entering the river in the studied area is due to irrigation return flow of which the biggest impact is during the summer months when there is low natural flow and high irrigation. These findings are backed up by the conclusions made by Kirchner *et al.* (1997). The outcomes of Chapter 6 show that the model can accurately simulate the change in salinity within rivers due to irrigation return flow, and that the model can be applied to ephemeral streams as well as permanently flowing rivers such as the Breede River.

Chapter 7 showed that it is possible to use the sparse DWA historical water quality monitoring data to approximately quantify the coefficients involved in nitrification and ammonification. The model investigated used flow, organic nitrogen and ammonium measures from DWA historical data to estimate the reaction coefficients involved in nitrification. This research once again highlights the importance of water quality measures taken at high flows, so as to obtain a good indication of diffuse inputs into a river. The measures taken at high flows were more useful in calibrating and confirming the model than measures taken at low flow, which typically show high variability because of equally variable point source influences. The research highlights the importance of organic nitrogen, or Kjeldahl nitrogen measures in DWA monitoring data for modelling nitrification. This conclusion is supported by the outcomes of Chapter 8, where it was found that measures of organic nitrogen were needed to accurately simulate nitrification in QUAL2K. In addition, it was found that the value of the reaction coefficient that controlled the simulated rate of nitrification of ammonium to nitrite was large compared to published values used in other models, as observed ammonium values had a very short residence time in the rivers investigated, and tended to drop in concentration in a very short time as they moved downstream. This is in accordance with the findings in Chapter 8, where the calibrated values of the nitrification coefficients were similarly high for both the Buffalo and Bloukrans Rivers. This research highlighted the fact that the paucity of measures of water quality at high flows and measures of Kjeldahl nitrogen within DWA historical monitoring data are an obstacle to the accurate modelling of nitrification. The estimations of nitrification coefficient values by this model can be used in more complex models such as QUAL2K, where often, data for accurately calibrating more complex and data intensive models may be lacking.

Chapter 8 investigated the application of the in-stream model QUAL2K to a stretch of the Buffalo River and the Bloukrans River. The Buffalo River is a river occurring in the Eastern Cape, South Africa, and the stretch of the Buffalo River investigated is influenced by two wastewater treatment plants, as well as textile effluent release. Because the study

was conducted during the dry season and during a major drought, the river was not influenced by diffuse sources. The Bloukrans River occurs in the Eastern Cape and flows through Grahamstown, where a waste water treatment works is a major point source introducing effluent as the stream leaves the city. Apart from the one major point source, the Bloukrans River receives diffuse sources of nutrients within the study area as the catchment in this region is extensively used for irrigated agriculture and irrigated pasture land.

This investigation showed that WWTW effluent flow dominated total flow in the section of the Buffalo River investigated during the time period the field work took place. This highlights the fact that in many smaller rivers and streams, effluent release flow from point sources form a major part of the total flow during low flow periods, and in this regard, it is vitally important to find methods, such as the model QUAL2K, that would allow managers to manage point sources so as to improve water quality downstream. South Africa is typically a dry country and receives rainfall that is below the global average. Therefore, effluent return flow probably dominates total flow in many smaller rivers and streams, except during the sporadic rainfall events. This investigation showed that the WWTWs on the Buffalo River released highly variable effluent in terms of both nutrient concentrations and flow. This perhaps indicates that WWTWs in South Africa have not been managed optimally, and indicates that it would be difficult to model the effects of WWTW effluent release on downstream water quality in many cases, as a constant effluent release and nutrient concentration cannot be assumed. This investigation showed that the QUAL2K model performed fairly well on the point source dominated Buffalo River.

The application of the QUAL2K model to the Bloukrans River could only be calibrated and confirmed by assuming a relatively large input of flow and nutrients from diffuse sources downstream of the WWTW. Even though the model gave fairly good confirmation results, there remain many uncertainties in that no actual observed data on the assumed downstream diffuse source inputs were available, and all diffuse inflow and

nutrient concentrations were assumed. The assumption that there was some diffuse input downstream of the WWTW is valid, as during field collection trips after relatively strong rainfall, flow became noticeably stronger at a certain point downstream even though there were no evident point sources or tributaries. The land use in this section of the Bloukrans is heavily utilized as dairy cow pastures, with the grazing land being irrigated by treated water obtained directly from the WWTW. The extra flow into the Bloukrans could not have been entirely ground water, as the extra inflow had to be assigned relatively high nutrient concentrations so that the model would give sensible results. The application of the QUAL2K model to the Bloukrans River shows that there is a high degree of uncertainty associated with calibrating the model to a river strongly affected by diffuse sources, as information on diffuse source flow and nutrient concentration is usually not available.

The application of both models showed that it is important to take measures of organic nitrogen, so as to simulate the process of ammonification and nitrification. Both applications of the QUAL2K model show that ammonium has a very short residence time, with high ammonium concentrations released in effluents decreasing rapidly as they move downstream. The QUAL2K models for both the Buffalo and the Bloukrans used high reaction coefficients for nitrification, so as to account for the rapid drop in ammonium concentrations. The drop in ammonium may in part be because aquatic flora are absorbing ammonium in preference to other nitrogen species. Although the QUAL2K model does simulate the uptake of nutrients by primary production, the model could only account for the rapid decrease in ammonium by setting the reaction coefficient that controls the rate of conversion of ammonium to nitrite to a high value of 7 and 5 for the Buffalo River and Bloukrans Stream respectively. This is higher than the upper range of 3 that Bowie *et al.* (1985) found from a review of the literature. This could be because organisms within the Buffalo and Bloukrans Rivers assimilate ammonium in preference to other forms of nitrogen, which the model was not set up to simulate because of a lack of information. Or perhaps nitrification coefficient values derived from models subsequent to the literature review by Bowie *et al.* (1985) are higher than the range given

by Bowie *et al.* (1985). Possibly, the microorganisms that occur within the Buffalo and Bloukrans Rivers facilitate a much faster rate of nitrification of ammonium. The QUAL2K model could not satisfactorily estimate phosphate concentrations for both the Buffalo River and the Bloukrans River, indicating that perhaps an important process is not being simulated by the model, or that there are incomplete data on point or diffuse sources of phosphate in the river stretches investigated.

9.2. Aims addressed in the research

Chapter 1 listed 4 aims that this thesis will attempt to address, namely:

Aim 1: Can the relationship between flow and water quality be accurately represented by simple statistical models?

Aim 2: Can relatively simple models accurately represent the relationship between flow and water quality?

Aim 3: Can the effect of diffuse sources be omitted from a water quality model and still obtain realistic simulations, and if so under what conditions?

Aim 4: Can models that solely use historical monitoring data, accurately represent the relationships between flow and water quality?

Simple statistical regression models that describe the relationship between flow and a chosen water quality variable are according to the Beck (1987) definition, Class III models. These models have been criticized for their lack of mechanistic capability, and are more suited to describing relationships within certain observed datasets, and are not appropriate for extrapolating the relationship into the future, or investigating management scenarios (Beck, 1987; Chapra, 2003). The results of Q-C regression models reinforce this assertion, as the method obtained a poor fit between flow and nutrients, while the model fit between flow and salinity is better. The poor fit between flow and nutrients within the regressions indicate that there are some mechanistic processes in play between flow and nutrients that simple regressions are not able to simulate. Chapter 3 addresses Aim 1, with the definite answer to the question being that in general, simple statistical

models have very limited use in representing the relationship between flow and water quality. The Q-C regression method uses historical monitoring data, but in some cases, there were not enough data available at particular gauging stations to produce valid regressions. Therefore, the method in certain cases cannot produce valid regressions using solely historical monitoring data, although for many other cases, there were enough data to investigate relationships through regression. Therefore, Aim 4 was positively answered in many cases using this method, but not for all cases due to a lack of data.

The Mechanistic/Statistical Nutrient Model investigated in Chapter 4, answered Aim 2 positively, by indicating that a relatively simple model that incorporates some mechanistic modelling capability, can reasonably accurately simulate the relationship between flow and nutrients. Although the point source component of the model incorporates some mechanistic understanding of important processes, the diffuse source component of the model is a simple regression model, and the Mechanistic/Statistical Nutrient Model would not be able to predict the effect of changing land cover/use on the diffuse nutrient input. This model is able to describe the relationship between flow and water quality, using solely historical monitoring water quality and flow data, and therefore answers Aim 4 positively.

The Land Cover Model, presented in Chapter 5, shows that a relatively simple statistical model may be able to give accurate predictions of diffuse source inputs of nutrients, by investigating the relationship between the parameters that signify the diffuse source input in the Mechanistic/Statistical Nutrient Model, and land cover within a catchment. The model gave results with high uncertainty because of a lack of land cover information, but the model does show that once again, Aim 2 can be answered positively. The Mechanistic/Statistical Nutrient Model in combination with the Land Cover Model, shows that in the context of modelling the relationship between flow and nutrients within catchments with varying land cover, it is important to consider diffuse sources emanating from different land cover types. Therefore, in this case, Aim 3 is answered negatively for this type of modelling.

The Mass – Balance Salinity Model presented in Chapter 6, once again indicates that a relatively simple model can accurately represent the relationship between flow and water quality. In this case, a limited number of processes that contribute to salinization were represented, i.e. natural salinization and salinization resulting from irrigation. This model once again answers Aim 2 positively.

The Simple Nutrient Model, presented in Chapter 7, once again answers Aim 2 positively, in showing the relatively simple models that focus on a few key water quality variables, and only attempt to simulate a few key processes, can be valuable in simulating relationships between flow and water quality. This model has specifically been designed to use the sparse DWA historical monitoring data, therefore, the relative success of the model indicates that certain models can use historical monitoring data to achieve a good description of the relationship between flow and a limited number of water quality variables.

The study of QUAL2K in Chapter 8, indicates that in certain circumstances, it is possible to disregard inputs of diffuse sources of nutrients, when studying the relationship between flow and water quality, and therefore answers Aim 3 positively. The model became much more uncertain once diffuse inputs became more important, and diffuse sources had to be incorporated.

9.3. The effect of data scarcity on model development and confirmation

Lack of data was a recurring problem in the application of all models tested in this study. The DWA historical monitoring data were used in many models and were found to suffer many shortcomings. Even though flow data at DWA gauging stations are relatively comprehensive, water quality measures tend to be few and sporadic. The paucity of water quality data hindered the investigated models in Chapter 3, as many gauging stations had to be discarded for lack of data. Lack of water quality data also led to many gauging

stations being discarded in Chapter 4. Chapter 5 built on the work done in Chapter 4, and the low number of gauging stations for which diffuse and point source signature parameters were available, seriously undermined the power of the models developed in Chapter 5. While there are shortcomings in the data within the DWA gauging site data for nutrient water quality constituents, generally salinity measures are fairly well represented within the DWA data. This, as well as the fact that salinity is a conservative water quality constituent, makes the modelling of salinity using the DWA data entirely plausible, as was shown in Chapter 6. This is backed up by Wimberley and Coleman (2005) who stated that the DWA hydrological database provides much of the data that would be needed for salinity modelling. The lack of DWA nutrient data meant that initial investigations of QUAL2K in Chapter 8 using DWA historical data, resulted in models that made little sense as there were too little data to accurately calibrate the QUAL2K model. Therefore, DWA data were not used for QUAL2K and dedicated field work was undertaken to collect data. The lack of DWA water quality data meant that few comparisons between model estimated nutrient values and observed values were possible for the model developed in Chapter 7, which affected the calibration and confirmation process. In addition, there are few water quality measures taken at high flows, which seriously hinder any investigation of the relationship between water quality and high flows. This affected the models developed in Chapter 4, as diffuse signatures were hidden from the observed data for many of the DWA gauging stations investigated. This would have had a major consequence on the power of the models developed in Chapter 5, as gauging stations with no apparent diffuse signature indicated within their historical monitoring data, may well have shown a diffuse signature if more water quality measures at higher flows were taken. Consequently, there were less data with which to find a correlation between land cover and diffuse signatures within the DWA data. The range of water quality measures routinely undertaken by DWA is limited, constraining the investigation to a few water quality variables, such as salinity, phosphate and nitrate, which are relatively well represented within the DWA data. Additional investigations into the relationship between flow and turbidity for example, could have been attempted had turbidity measures been better represented within the DWA monitoring data. Chapter 7

highlighted the role of the paucity of organic nitrogen observations in the modelling of nitrification. The lack of chlorophyll-a concentrations forces models based on DWA historical data to exclude primary production processes (see Chapter 7). Chapter 8 showed that complex models with a time step of a day or shorter, are data intensive, and that while it is possible to obtain reasonable results with QUAL2K using daily grab samples, the models developed would have benefitted from field measures taken at shorter time intervals such as hourly. The models developed would have benefitted from field measures of organic nitrogen.

In most of the research chapters, lack of data contributed to an increase in uncertainty in the model results. In Chapter 5 for example, 95 % prediction limits were very wide in the land cover models. This was due to the high variance in the diffuse signature parameters for the DWA monitoring points used. A larger data set of data might well have decreased the uncertainty around the results.

9.4. Shortcomings and advantages of the investigated models in representing the relationship between flow and water quality

The statistical models outlined in Chapter 3 are the most simple to understand and to implement. Unfortunately, they really only give a good model fit to salinity (EC) data. Since the statistical models are developed using monitoring data obtained in the past, changes to rivers, such as changes in land use, and changes to the hydrological conditions of rivers such as additional reservoirs or interbasin transfers, could make Q-C models based on past data inaccurate. Accordingly, Q-C models are not appropriate for ‘what –if’ scenario investigations, unless the regression coefficients can be related in some way to measures of the factors forcing water quality variations. There does not appear to be enough data within the DWA database to establish such relationships.

The models presented in Chapter 4 incorporate some mechanistic understanding of the

relationship between flow and nutrients, depending on whether the source of nutrients is from point or diffuse sources. The model also manages to estimate the uncertainty of nutrient concentrations at low flows from point source signatures, by incorporating an element of randomness into the model. The model provides an estimation of a point source signature within observed data defined by four parameters, stipulating maximum point source flow, minimum point source flow, maximum point source concentration, and minimum point source concentration. These parameters would allow users of the model to investigate scenarios such as an increase or decrease in point source flow or concentration, by simply changing the parameters to reflect the point source changes expected under different scenarios. Alternatively, the same water quality parameters could be used with different scenarios of upstream flow and the consequences examined (in terms of changes in maximum concentration for example). The model is very simplistic in its conceptual understanding of the relationship between nutrients and flow, and does not attempt to simulate processes such as the background concentration of nutrients, re-suspension of nutrients due to scouring of the river bed during high flow, and many other processes. Therefore, it is prudent to restrict the application of this model to relatively small rivers and streams where there would not be as many additional processes in play, and where the model is applied, to recognize the model limitations. The model is relatively easy to understand and use.

The models in Chapter 5 that link land cover and flow to model estimated diffuse signatures in measured water quality data, are useful for obtaining an idea of what possible diffuse signature could be expected in a catchment where there are little or no water quality data available, but where land cover information is available, and daily flow data is measured or can be estimated. The models use the best information that is readily available at the scale needed, but various factors limit the power of the models, and increase the uncertainty in the estimations, which must be considered when using the models. These land cover models could be of great use in scenario investigations, where managers can obtain some idea of possible changes to diffuse signatures with flow in response to changing land cover. It is possible to combine the land cover models with the

point source component of the models presented in Chapter 4, to obtain complete hypothetical profiles of nutrient concentrations in response to flow, where different scenarios of point source input, land cover or changes in the flow regime can be investigated. The land cover models in Chapter 5 are simple to use as they are equations that can be implemented in Excel along with observed or predicted flow data. The land cover information used in the models is readily available.

The water quality model outlined in Chapter 6, which was extended from the model by Hughes (2008), uses the well established Pitman Model (Hughes, 2004) as its hydrological module. There is a great deal of experience of the use of this model in South Africa and it is widely used in a variety of resource assessment projects. Regional parameters are available for the whole of South Africa (Middleton and Bailie, 2005). The results of Chapter 6 indicate that the water quality model can accurately simulate in-stream salinity within regions of little or no irrigation, to regions of intense irrigation, and the model can be applied to both ephemeral streams and large permanently flowing rivers. The parameters of the water quality component of the model can be obtained by calibrating the model to observed data, or by examining observed water quality data for boreholes and springs in the catchment of the modelled reach. There is a strong trend of increasing salinity within South African water resources, therefore, a model to estimate in-stream salinity would be of great value for managing water resources. The model is especially applicable to a region such as the middle Breede River which is dramatically affected by saline irrigation return flow. ‘What if’ scenario investigations could be performed with the model by increasing or decreasing the hypothetical irrigation area within the modelled catchment. The model is simpler than that given by Herold and le Roux (2004) which is also designed to simulate the effects of irrigation return flow on salinity. However, the preliminary investigations of the model investigated in Chapter 6 show that it can accurately simulate in stream effects of saline irrigation return flow, despite its simplicity. The simplicity of the model may well be an advantage as it may be easier to calibrate and would require less data than the model given by Herold and le Roux (2004).

The nutrient model outlined in Chapter 7 has been specifically designed to be able to predict the nitrification process by using the sparse DWA historical monitoring data, a perceived gap in the available modelling tools within South Africa. Because of the DWA data limitations, the model simulates only the fate of the nitrogen species due to ammonification and nitrification. Therefore, it would not be appropriate to use this model as the final predictor of nutrient concentrations downstream, if factors such as primary production and sediment processes were to be considered. Rather, the model would be used to obtain some idea of what reaction coefficients to use for nitrification in a more comprehensive model, in a situation where there is a lack of data with which to calibrate a more comprehensive model. Even though the model has been designed to use sparse DWA monitoring data, it was found that there are very few DWA gauging station data that can actually be used to obtain accurate results from the model. This is because of the small number of observations of organic nitrogen in the DWA datasets.

The investigation of the QUAL2K model in Chapter 8 shows that the model has some use in predicting the effect of point sources on water quality downstream. This model could be of great use for management of rivers dominated by point sources, or during low flow periods when point sources are dominant in affecting water quality. QUAL2K can allow management scenarios to be investigated, as the model will predict changes to water quality downstream in response to changes to the flow or concentration of the point source effluent, or in response to changes to the amount of natural flow in the reach. The research in Chapter 8 indicates that QUAL2K may not be able to estimate phosphate concentrations accurately, although further research and better calibration of the model may rectify this problem in the future. QUAL2K does however require a relatively large amount of field data to give accurate results. The model is not simple to use, and potential users of the model would have to have some background knowledge of how the model works, or at least some knowledge of the processes the model attempts to simulate. At this stage, there do not appear to be many examples of published work where researchers used QUAL2K, neither in South Africa nor globally. This could be because QUAL2K is a

relatively new model, and current research on the model is yet to be published. Unfortunately, there are few critical assessments of the model in the literature, nor examples that one could follow in applying the model.

9.5. Recommendations for model use in the context of IWRM in South Africa

The statistical models developed in Chapter 3 are really only appropriate for predicting the response of salinity to changing flow patterns. One must in addition consider that any change in the hydrological profile of the river, such as additional reservoirs since the model was constructed, would compromise the predictive ability of the model. As there are no mechanistic components to the models, they are of little use in situations where the sources of salinity and/or the flow regimes of a river are likely to change after different types of water resources development. The statistical models have the advantage of being simple and easy to understand, and information derived from the models should be obtainable fairly quickly and easily, using DWA historical monitoring data.

The mechanistic model developed in Chapter 4 could give an indication of what possible nutrient signature to expect due to diffuse sources during high natural flow. The separation of the point source signature from the diffuse source signature, and the ability to adjust the point signature parameters, allows for investigations of the effect of different magnitudes of point source loadings on water quality downstream. The model includes some indication of uncertainty around the point source signature component. This is important, as the model would give some indication of risk if it were used in management. This model could be used in place of more complex models such as QUAL2K, to manage point sources, using only DWA historical monitoring data, and hypothetical additions or reductions to point source loading. Of course, an instream model such as QUAL2K is preferable, but data limitations and resources often preclude the use of such models. It is, however, recommended that this model only be used on

smaller rivers and streams, as many more complex processes such as scouring of the river channel during high flow occur in larger rivers which could lead to higher nutrient concentrations at higher flow which are unrelated to diffuse sources. The model could be used within the IWRM context to allow decision makers to determine what quantities and qualities of effluent flow released by point sources, would maintain downstream pollution levels within acceptable limits. The model could also be useful within scenario analyses, where hypothetical increases or decreases of released effluent effect on downstream water quality can be investigated. Predicting water quality variations in ungauged catchments is an internationally recognized problem that has been perceived as a research priority (Sivapalan *et al.*, 2003). If there are some data or estimation of point source load within a catchment, and some data on possible diffuse source loading due to land use, the model could be of particular use for determining the water quality profile in relation to flow in ungauged catchments. The models have been shown to be able to generate data that is sufficiently accurate for decision making, in that the models provide an indication of the range of nutrient values that can be expected relative to water quality standards. They are fairly easy to implement, and use available DWA historical monitoring data.

The land cover models developed in Chapter 5 are an extension of the models developed in Chapter 4, as they aim to quantify the diffuse source signatures using land cover data. The land cover models could be of great use to quantify diffuse input of nutrients in relation to flow, in ungauged catchments where there is information on land cover. Of course, as Chapter 5 has shown, one must be aware of the uncertainty surrounding these predictions when applying the model. It is preferable to use the regional model or the regional model considering just the riparian zone, than the model that incorporates data from all regions. This is because Principal Component Analysis (PCA) indicated that stronger relationships were evident between land cover and the diffuse source parameters for regional data as compared to data for all regions. If only flow and point source loading data were available in a catchment, one could hypothetically obtain the profile of the response of nutrient concentration to flow by using the point source component of the model from Chapter 4, with the appropriate regional land cover model from Chapter 5.

The models should be reasonably understandable and easy to implement, as they are simple equations that can be implemented within a spreadsheet. Figure 9.1 shows an example of how the models developed in Chapters 4 and 5 can be used in scenario analysis, where management scenarios such as increased abstraction, changes in land cover, and changes to point source effluent load can be investigated.

The mass-balance salinity model described in Chapter 6 could be of great value in managing rivers and catchment land use within regions of intense irrigation where saline irrigation return flow is likely to be a problem. By changing the hypothetical irrigated land use area within a catchment, the model can show what area of irrigated land could be utilized within a catchment before a certain upper limit of in-stream salinity is exceeded. It has been demonstrated within a limited number of case studies, that the model is able to simulate the variability of salinity in an acceptable manner. Potentially, the model could be incorporated into a model framework, which would be relatively easy for managers to use.

The model investigated in Chapter 7 could be used in an initial investigation of catchments where there are some DWA historical monitoring data, to obtain an indication of what nitrification coefficients to use in the calibration of a more complex model such as QUAL2K. The advantage of this model to decision makers is that the model is able to

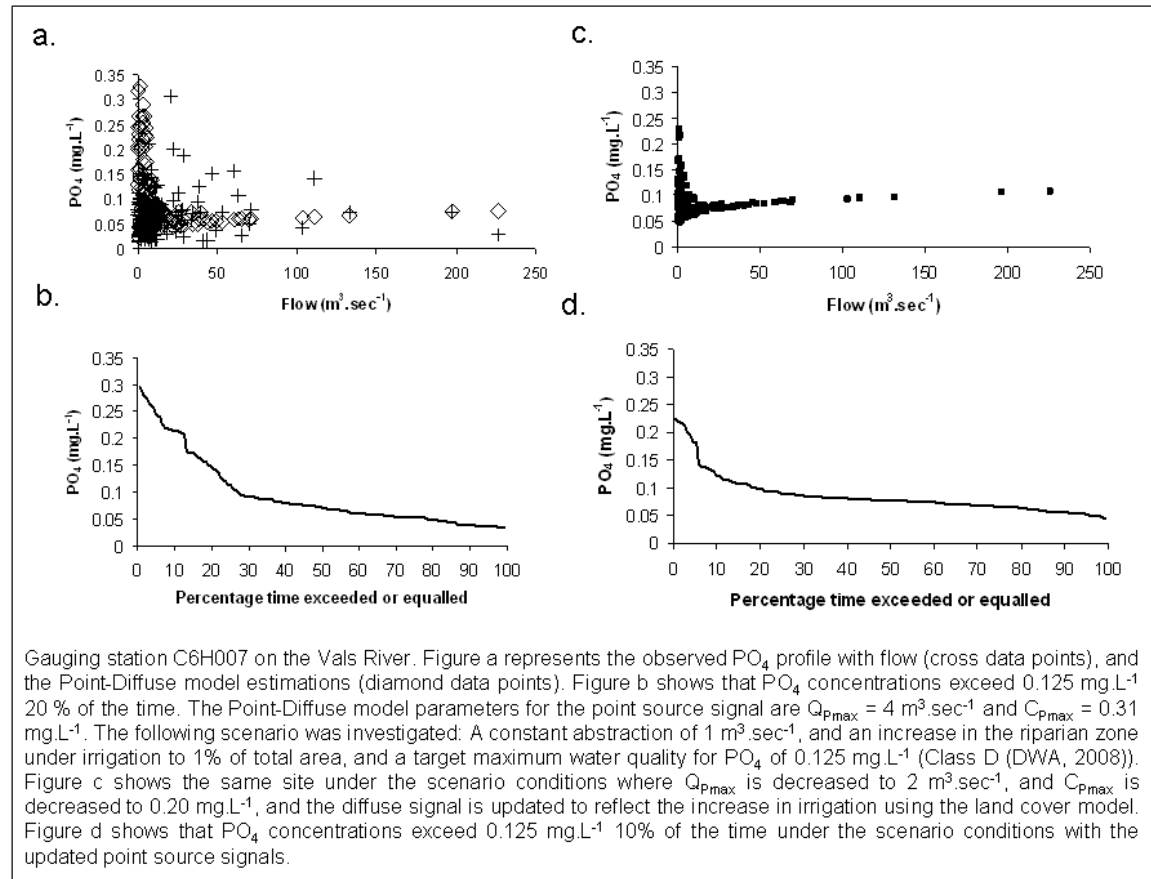


Figure 9.1. An example of how the Mechanistic/Statistical Nutrient model and the land cover models developed in Chapters 4 and 5 can be used in scenario analysis for management.

quantify nitrification coefficients, using available DWA historical monitoring data. Unfortunately, although there is some information on organic nitrogen, many DWA datasets do not have organic nitrogen measures, and therefore the model is precluded from being run on these data sets. In situations where the model can be run, information can be obtained fairly quickly. The model in its present state would have to be run by an expert, unless the model can be incorporated within a modelling framework that is relatively easy to use.

The model QUAL2K investigated in Chapter 8 would be appropriate for estimating the effect of point sources on water quality downstream on a river stretch that is dominated by point sources, or during low flow periods when diffuse sources will not come into play. This model takes some initial field data collection to calibrate, but after calibration, and provided that point source flow and water quality is monitored accurately, the model could give accurate estimations of water quality downstream. QUAL2K is a complex model, and should be used in place of a model such as that from Chapter 4, if processes such as primary production and sediment processes are important. The model is also applicable to larger rivers, as opposed to the model in Chapter 4 which should be restricted to smaller rivers and streams. QUAL2K predicts the concentrations of a range of water quality measures such as oxygen, while the simpler model from Chapter 4 does not. Dedicated data collection would have to be performed to obtain useful information from this model, and this could delay a decision making processes if the model was used. The model would require substantial investment in time and money to collect additional data. Calibration of the model would require an expert, while running the calibrated model would require managers to be trained. The model itself is free of charge and can be downloaded over the internet. QUAL2K is unlikely to be used by decision makers, unless a specific case of predicting the effect of effluent flow on downstream water quality within a complex system allows no other alternative models to be used.

9.6. The argument for investigating multiple models in this research

This research presents a range of models with which to investigate the relationship between flow and water quality. The models range from simple statistical models to complex mechanistic models, and from models that simulate one or two processes to a model that attempts to simulate a range of complex processes. In addition, the majority of models presented, simulate the relationship between flow and a few important water quality constituents, such as salinity or nutrients, while the more complex model QUAL2K, has been designed to estimate the fate of a large range of water quality constituents such as carbonaceous biological oxygen demand (CBOD) and dissolved oxygen. The question may be asked whether the investigation of one complex watershed scale modelling framework such as BASINS (Wimberley and Coleman, 2005) would have been better suited for addressing the aims of this research. While the investigation of a single model would have been easier, there are many benefits derived from exploring multiple modelling approaches.

The overall aim of this thesis is to explore the relationship between water quality and flow. While existing water quality models would certainly incorporate the effects of flow on water quality, this would only be one of many processes affecting water quality that models would simulate. For example, while QUAL2K would be able to simulate the effect of point source input into a river or changes in natural flow on water quality downstream, the model also attempts to simulate many other processes which are not directly or strongly linked to flow, such as the effect of primary production on dissolved oxygen levels over a 24 hour period as light levels change, or temperature effects on reaction coefficients controlling chemical processes within the water column or sediment. It would be difficult to explore the relationship between flow and water quality in such complex models, as fundamental relationships between flow and water quality represented in the model are hidden behind extra model complexity that is not relevant to this research. In contrast, this research investigated modelling techniques that explored the basic and most fundamental relationships between flow and water quality.

This research investigated various models of varying degrees of complexity. In an implementation context, this has several advantages. Specific models are suitable for specific circumstances which are linked to modelling requirements, data availability, costs, expertise and time. Q-C models of the relationship between flow and salinity may be entirely suitable for some modelling requirements, while complex models such as QUAL2K would be better suited in cases where point sources need to be controlled to achieve downstream water quality targets. The presented models operate over a range of temporal scales. The models investigated used data ranging from long term historical data such as the models presented in Chapters 3, 4, 5, 6 and 7 to the daily time step model QUAL2K investigated in Chapter 8. The models investigated operate at different spatial scales, such as the in-stream QUAL2K, to the regional catchment scale land cover models presented in Chapter 5. Data availability precludes the use of many complex models in most cases and the research presented here has concentrated on developing models that can use the readily available DWA historical monitoring data. Many of the models presented in this research are relatively simple and would be cost effective to implement.

The Q-C statistical regressions presented in Chapter 3 would fall into the Class III group of models as defined by Beck (1987), while QUAL2K investigated in Chapter 8 would fall into the Class I group of models. Beck (1987) warns that Class III models are too simple to provide realistic simulations, and this was precisely the conclusion reached in Chapter 3, where the salinity Q-C regressions were based on past data, and would provide erroneous simulations under changed future conditions. Of even greater concern is that simple Class III models could give erroneous simulations with high confidence. Beck (1987) states that complex Class I models provide simulations of reality that have a high degree of uncertainty, as they consist of a collection of hypotheses that are impossible to verify as correct. The reasons for this are given in Chapter 2. The development of Class II models which simulate a few essential processes that drive ecological functioning should therefore be encouraged as the model predictions can be assigned some indication of uncertainty (Beck, 1987; McIntyre, 2003). The majority of models investigated in this

research can be classified as Class II models as defined by Beck (1987), for example the models presented in Chapters 4, 5, 6 and 7. While scientists and engineers at universities and research institutes have tended to prefer more complex models, it has been shown that managers who routinely use models for decision making, tend to use relatively simple models (Reckhow, 1994). Successful cases studies of large mechanistic models aiding decision making, have generally been rare (Reckhow, 1994). This tends to support the argument for the development of relatively simple models that achieve specific management requirements.

It must be considered that many existing models have been developed in countries outside of South Africa, and might not be entirely suitable for South African conditions. For example, QUAL2E was developed to be well suited to the U.S. regulatory framework, as polluters are set a wasteload allocation. A wasteload allocation is the maximum amount of waste that can be discharged to a river while still meeting water quality standards under low flow conditions. QUAL2E was designed specifically to simulate steady streamflow conditions where there is steady effluent discharge as specified in the water quality regulations for wasteload allocation (Shanahan *et al.*, 1998). While source directed controls are part of the regulatory framework in South Africa, it has been demonstrated in Chapter 8, that effluent releases from point sources in South Africa are generally highly temporally variable in both effluent pollutant concentration and effluent flow rate. The models developed in this research have used exclusively South African monitoring data in the model construction and are therefore, appropriate for South African conditions, except for the investigation of QUAL2K which is an internationally developed model.

9.7. Possible further research directions

This research has identified the main processes that determine the effect of flow on water quality, and various models have been developed to simulate these processes. While these models are important as they fulfill the objectives of this research, a modelling

framework that is broad enough to be applicable to many situations, but would still allow modelling of specific processes or water quality variables without being data intensive, might be suitable for management of water resources. In this regard, future research could investigate modelling frameworks such as the Integrated Nitrogen Model for Multiple Source Assessment in Catchments (INCA) (Jarvie *et al.*, 2002; Wade *et al.*, 2002; Whitehead *et al.*, 1998), or the Better Assessment Science Integrating Point and Non-point Sources (BASINS) framework (Wimberley and Coleman, 2005). These modelling frameworks could be investigated to determine whether the main processes that determine the effect of flow on water quality, are adequately represented within the frameworks.

While some of the models investigated in this thesis have some estimation of uncertainty, the issue of uncertainty was not a central theme in this research. However, without some estimation of uncertainty, model predictions for management decisions do not give an indication of the risk involved in making a management decision. Incorporation of uncertainty into the investigated models has been left as an issue for further research.

The mechanistic understanding behind the Mechanistic/Statistical Nutrient models developed in Chapter 4 is relatively simple, and it has been recommended that the models be applied to relatively small rivers and streams, as the models do not simulate certain processes that can be expected in larger rivers such as re-suspension of nutrients from the sediments during higher flows. Further research is needed to incorporate simulation of a larger number of processes. For example, the effect of antecedent rainfall on the diffuse source signature is something that the present model structure does not consider.

The land cover models developed in Chapter 5 lack predictive power as the land cover data were perhaps not entirely appropriate for correlation with diffuse sources, although the land cover data are the only relevant data that is readily available. Further research could investigate what other sort of land use data could be associated with diffuse source signatures, such as fertilizer application rates on agricultural land, or population density

in urban areas. Future research on this model could also investigate seasonality in relation to rainfall, irrigation and fertilizer application and the effect of these on a diffuse signature of nutrients.

The salinity model investigated in Chapter 6 incorporates the effect of saline irrigation return flow. If it is perceived that there is value in extending the model further, other processes that affect salinity, such point source inputs of salinity for example, could be added to the model. There were also limited applications of the model in Chapter 6, and further case studies of the model are needed to further assess the model's accuracy and usefulness.

The investigation of QUAL2K in Chapter 8 was limited in that the model was applied to two river reaches of relatively low order, and both river reaches occur in the Eastern Cape. Further investigation is required where the model is applied to larger rivers, or rivers in a different part of the country.

All the models investigated in this research, require further investigation in regards to use of the models in scenario analysis for management. An important scenario to investigate is that of changed climatic conditions, especially in regards to higher temperatures, as climate change is a major concern.

Appendix A

Appendix A Table 1: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
A2H012	Crocodile River	25° 48' 37.72"	27° 54' 34.37"	Kalkheuwel 493 Jq on Krokodilrivier	1990	2008
A2H014	Hennops River	25° 47' 54.31"	27° 59' 7.188"	Schurveberg 488 Jq at Skurveberg on Hennopsrivier	1990	2007
A2H021	Pienaars River	25° 7' 40.00"	27° 37' 44.00"	Pienaars River at Buffelspoort	1990	2008
A2H048	Crocodile River	25° 34' 23.77"	27° 45' 16.01"	Krokodilpoort 418 Jo /Thaba Moya on Krokodilrivier	1990	2008
A2H059	Crocodile River	25° 12' 23.00"	27° 33' 28.79"	Vaalkop 192 Jq at Atlanta on Krokodilrivier	1990	2008
A2H060	Crocodile River	25° 3' 43.99"	27° 31' 15.99"	Crocodile River at Nooitgedacht	1990	2008
A2H061	Apies River	25° 28' 0.012"	28° 15' 48.99"	Apies River at Rondavel	1990	2007
A2H083	Crocodile River	25° 43' 28.99"	27° 51' 5.115"	Hartbeespoort Dam on Crocodile Riv: Down Stream Weir	1992	2008
A2H094	Hex River	25° 32' 51.68"	27° 21' 8.387"	Down Stream Weir for Bospoort Dam	1992	2004
A2H106	Pienaars River	25° 7' 51.99"	27° 48' 39.99"	Klipvoor Dam on Pienaars River: Down Stream Weir	1992	2007
A2H116	Krokodil River	24° 41' 42.50"	27° 24' 32.61"	Haakdoordrift 373 Kq Down Stream Weir for Paul Hugo	1990	1995
A4H002	Mokolo River	24° 16' 55.99"	28° 5' 25.00"	Mokolo River at Zandrivier/Vaalwater	1990	2006
A4H004	Matlabas River	24° 9' 33.98"	27° 28' 46.99"	Matlabas River at Haarlem East	1990	2006
A4H005	Mokolo River	24° 4' 58.00"	27° 46' 23.01"	Mokolo River at Dwaalhoek	1990	2001
A4H007	Tambotie River	23° 45' 47.01"	27° 54' 30.99"	Tambotie River at Blakeney	1991	2006
A4H008	Sterkstroom River	24° 12' 56.98"	27° 58' 24.99"	Sterkstroom River at Doornspruit	1990	2007
A5H004	Lephalala River	23° 58' 51.99"	28° 23' 59.99"	At Muisvogelkraal on Lephalala	1994	2001

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
A5H006	Limpopo River	22° 56' 5.999"	28° 0' 15.01"	At Botswana Sterkloop on Limpopo River	1991	2006
A6H006	Little Nyl	24° 41' 57.01"	28° 24' 33.01"	Little Nyl River at Nylstroom	1990	2007
A6H009	Mogalakwena River	22° 35' 49.99"	28° 53' 11.00"	Mogalakwena River at Leniesrus/Aden	1990	1996
A6H010	Bad Se Loop	24° 34' 41.01"	28° 38' 24.00"	At Vischgat on Bad Se Loop	1990	2007
A6H011	Groot-Nylrivier	24° 45' 39.99"	28° 20' 44.01"	At Modderpoort on Groot-Nylrivier	1990	2007
A6H012	Olifant Spruit	24° 39' 52.99"	28° 28' 32.01"	Olifant Spruit at Olifantspoort	1990	2008
A6H018	Rasloop River	24° 46' 14.98"	28° 20' 54.99"	Rasloop River at Modderpoort	1993	2007
A6H019	Hessie Se Water	24° 39' 45.00"	28° 27' 19.00"	At Rietspruit on Hessie Se Water	1997	2007
A7H001	Sand River	22° 54' 29.98"	29° 36' 51.01"	At Waterpoort on Sandrivier	1990	1999
A9H001	Luvuvhu River	23° 6' 42.01"	30° 23' 22.99"	Luvuvhu River at Weltevreden/Schuynshoog	1990	2006
A9H013	Mutale River	22° 26' 8.015"	31° 4' 33.99"	At Mutale Bend Kruger National Park on Mutale	1990	2007
B1H005	Olifants River	26° 0' 23.00"	29° 15' 14.00"	Olifants River at Wolvekrans	1990	2007
B1H010	Olifants River	25° 53' 30.01"	29° 18' 15.01"	Witbank Dam on Olifants River: Down Stream Weir	1990	2008
B1H012	Little Olifants River	25° 48' 29.01"	29° 35' 12.01"	At Rondebosch U/S Middelburg on Klein Olifants	1990	2007
B1H015	Little Olifants River	25° 46' 23.98"	29° 32' 36.99"	Middelburg Dam on Lit..Olifants Riv: Down Stream	1990	2007
B1H020	Koringspruit River	26° 6' 20.98"	29° 19' 50.98"	At Vaalkranz U/S Vandyksdrift on Koringspruit	1990	2006
B1H021	Steenkool Spruit	26° 8' 9.995"	29° 16' 11.99"	Steenkool Spruit at Middeldrift	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
B2H003	Bronkhorstspuit	25° 47' 56.00"	28° 44' 8.987"	At Bronkhorstspuit on Bronkhorstspuit	1991	2008
B2H014	Wilgerivier	25° 49' 36.01"	28° 52' 50.98"	At Onverwacht on Wilgerivier	1991	2008
B2H015	Wilgerivier	25° 36' 57.99"	29° 0' 57.99"	At Zusterstroom on Wilgerivier	1994	2007
B3H001	Olifants River	24° 55' 0.011"	29° 23' 3.012"	Olifants River at Loskop North	1993	2008
B3H021	Elands River	24° 55' 31.00"	29° 19' 27.98"	Elands River at Scherp Arabie	1994	1998
B4H003	Steelpoort River	25° 1' 44.00"	29° 51' 24.01"	Steelpoort River at Buffelskloof	1990	2008
B4H005	Waterval River	25° 4' 6.995"	30° 36' 5.003"	Waterval River at Modderspruit	1990	2007
B4H007	Little Spekboom River	25° 0' 29.01"	30° 29' 57.98"	Little Spekboom River at Potloodspruit	1990	2008
B4H009	Dwars River	24° 54' 45.00"	30° 6' 11.98"	Dwars River at Dwarsrivier	1990	2007
B4H010	Dorps River	25° 4' 31.00"	30° 26' 20.00"	At Lydenburg Nature Reserve on Dorpsrivier	1990	2008
B6H001	Blyde River	24° 40' 45.01"	30° 48' 8.999"	Blyde River at Willemsoord	1990	2007
B6H003	Treurrivier	24° 41' 9.995"	30° 48' 54.00"	Willemsoord on Treurrivier	1990	2008
B6H004	Blyde River	24° 27' 30.99"	30° 49' 39.00"	Blyde River at Chester	1990	2008
B6H006	Kranskloof Spruit	24° 55' 38.99"	30° 32' 45.99"	Kranskloof Spruit at Krugerspost	1990	2007
B7H015	Olifants River	24° 3' 32.00"	31° 14' 13.99"	Olifants River at Mamba/Kruger National Park	1990	2008
B7H019	Ga-Selati River	24° 2' 3.011"	31° 7' 24.99"	Ga-Selati River at Loole/Foskor	1990	2008
B8H008	Letaba River	23° 39' 29.01"	31° 3' 2.557"	At Letaba Ranch on Groot Letaba	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
B8H009	Letaba River	23° 52' 49.00"	30° 22' 0.983"	The Junction on Groot-Letaba	1990	2007
B8H014	Letaba River	23° 52' 50.01"	30° 4' 46.99"	At Grysappel on Groot Letaba	1990	2007
B8H033	Little Letaba River	23° 16' 51.59"	30° 32' 35.01"	Tabaan State Land on Klein-Letaba	1996	2007
C1H002	Klip River	27° 10' 9.984"	29° 14' 2.003"	Sterkfontein Delangesdrift on Kliprivier	1990	2006
C1H007	Vaal River	26° 50' 23.99"	29° 43' 24.99"	Vaal River at Goedgeluk/Bloukop	1990	2008
C1H008	Waterval River	26° 51' 39.99"	28° 53' 4.992"	Elandslaagte on Watervalrivier	1990	2008
C1H015	Klip River	27° 10' 18.98"	29° 14' 11.00"	Sterkfontein Delangesdrift at Steel Bridge on Kliprivier	1995	2008
C2H001	Mooi River	26° 38' 53.01"	27° 5' 21.98"	Mooi River at Witrand	1990	2007
C2H004	Suikerbosrant River	26° 40' 14.70"	28° 1' 49.58"	Suikerbosrant River at Vereeniging Weir	1995	2008
C2H005	Rietspruit	26° 43' 46.99"	27° 43' 4.008"	Rietspruit at Kaalplaats Rw RV2	1990	2008
C2H007	Vaal River	27° 0' 36.39"	26° 41' 53.08"	Pilgrims Estate 272 at Orkney on Vaalrivier	1990	2008
C2H008	Vaal River	26° 44' 7.007"	27° 36' 30.99"	Vaal River at De Pont/Lindequesdrift	1990	1996
C2H018	Vaal River	26° 58' 13.00"	27° 12' 39.99"	Vaal River at De Vaal/Schoemansdrift	1990	2008
C2H021	Klip River	26° 27' 12.99"	28° 5' 8.988"	Klip River at Witkop Rw K25	1990	1996
C2H061	Vaal River	27° 23' 22.99"	26° 27' 50.00"	Palmietfontein 250 at Klipplaatdrift on Vaalrivier	1990	2008
C2H069	Moorivierloop River	26° 22' 32.01"	27° 13' 50.98"	Moorivierloop River at Blaauwbank	1990	2008
C2H073	Skoonspruit River	26° 59' 4.991"	26° 37' 56.20"	At Goedgenoeg 150M U/S Orkney Bridge on Skoonspruit River	1990	2008

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
C2H085	Mooi River	26° 52' 49.00"	26° 57' 53.99"	Mooi River at Hoogekraal/Kromdraai	1990	2008
C2H140	Vaal River	26° 44' 11.00"	27° 35' 33.00"	Vaal River at Woodlands/Goose Bay Canyon	1997	2008
C3H003	Harts River	27° 34' 23.01"	24° 44' 47.00"	At Taung on Hartsrivier	1990	2007
C3H007	Harts River	27° 54' 10.00"	24° 36' 56.01"	Espagsdrif Seoding 25 Bridge at The Weir on Harts River	1990	2008
C3H016	Harts River	28° 22' 36.98"	24° 18' 11.01"	At Delpportshoop Lloyds Weir on Hartsrivier	1995	2007
C4H017	Sand River	28° 7' 0.011"	26° 43' 31.00"	Sand River at Doringrivier/Bloudrif	1996	2007
C5H003	Modder River	29° 9' 37.00"	26° 34' 23.98"	At Likatlong /Sannaspos on Modderrivier	1991	2007
C5H007	Renosterspruit	29° 8' 39.98"	26° 19' 5.015"	At Shannon Valley on Renosterspruit	1990	2007
C5H012	Riet River	29° 39' 29.01"	25° 58' 23.98"	Riet River at Kromdraai/Rietwater	1990	2007
C5H014	Klipdrift River	29° 2' 31.99"	24° 36' 5.115"	Klipdrift And Part of Kookfontein 109 at Klipdrift River	1992	2006
C5H016	Riet River	28° 57' 36.00"	24° 14' 32.99"	At Estate Biesiesbult Aucampshoop on Rietrivier	1990	1999
C5H018	Modder River	29° 2' 35.98"	24° 38' 26.98"	Modder River at Tweerivier	1992	1998
C5H022	Kgabanyane River	29° 17' 8.016"	26° 55' 18.98"	Kgabanyane River at Bedford	1992	2007
C5H023	Kgabanyane River	29° 17' 9.996"	26° 45' 51.01"	Kgabanyane River at Dankbaar	1990	2002
C5H035	Modder River	29° 1' 41.98"	24° 38' 21.01"	@ Twee Rivier D/S Twee Rivier on Modder River	1992	2007
C5H048	Riet River	29° 1' 59.98"	23° 58' 59.98"	At Zoutpansdrift on Rietrivier	1990	2008
C5H053	Modder River	28° 56' 56.00"	26° 19' 18.01"	Modder River at Glen	1999	2008

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
C5H054	Renosterspruit	28° 58' 0.012"	26° 19' 59.01"	At Bishops Glen on Renosterspruit	1995	2007
C6H001	Vals River	27° 26' 29.00"	26° 59' 11.00"	Vals River at Roodewal	1994	2008
C6H002	Vals River	27° 23' 54.99"	26° 36' 52.99"	Vals River at Grootdraai/Bothaville	1990	2008
C6H003	Vals River	27° 23' 59.99"	26° 37' 28.99"	Vals River at Mooifontein/Bothaville	1992	2005
C6H007	Vals River	27° 40' 15.99"	27° 14' 12.98"	Vals River at Kroonstad Bridge Old Barend Wessel	1995	2007
C7H006	Renoster River	27° 2' 39.98"	27° 0' 17.99"	Renoster River at Arriesrust	1990	2007
C8H001	Wilge River	27° 16' 26.00"	28° 29' 23.99"	Wilge River at Frankfort	1990	2008
C8H003	Cornelisrivier	27° 50' 41.99"	28° 57' 43.99"	At Warden on Cornelisrivier	1990	2008
C8H004	Liebenbergsvlei River	27° 42' -2.55"	28° 19' 18.01"	Liebenbergsvlei River at De Molen/De Welkom	1990	1996
C8H011	Elandsrivier	28° 9' 38.98"	28° 52' 28.99"	Killarney 604 on Elandsrivier	1990	1997
C8H020	Liebenbergsvlei River	27° 41' 21.01"	28° 22' 41.98"	Liebenbergsvlei River at Roodekraal	1996	2008
C8H022	Wilge River	27° 17' 56.00"	28° 29' 45.99"	Wilge River at Slabberts/Kimberley	1999	2008
C8H026	Liebenbergsvlei River	27° 25' 38.99"	28° 31' 32.98"	At Frederiksdal on Liebenbergsvlei River	1990	2008
C8H027	Wilge River	27° 18' 2.557"	28° 35' 12.98"	At Ballingtomp on Wilge River	1990	2008
C8H028	Wilge River	27° 48' 10.00"	28° 46' 5.987"	Wilge River at Bavaria Flood Section	1992	2008
C9H009	Vaal River	28° 30' 56.98"	24° 36' 3.995"	Vaal River at De Hoop	1990	2007
C9H010	Vaal River	28° 24' 20.98"	24° 16' 18.01"	Wilmea Vaal Gamagara 0.85KM After Confluence of Harts	1991	2008

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
C9H021	Vaal River	27° 40' 9.012"	25° 37' 5.015"	Bloemhof Dam on Vaal River: Down Stream Weir	1990	2008
C9H024	Vaal River	28° 42' 41.40"	24° 4' 22.40"	Smidts Drift Outspan 23 Schmidtsdrift @ Weir	1995	2007
D1H001	Wonderboom Spruit	31° 0' 2.988"	26° 21' 11.01"	Wonderboom/Stormb..Spruit at Diepkloof/Burgersdorp	1990	2007
D1H003	Orange River	30° 40' 46.99"	26° 42' 44.99"	Orange River at Aliwal North	1990	2008
D1H006	Kornet Spruit	30° 9' 37.00"	27° 24' 6.011"	Kornet Spruit at Maghaleen	1990	2008
D1H009	Orange River	30° 24' 20.87"	27° 20' 19.67"	Orange River at Oranjedraai	1990	2008
D1H011	Kraai River	30° 49' 50.01"	26° 55' 17.00"	Kraai River at Roodewal	1990	2007
D1H033	Malibamatso River	29° 28' 0.012"	28° 37' 59.98"	Malibamatso River at Paray Lesotho	1990	2007
D2H035	Caledon River	28° 52' 59.98"	27° 53' 24.00"	Caledonriver at Ficksburg/Ficksburg Bridge	1994	2007
D2H037	Caledon River	29° 36' 33.01"	27° 3' 56.01"	Caledon River at Wilgedraai/Hobhouse	1995	2008
D3H008	Orange River	28° 57' 47.01"	19° 9' 8.999"	Orange River at Pella Mission	1992	2008
D3H012	Orange River	29° 59' 27.99"	24° 43' 27.98"	Orange River at Dooren Kuilen Down Stream D3R003	1990	2008
D3H013	Orange River	30° 35' 2.004"	25° 25' 10.99"	Roodepoort on Oranjerivier	1991	2008
D3H015	Seekoei River	30° 32' 3.011"	24° 57' 42.98"	Seekoei River at De Eerste Poort	1991	2008
D7H002	Orange River	29° 39' 5.003"	22° 44' 47.00"	At Prieska on Orange	1990	2003
D7H005	Orange River	28° 27' 38.98"	21° 14' 56.00"	Orange River at Upington	2002	2007
D7H008	Orange River	29° 1' 46.99"	22° 11' 16.00"	Orange River at Boegoeberg Reserve/Zeekoebaart	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
D7H014	Orange River	28° 46' 5.015"	20° 43' 14.01"	Orange River at Kakamas South/Neusberg Left Side	1995	2007
E1H013	Olifants River	32° 35' 44.98"	19° 0' 33.98"	Middelpos 553 at Citrusdal on Olifantsrivier	1995	2008
E2H002	Doring River	32° 30' 10.00"	19° 32' 8.988"	At Elands Drift Aspoort on Doringrivier	1990	2007
E2H003	Doring River	31° 51' 37.00"	18° 41' 15"	At Melkboom on Doringrivier	1990	2007
G1H013	Berg River	33° 7' 30"	18° 51' 20.98"	Berg River Site 5 -D/S of G1H013Q01 Drieheuvels	1990	2008
G1H031	Berg River	32° 59' 48.98"	18° 46' 44.00"	At Misverstand Die Brug on Bergrivier	1990	2008
G1H036	Berg River	33° 26' 6.000"	18° 57' 24.98"	At Vleesbank Hermon Bridge on Bergrivier	1990	2008
G1H043	Sandspruit River	33° 9' 41.00"	18° 53' 35.01"	At Vrisgewaagd on Sandspruit	1990	2007
G2H015	Eerste Rivier	34° 1' 49.00"	18° 44' 53.98"	At Faure on Eersterivier	2002	2004
G2H020	Eerste Rivier	33° 56' 57.98"	18° 50' 18.99"	At Fleurbaai Stellenbosch on Eersterivier	1990	2007
G4H005	Palmiet River	34° 11' 48.98"	18° 58' 50.01"	Palmiet River at Van Aries Kraal/Applethwaite	1990	2008
G4H006	Klein River	34° 24' 20.98"	19° 36' 2.016"	Klein River at Can Q5-8/Wagenboomsdrift	1990	2007
G4H007	Palmiet River	34° 19' 46.99"	18° 59' 25.00"	Palmiet River at Farm 562-Welgemoed/Kleinmond	1990	2007
G4H014	Botrivier	34° 14' 7.008"	19° 12' 55.00"	At Roode Heuvel on Botrivier	1990	2008
G5H008	Sout River	34° 17' 30.98"	20° 1' 24.99"	Sout River at Kykoedy	1990	2007
H1H003	Bree River	33° 22' 51.99"	19° 18' 10.00"	Bree River at Ceres Commonage	1990	2007
H1H006	Bree River	33° 25' 18.01"	19° 16' 5.987"	Bree River at Ceres Commonage/Witbrug	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
H1H007	Wit River	33° 34' 5.016"	19° 8' 53.98"	Wit River at Drosterskloof	1990	2007
H1H013	Koekedou River	33° 21' 32.00"	19° 17' 53.98"	Koekedou River at Ceres/Persephone	1990	2007
H2H006	Hex River	33° 34' 39.00"	19° 30' 11.98"	Hex River at Glen Heatlie	1990	2007
H3H011	Kogmanskloof River	33° 52' 14.98"	20° 0' 11.98"	Kogmanskloof River at Goudmyn	1990	2007
H4H015	Houtbaais River	33° 59' 34.00"	19° 49' 14.98"	Houtbaais River at Schurfberg	1990	2007
H4H016	Keisers River	33° 56' 25.00"	19° 50' 27.99"	Keisers River at Mc Gregor Commonage/Vrolykheid	1990	2007
H4H017	Bree River	33° 49' 5.016"	19° 41' 40.99"	Bree River at La Chasseur	1990	2007
H4H018	Poesjenels River	33° 52' 2.999"	19° 43' 1.992"	Poesjenels River at La Chasseur	1990	2007
H4H019	Vink River	33° 49' 9.984"	19° 47' 43.00"	Vink River at De Gorree	1990	2006
H4H020	Nuy River	33° 43' 5.016"	19° 28' 55.99"	Nuy River at Doornrivier	1990	2008
H5H002	Bree River	33° 53' 18.99"	20° 0' 47.98"	Bree River at Goudmyn/Rooibrug	1990	1995
H5H003	Boesmans River	34° 2' 25.00"	19° 58' 48.00"	Boesmans River at Boschjesmans Rivier	1990	2007
H5H004	Bree River	33° 53' 52.00"	20° 0' 46.00"	Bree River at Wolvendrift/Secunda	1990	2007
H6H005	Baviaansrivier	34° 1' 44.00"	19° 33' 27.00"	At Genadendal Mission Station on Baviaansrivier	1990	2007
H6H009	Riviersonderend	34° 4' 32.01"	20° 8' 44.01"	Riviersonderend at Reenen	1990	2008
H7H006	Bree River	34° 3' 56.98"	20° 24' 15.01"	At Swellendam on Bree River	1990	2008
H8H001	Duiwenhoks River	34° 15' 2.016"	20° 59' 32.99"	Duiwenhoks River at Dassjes Klip	1990	2007

Appendix Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
H9H005	Goukou River	34° 5' 31.99"	21° 17' 43.00"	At Farm 216 Swq 4A-11 on Goukou	1990	2007
J1H018	Touws River	33° 41' 49.99"	21° 8' 45.99"	Touws River at Okkerskraal	1990	2007
J1H019	Grootrivier	33° 45' 0"	21° 26' 40.99"	At Buffelsfontein Van Wyksdorp on Grootrivier	1990	2007
J4H002	Gourits River	33° 58' 50.01"	21° 39' 11.98"	Gourits River at Zeekoedrift/Die Poort	1990	2007
J4H003	Weyers River	34° 1' 53.00"	21° 35' 14.99"	Weyers River at Weyers Rivier	1990	2007
J4H004	Langtou River	33° 59' 14.99"	21° 46' 36.98"	Langtou River at Langfontein	1990	1996
K1H004	Brandwag River	34° 1' 54.98"	22° 3' 11.98"	At Brandwacht on Brandwagrivier	1990	2007
K1H005	Moordkuil River	34° 2' 22.99"	22° 7' 59.98"	Moordkuil River at Banff	1990	2007
K3H001	Kaaimans River	33° 58' 14.98"	22° 32' 53.98"	Kaaimans River at Upper Barbiers Kraal	1990	2007
K3H003	Maalgate River	34° 0' 20.98"	22° 21' 3.995"	Maalgate River at Knoetze Kama/Buffelsdrift	1990	2007
K4H001	Hoekraal River	33° 58' 46.99"	22° 48' 2.557"	Hoekraal River at Eastbrook	1990	1993
K4H002	Karatara River	33° 52' 51.99"	22° 50' 18.99"	Karatara River at Karatara Forest Reserve	1990	2007
K4H003	Diep River	33° 54' 42.01"	22° 42' 20.98"	Diep River at Woodville Forest Reserve	1990	2007
K5H002	Knysna River	33° 53' 24.00"	23° 1' 54.01"	Knysna River at Milwood Forest Reserve	1990	2007
K6H001	Keurbooms River	33° 48' 10.00"	23° 8' 9.995"	Keurbooms River at Mkama/Peters River	1990	2007
K7H001	Bloukrans River	33° 57' 15.01"	23° 38' 30.01"	Bloukrans River at Lottering Forest	1990	2007
L6H001	Heuningkliprivier	33° 12' 10.00"	24° 14' 8.015"	At Campherspoort on Heuningkliprivier	1993	2006

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
N2H007	Sundays River	33° 5' 39.98"	25° 0' 46.00"	Sundays River at De Draay	1991	1996
N4H001	Sundays River	33° 22' 40.00"	25° 21' 16.99"	Sundays River at Korhaanspoort/Courans Drift	1997	2007
N4H003	Sundays River	33° 34' 53.00"	25° 40' 27.98"	Sundays Riv at Addo Drift East/Addo Bridge	1992	1997
N4H005	Coerney River	33° 30' 45.00"	25° 39' 33.01"	Coerney River at Selborne/Carlton	1994	2007
P1H003	Boesmans River	33° 19' 45.01"	26° 4' 39.00"	Boesmans River at Donker Hoek/Alicedale	1990	2007
P3H001	Kariega River	33° 33' 15.98"	26° 36' 12.99"	Kariega River at Smithfield/Lower Waterford	1990	2007
P4H001	Kowie River	33° 30' 23.00"	26° 44' 40.99"	Kowie River at Bathurst/Wolfscrag	1990	2007
Q1H001	Great Fish River	31° 54' 11.01"	25° 28' 55.99"	At Katkop on Groot-Visrivier	1972	1993
Q1H012	Teebus River	31° 33' 29.98"	25° 32' 35.98"	Teebus River at Jan Blaauws Kop/Beaconsfield	1978	2007
Q1H013	Klein-Brakrivier	31° 46' 40.00"	25° 19' 5.987"	Zeeven Fonteynen 254 on Klein-Brakrivier	1982	2005
Q2H002	Great Fish River	31° 54' 18.00"	25° 25' 47.99"	At Zoutspans Drift Zoutpan on Groot-Visrivier	1977	2008
Q3H004	Pauls River	32° 2' 8.015"	25° 31' 14.98"	Pauls River at Coutzenburg	1977	2007
Q3H005	Great Fish River	32° 5' 17.98"	25° 34' 33.99"	At Rietfontyn Waaikraal on Groot-Visrivier	1977	1993
Q4H003	Vlekpoort River	32° 37' 44.00"	25° 52' 59.98"	Vlekpoort River at Roberts Kraal	1972	1990
Q4H013	Tarka River	32° 18' 50.00"	25° 44' 29.00"	Tarka River at Bridge Farm/Tarka Bridge New Weir	1993	2007
Q6H002	Baviaansrivier	32° 37' 44.00"	25° 52' 59.98"	At Melrose on Baviaansrivier	1977	1980
Q6H003	Baviaansrivier	32° 36' 19.00"	25° 53' 6.000"	At Botmansgat De Klerkdal on Baviaansrivier	1980	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
Q7H005	Little Fish River	33° 5' 35.98"	25° 53' 36.99"	At Sout Vleij Sheldon on Klein-Visrivier	1976	2007
Q8H008	Little Fish River	32° 47' 9.996"	25° 36' 53.99"	Little Fish River -Doorn Kraal	1980	2007
Q9H002	Koonap River	32° 42' 50.00"	26° 17' 48.01"	Koonap River at Adelaide	1972	2007
Q9H012	Great Fish River	33° 5' 53.98"	26° 26' 44.01"	At Brandt Legte Piggots Bridge on Groot-Visrivier	1972	2007
Q9H013	Kap River	33° 21' 19.00"	26° 51' 42.98"	Kap River at Kap River Mountains/Forest View	1979	1991
Q9H016	Koonap River	32° 29' 57.01"	26° 21' 56.01"	Koonap River at Schurftkop	1981	1993
Q9H018	Great Fish River	33° 14' 16.00"	26° 59' 25.00"	At Matomelas Reserve Outspan on Groot-Visrivier	1972	2007
Q9H019	Balfour River	32° 33' 05.00"	26° 40' 17.00"	At Grey Kirk	1970	2005
Q9H029	Kat River	32° 45' 40.00"	26° 37' 46.00"	At Fort Beaufort	1970	2005
Q9H030	Koonap River	32° 27' 52.99"	26° 30' 38.98"	Koonap River at Frisch Gewaagd/Groenkop New Weir	1995	2007
R1H001	Tyume River	32° 45' 33.98"	26° 51' 19.00"	Tyume River at Goumahashe Reserve	1974	1980
R1H005	Keiskamma River	32° 45' 6.011"	27° 5' 26.98"	Keiskamma River at Zanyokwe/Sa Native Trust	1972	1995
R1H013	Keiskamma River	33° 0' 42.01"	26° 57' 16.99"	Keiskamma River at Kammas/Naudeshoek	1977	1986
R1H014	Tyume River	32° 38' 24.00"	26° 56' 9.995"	Tyume River at Kwa Khayaletu/Yantolas	1972	2007
R1H015	Keiskamma River	33° 11' 7.296"	27° 23' 26.70"	Farm 7 About 220M U/S of Howard Shaw Bridge on Keiskamma River	1972	2007
R2H001	Buffalo River	32° 43' 55.00"	27° 17' 37.00"	At Pirie Forest Reserve	1970	2005

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
R2H005	Buffalo River	32° 52' 31.00"	27° 22' 23.00"	At King Williams Town	1970	2005
R2H006	Mgqakwebe River	32° 51' 24.01"	27° 22' 35.00"	Mgqakwebe River at Msenge Ridge	1972	2007
R2H007	Zele River	32° 46' 45.01"	27° 23' 8.016"	Zele River at Braunschweig	1977	1981
R2H008	Quencwe River	32° 46' 5.015"	27° 22' 27.01"	Quencwe River at Braunschweig/Edendale	1972	2007
R2H009	Ngqokweni River	32° 55' 0.012"	27° 22' 23.01"	Ngqokweni River at Sheshegu 5/Mgqokweni 19	1972	2007
R2H010	Buffalo River	32° 56' 26.00"	27° 27' 41.00"	At 135 kwq U/S James McInt	1970	2005
R2H011	Yellowwoods River	32° 55' 29.60"	27° 28' 44.79"	Fort Murray North Outspan on Yellowwoods River	1972	1985
R2H012	Mgqakwebe River	32° 47' 12.98"	27° 15' 47.98"	Mgqakwebe River at Jefta 29/Pirie Mission	1972	1997
R2H015	Yellowwoods River	32° 55' 57.10"	27° 28' 22.11"	Fort Murray North Outspan at Bridge Ds of R2H015 on Yellowwoods River	1989	2003
R2H016	Zwelitsha Spruit	32° 56' 6.000"	27° 26' 48.01"	Jan Tzatzoes Location North 1924 at Malakalaka on Zwelitsha Spruit	1989	2007
R2H027	Buffalo River	32° 59' 37.00"	27° 37' 00.00"	At Mhlabati Needs Camp	1970	2005
R3H001	Gqunube River	32° 48' 10.00"	27° 51' 23.00"	Gqunube River at Outspan	1974	2003
S3H004	Swart - Keirivier	32° 2' 59.99"	26° 47' 17.01"	At Cathcarts Gift Endwell on Swart -Keirivier	1990	2007
S3H005	Oskraal River	32° 10' 51.99"	26° 49' 14.98"	Oskraal River at Whittlesea	1990	1997
S3H006	Klaas Smits River	31° 55' 23.98"	26° 47' 11.00"	Klaas Smits River at Weltevreden/Queenstown	1990	2007
S5H002	Tsomo River	32° 2' 35.98"	27° 49' 22.00"	At Wyk Maduma Tsomo on Tsomo	1995	2007
S5H004	Tsomo River	31° 47' 15.00"	27° 40' 45.01"	Tsomo River at Famini Location/Ncora Dam	1999	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
S6H001	Kubusi River	32° 34' 45.01"	27° 22' 0.011"	Kubusi River at Stutterheim	1990	2007
S6H002	Kubusi River	32° 34' 32.01"	27° 37' 23.01"	Kubusi River at Hammerhead/Thornhill	1990	1995
S6H003	Toise River	32° 30' 57.99"	27° 31' 28.99"	Toise River at Forkroad	1990	2007
S7H001	Gcuwa River	32° 19' 39.00"	28° 8' 40.99"	Gcuwa River at Butterworth	1998	2008
S7H004	Great Kei River	32° 30' 55.00"	28° 0' 56.01"	At Area 8 Springs B on Groot-Keirivier	1990	2007
T1H001	Xuka River	31° 40' 18.98"	28° 6' 38.98"	At Caca 45 Xukadrift on Xuka	1999	2007
T1H004	Mbashe River	31° 55' 8.004"	28° 26' 52.00"	At Bashee Bridge on Mbashe	1998	2007
T2H002	Mtata River	31° 35' 3.012"	28° 47' 6.000"	At Norwood Umtata on Mtata	1995	2006
T3H004	Mzimntlana River	30° 34' 5.987"	29° 25' 22.00"	Mzimntlana River at Slangfontein/Kokstad	1990	2007
T3H005	Tina River	31° 1' 53.00"	28° 52' 59.98"	Tina River at Mahlungulu	1995	2007
T3H006	Tsitsa River	31° 14' 12.98"	28° 51' 15.01"	Tsitsa River at Xonkonxa/Tsitsa Bridge	1995	2007
T3H007	Mzimvubu River	30° 51' 5.115"	29° 4' 13.00"	At N2 Umzimvubu Bridge Ku Makhola Mzinto on Mzimvubu River	1994	2007
T3H008	Mzimvubu River	30° 34' 14.98"	29° 9' 2.015"	Mzimvubu River at Kromdraai/Inungi	1990	2007
T4H001	Mtamvuna River	30° 44' 2.003"	29° 49' 41.98"	Mtamvuna River at Gundrift/Mtamvuna	1990	2007
T5H002	Bisi River	30° 24' 29.01"	29° 53' 59.99"	At Nooitgedacht Bisi on Bisi	1999	2007
T5H003	Poela River	29° 44' 48.98"	29° 32' 21.98"	Polela River at Coxhill/Himeville	1990	2007
T5H004	Mzimkhulu River	29° 46' 38.99"	29° 28' 14.98"	At Fp 1609030/The Banks on Mzimkhulu	1990	1992

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
T5H005	Nkonzo River	29° 59' 16.00"	29° 51' 6.011"	Nkonzo River at Dronkvlei/Kleinhoek	1990	1992
T5H007	Mzimkhulu River	30° 14' 48.98"	29° 55' 49.00"	At Bezweni/Island View on Mzimkhulu	1995	2007
T6H001	Mntafufu River	31° 29' 39.98"	29° 31' 45.01"	Mntafufu River at Lower Ntafufu 35	1998	2007
T6H004	Lusikisiki River	31° 19' 40.00"	29° 31' 42.99"	Xura River at Xura 27/Lusikisiki	1995	2007
U1H005	Mkomazi River	29° 44' 39.01"	29° 54' 20.98"	Mkomazi River at Lot 931821/Camden	1990	2004
U1H006	Mkomazi River	30° 10' 5.988"	30° 41' 52.00"	Shozi Delos Estate on Mkomazi	1990	2007
U2H022	Msunduze River	29° 39' 38.98"	30° 38' 12.98"	Msunduze River at Inanda/Nomfihlelo	1990	2008
U2H041	Msunduze River	29° 36' 27.00"	30° 27' -2.55"	Msunduze River at Hampstead Park/Moto-X Darv	1996	2008
U2H055	Mgeni River	29° 38' 30.98"	30° 41' 15"	At Inanda Location Egugwini on Mgeni	1990	2008
U4H002	Mvoti River	29° 9' 42.01"	30° 37' 46.99"	Mvoti River at Mistley	1990	2007
U6H002	Mlazi River	29° 44' 54.99"	30° 19' 8.003"	Bainsfield Nooitgedacht on Mlazi	1990	2007
U6H003	Mlazi River	29° 48' 12.99"	30° 30' 57.99"	At Umlaas Road on Mlazi	1990	2008
U8H003	Mpambanyoni River	30° 16' 18.01"	30° 41' 43.00"	Mpambanyoni River at Umbeli Belli	1994	2007
V1H001	Tugela River	28° 44' 8.015"	29° 49' 14.01"	Tugela River at Tugela Drift/Colenso	1990	2007
V1H010	Little Tugela	28° 49' 5.015"	29° 32' 42.00"	Little Tugela River at Winterton	1990	2007
V1H026	Tugela River	28° 43' 14.98"	29° 21' 33.01"	Tugela River at Kleine Waterval	1990	2008
V1H038	Klip River	28° 33' 42.01"	29° 45' 9.000"	Klip River at Ladysmith Townlands/Army Camp	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
V1H041	Mlambonja River	28° 48' 42.01"	29° 18' 42.98"	Mlambonja River at Kleinerivier	1990	2007
V1H058	Tugela River	28° 45' 43.99"	29° 17' 33.00"	Driel Barrage on Tugela River: Down Stream Weir	1990	2008
V2H002	Mooi River	29° 13' 9.983"	29° 59' 36.99"	At Mooirivier on Mooirivier	1990	2008
V2H004	Mooi River	29° 4' 14.98"	30° 14' 44.98"	Mooi River at Doornkloof	1990	2008
V2H006	Little Mooi River	29° 15' 29.01"	29° 52' 9.012"	Little Mooi River at Dartington	1995	2007
V3H010	Buffels River	28° 3' 32.00"	30° 22' 24.99"	At Tayside on Buffelsrivier	1990	2008
V5H002	Tugela River	29° 8' 26.01"	31° 23' 30.98"	At Mandini on Tugela River	1990	2007
V6H002	Tugela River	28° 45' 0"	30° 26' 34.00"	At Tugela Ferry on Tugela	1990	2007
V6H003	Wasbank River	28° 18' 33.98"	30° 8' 53.01"	Wasbank River at Kuick Vlei	1990	2007
V6H004	Sundays River	28° 24' 15.98"	30° 0' 47.01"	Klein Fontein 1262 Gt on Sundays River	1990	2001
V6H006	Sundays River	28° 14' 22.99"	29° 45' 15.98"	Sundays River at Waterfall	1990	2006
W1H009	Mhlatuze River	28° 44' 52.00"	31° 44' 44.98"	Mhlatuze River at Riverview 11459	1994	2008
W2H005	Wit-Mfolozi	28° 20' 17.98"	31° 22' 24.99"	At Overvloed/Ulundi on Wit-Mfolozi	1990	2007
W2H009	Wit-Mfolozi	27° 53' 49.99"	30° 53' 2.004"	At Doornhoek on Wit-Mfolozi	1990	2008
W3H008	Mkuze River	27° 36' 33.01"	31° 57' 26.99"	Mkuze River at Doornhoek	1993	2001
W3H015	Hluhluwe River	28° 2' 22.99"	32° 21' 5.115"	Hluhluwe River at Valsbaai/St Lucia Inflow	1990	2001
W4H003	Phongolo River	27° 25' 10.99"	31° 30' 36.00"	Phongolo River at The Bokfontein/Grootdraai	1990	1990

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
W4H004	Bivana River	27° 31' 38.99"	30° 51' 29.01"	At Welgelegen Pivaansbad on Bivane	1990	2007
W4H006	Phongolo River	27° 21' 48.99"	31° 46' 59.98"	Phongolo River at Mhlati	1990	2007
W5H005	Hlelo River	26° 49' 44.00"	30° 43' 41.98"	Hlelo River at Ishlelo	1992	2000
W5H006	Swartwater River	27° 6' 52.81"	30° 49' 53.39"	Swartwater River at Zwartwater	1992	2000
W5H008	Bonnie Brook	26° 28' 58.00"	30° 38' 4.992"	Bonnie Brook at Broadholms	1990	2007
W5H022	Assegaai River	27° 3' 54.68"	30° 59' 36.81"	At Zandbank on Assegaairivier	1993	2008
W5H024	Mpuluzi River	26° 23' 11.00"	30° 50' 44.01"	Mpuluzi River at Dumbarton	1990	2007
W5H025	Usutu River	26° 30' 44.99"	30° 47' 11.00"	Usutu River at Stafford	1990	2007
W5H026	Ngwempisi River	26° 40' 38.99"	30° 42' 6.984"	Ngwempisi River at Merriekloof	1992	2007
X1H001	Komati River	26° 2' 7.008"	30° 59' 50.99"	Komati River at Hooggenoeg	1990	2007
X1H003	Komati River	25° 40' 51.99"	31° 46' 59.98"	At Tonga on Komati River	1990	2007
X1H014	Mlumati River	25° 40' 18.01"	31° 34' 32.98"	Mlumati River at Lomati	1990	2007
X1H016	Buffel Spruit	25° 56' 49.99"	30° 34' 6.995"	Buffel Spruit at Doornpoort	1990	2007
X1H018	Komati River	25° 50' 16.00"	30° 24' 14.00"	Komati River at Gembokhoek	1990	2007
X2H005	Nels River	25° 25' 50.01"	30° 58' 0.012"	Nels River at Boschrand	1990	2007
X2H006	Crocodile River	25° 28' 9.983"	31° 6' 5.115"	At Karino on Crocodile	1990	2007
X2H015	Elands River	25° 29' 16.00"	30° 41' 51.00"	At Lindenau on Elandsrivier	1990	2007

Appendix A Table 1 continued: Department of Water Affairs (DWA) flow and water quality monitoring sites

Site	River Name	Lat	Long	Description	Data Availability	
					From	To
X2H016	Crocodile River	25° 21' 43.99"	31° 57' 24.01"	At Ten Bosch Kruger National Park on Crocodile River	1990	2007
X2H017	Crocodile River	25° 26' 16.00"	31° 38' 4.992"	Crocodile River at Thankerton/Kruger National Park	1990	1996
X2H022	Kaap River	25° 32' 31.99"	31° 19' 1.991"	Kaap River at Dolton	1990	2007
X2H031	South Kaap River	25° 43' 45.01"	30° 58' 44.00"	South Kaap River at Bornmans Drift	1990	2007
X2H032	Crocodile River	25° 30' 50.00"	31° 13' 27.98"	Crocodile River at Weltevrede	1990	2007
X2H036	Komati River	25° 26' 9.995"	31° 58' 55.99"	@ Komatipoort Kruger National Park on Komati River	1990	2007
X2H046	Crocodile River	25° 23' 56.00"	31° 36' 38.01"	Crocodile River at Riverside/Kruger National Park	1990	2007
X3H004	North Sand River	25° 4' 31.00"	31° 7' 53.00"	North Sand River at De Rust	1990	2007
X3H006	Sabie River	25° 1' 48.00"	31° 7' 36.01"	Sabie River at Perrys Farm	1990	2000
X3H008	Sand River	24° 46' 8.003"	31° 23' 24.00"	Sand River at Exeter	1991	2007
X3H015	Sabie River	25° 8' 12.98"	31° 56' 42.00"	Sabie River at Lower Sabie Rest Camp/Kruger Nat Park	1990	2007

Appendix A Table 2: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
A2H012	12.00	1.57	2.95	0.00		
A2H014	0.80	0.31	7.73	0.01		
A2H021	12.00	0.02	2.06	0.02		
A2H059	7.00	0.00	0.44	0.00		
A2H060	48.00	0.01	0.99	0.01		
A2H061	1.20	0.18	8.99	0.00		
A2H083	22.00	0.13	0.28	0.00		
A2H094	0.90	0.00	1.88	0.00		
A2H106	10.00	0.00	1.94	0.03		
A2H116	0.50	0.00	0.28	0.10	0.05	0.22
A4H002	1.60	0.50	0.13	0.00		
A7H001	1.50	0.00	0.10	0.00	0.02	0.32
A9H001	3.50	0.00	0.10	0.00		
B1H005	15.00	0.00	0.13	0.00	0.00	0.31
B1H010	19.00	0.00	0.09	0.00	0.00	0.28
B1H012	5.00	0.00	0.13	0.00	0.01	0.27
B1H015	0.70	0.00	0.23	0.00	0.01	0.19
B1H020	0.05	0.00	0.16	0.00	0.02	0.17
B1H021	0.40	0.00	4.07	0.00		
B2H003	2.30	0.00	0.18	0.00	0.01	0.29
B2H014	0.50	0.01	0.12	0.05	0.01	0.38
B3H021	0.20	0.00	0.13	0.01	0.02	0.28
B4H003	5.00	0.00	0.26	0.00		
B4H010	2.00	0.09	0.15	0.00		
B6H001	2.00	0.64	0.14	0.00		
B6H004	8.00	0.17	0.08	0.00	0.01	0.12
B7H015	15.00	0.00	0.34	0.00		
B7H019	5.00	0.00	1.00	0.00		
B8H008	15.00	0.03	0.21	0.00		
B8H009	0.80	0.01	0.39	0.00		
B8H014	0.50	0.01	0.34	0.00		

Appendix A Table 2. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
C1H002	11.00	0.01	0.55	0.00		
C1H007	6.00	0.01	0.66	0.00		
C1H008	7.00	0.01	3.06	0.00		
C2H001	0.80	0.05	0.51	0.00		
C2H004	1.80	0.55	1.40	0.00		
C2H021	13.00	0.18	1.43	0.09		
C2H069	0.30	0.04	3.55	0.00		
C2H073	0.50	0.03	12.98	0.00		
C2H085	12.00	0.00	7.02	0.01		
C3H003	0.30	0.00	0.22	0.00	0.04	0.07
C3H007	0.80	0.29	0.89	0.00		
C3H016	0.08	0.08	0.02	0.00	0.02	0.22
C5H012	5.00	0.01	0.18	0.00	0.05	0.28
C5H014	5.00	0.01	0.33	0.00	0.03	0.13
C5H016	4.00	0.00	0.09	0.00	0.01	0.35
C5H018	5.00	0.00	0.17	0.00	0.01	0.26
C5H035	0.60	0.00	0.29	0.00	0.04	0.25
C5H048	1.50	0.00	0.30	0.00	0.02	0.25
C5H053	1.00	0.01	4.57	0.01		
C6H001	0.80	0.00	4.56	0.02		
C6H003	0.01	0.00	6.23	0.02		
C6H007	4.00	0.02	0.31	0.01	0.02	0.24
C7H006	6.00	0.01	0.50	0.00	0.02	0.23
C8H001	17.00	0.01	0.79	0.00		
C8H003	2.00	0.00	0.66	0.00		
C8H004	10.00	0.00	0.21	0.00		
C8H011	1.30	0.08	0.78	0.01		
C8H020	18.00	0.17	0.36	0.01	0.03	0.15
C8H026	20.00	0.00	0.51	0.00		
C9H021	55.00	0.10	0.28	0.00	0.01	0.19
D1H001	0.10	0.00	4.36	0.01		

Appendix A Table 2. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
D1H011	30.00	0.00	0.19	0.00	0.01	0.34
D3H015	1.50	0.00	0.26	0.00	0.03	0.20
E1H013	11.00	0.26	0.06	0.00	0.01	0.19
G1H036	1.10	0.03	1.00	0.50	0.03	0.34
G2H015	3.00	0.59	3.50	0.06		
G2H020	2.50	0.00	0.21	0.00	0.02	0.20
G4H007	10.00	0.12	0.20	0.00	0.01	0.12
H1H003	0.30	0.01	1.63	0.00		
H1H006	40.00	0.01	0.18	0.00		
H3H011	0.40	0.11	0.94	0.00		
H4H020	0.25	0.01	0.35	0.00	0.03	0.23
H5H002	2.00	1.92	0.08	0.00	0.01	0.25
H6H009	0.30	0.23	0.12	0.00	0.01	0.18
H8H001	1.00	0.00	0.11	0.00	0.02	0.32
H9H005	1.00	0.00	0.15	0.00		
J1H018	0.00	0.00	0.10	0.01	0.05	0.30
J1H019	1.50	0.00	0.25	0.00		
J4H002	1.40	0.00	0.62	0.00	0.02	0.30
K1H004	0.20	0.00	0.18	0.00	0.02	0.23
K1H005	0.30	0.02	0.11	0.01	0.03	0.24
N4H001	0.10	0.02	0.15	0.02	0.06	0.25
N4H003	1.50	0.25	0.41	0.00	0.03	0.31
P1H003	2.00	0.00	0.18	0.01		
P3H001	0.40	0.00	0.29	0.00		
P4H001	0.40	0.00	0.63	0.00		
Q3H004	0.60	0.00	0.73	0.02	0.10	0.22
Q4H013	1.00	0.04	1.04	0.01		
Q6H003	0.30	0.00	1.29	0.00		
Q8H008	3.00	0.05	0.48	0.00		
Q9H002	0.50	0.00	1.43	0.00		
Q9H012	15.00	1.60	0.69	0.01	0.08	0.04

Appendix A Table 2. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q _{pmax}	Q _{pmin}	C _{pmax}	C _{pmin}	A	B
Q9H018	10.00	1.57	2.20	0.01		
R1H005	0.60	0.02	0.13	0.01	0.01	0.25
R1H015	4.00	0.00	0.49	0.00		
R2H027	7.00	0.01	0.20	0.01		
S3H004	0.40	0.00	0.60	0.01	0.04	0.31
S3H005	0.20	0.01	0.25	0.00		
S3H006	2.00	0.00	0.26	0.01		
S5H002	10.00	0.10	0.14	0.01		
S5H004	13.00	0.01	0.14	0.01	0.01	0.28
S6H002	0.40	0.03	0.16	0.00		
S7H001	1.50	0.01	0.90	0.01		
T1H001	14.00	0.20	0.17	0.01		
T1H004	14.00	0.07	0.12	0.01	0.02	0.27
T3H004	5.00	0.01	0.08	0.00	0.02	0.25
T4H001	12.00	0.69	0.12	0.01		
T5H002	1.00	0.10	0.04	0.00	0.02	0.23
T5H004	0.10	0.10	0.04	0.00	0.01	0.20
U1H005	14.00	0.47	0.22	0.00	0.01	0.21
U6H003	1.50	0.00	0.23	0.00		
U8H003	0.10	0.00	0.06	0.00	0.03	0.42
V1H001	0.59	0.59	0.08	0.00	0.01	0.21
V1H010	8.00	0.01	0.18	0.00		
V1H038	8.00	0.01	0.18	0.00		
V1H041	5.00	0.25	0.17	0.00		
V1H058	12.00	0.35	0.15	0.00		
V2H002	4.00	0.07	0.45	0.00		
V2H004	8.00	0.02	0.19	0.00		
V2H006	3.00	0.02	0.07	0.00		
V3H010	3.00	0.15	1.07	0.01		
W1H009	2.00	0.41	0.18	0.01	0.02	0.19

Appendix A Table 2 continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse phosphate signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
W2H009	0.80	0.03	0.34	0.00		
W3H008	1.00	0.01	0.05	0.00	0.01	0.28
W3H015	0.01	0.00	0.05	0.00	0.02	0.32
W4H004	4.00	0.11	0.12	0.00		
W5H005	3.00	0.01	0.09	0.00		
W5H022	20.00	0.32	0.09	0.00		
W5H024	4.00	0.08	0.16	0.00		
W5H025	1.00	0.00	0.33	0.00		
W5H026	0.80	0.01	0.33	0.00		
X1H001	3.00	0.06	0.21	0.00		
X1H016	2.20	0.25	0.09	0.00		
X1H018	2.20	0.00	0.10	0.01	0.01	0.17
X2H005	7.00	0.01	0.10	0.00		
X2H006	8.00	1.64	0.28	0.01		
X2H015	2.00	0.58	0.30	0.00		
X2H022	11.00	0.00	0.08	0.00	0.01	0.29
X2H031	11.00	0.04	0.08	0.00		
X2H032	8.00	0.04	0.56	0.00		
X3H004	0.10	0.00	0.08	0.00	0.01	0.31
X3H006	0.88	0.88	0.05	0.00	0.05	0.46
X3H008	3.00	0.01	0.19	0.00	0.02	0.15

Appendix A Table 3.: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
A2H012	8.00	1.33	56.53	0.02		
A2H014	2.50	0.31	12.59	0.02		
A2H021	2.10	0.02	2.50	0.02		
A2H059	10.00	0.00	2.24	0.02	0.10	0.33
A2H060	10.00	0.01	2.24	0.02	0.13	0.28
A2H061	2.30	0.18	13.11	0.05		
A2H083	7.00	0.13	3.39	0.02		
A2H094	0.20	0.00	2.00	0.02		
A2H106	0.50	0.00	2.15	0.02		
A2H116	0.30	0.00	0.30	0.02	0.09	0.41
A4H002	0.01	0.01	0.30	0.02	0.08	0.15
A7H001	0.10	0.00	0.40	0.02		
A9H001	0.20	0.00	0.40	0.02	0.17	0.33
B1H005	1.00	0.00	4.77	0.02	0.00	0.00
B1H010	8.00	0.00	1.30	0.02	0.03	0.35
B1H012	6.00	0.00	0.60	0.02		
B1H015	6.00	0.00	0.53	0.02		
B1H020	0.02	0.00	0.77	0.02		
B1H021	1.20	0.00	5.50	0.02		
B2H003	1.10	0.00	0.86	0.02	0.04	0.17
B2H014	1.20	0.01	0.99	0.02	0.08	0.14
B2H015	0.10	0.02	0.30	0.02	0.07	0.34
B3H001	7.00	0.00	1.86	0.02	0.13	0.13
B3H021	2.00	0.00	1.86	0.02		
B4H003	7.00	0.00	0.74	0.02		
B4H010	0.10	0.09	0.35	0.02	0.09	0.21
B6H001	1.00	0.64	0.40	0.02	0.16	0.15
B6H004	0.20	0.17	0.40	0.02	0.07	0.28
B7H015	6.00	0.00	4.81	0.02		
B7H019	1.00	0.00	4.81	0.02		
B8H008	3.00	0.03	3.96	0.02		

Appendix A Table 3. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q _{pmax}	Q _{pmin}	C _{pmax}	C _{pmin}	A	B
B8H009	2.00	0.01	1.91	0.02		
B8H014	0.50	0.01	0.40	0.02	0.11	0.32
C1H002	4.00	0.01	1.29	0.02		
C1H007	6.00	2.75	1.29	0.02		
C1H008	6.00	0.01	18.35	0.02		
C2H001	0.80	0.05	1.20	0.02		
C2H004	6.00	0.55	1.50	0.02		
C2H021	8.00	3.00	7.19	1.45		
C2H069	0.50	0.04	18.00	0.02		
C2H073	0.50	0.03	17.74	0.02		
C2H085	0.50	0.00	10.00	0.02		
C3H003	0.50	0.00	2.14	0.02		
C3H007	3.00	0.29	7.59	0.02		
C3H016	0.08	0.08	0.00	0.02	0.22	0.22
C5H012	0.01	0.01	0.10	0.02	0.04	0.20
C5H014	5.50	0.48	1.55	0.02	0.18	0.14
C5H016	1.50	0.00	1.60	0.02	0.09	0.23
C5H018	0.30	0.00	1.23	0.02	0.11	0.25
C5H035	0.20	0.00	4.42	0.02	0.20	0.26
C5H048	4.00	0.00	0.40	0.02	0.09	0.24
C5H053	2.00	0.01	8.55	0.02		
C6H001	0.30	0.00	8.00	0.02		
C6H003	2.00	0.00	3.73	0.02		
C6H007	10.00	0.02	0.58	0.20		
C7H006	7.00	0.01	2.00	0.02		
C8H001	10.00	0.01	2.49	0.02		
C8H003	2.00	0.00	0.60	0.02		
C8H004	2.00	0.00	0.90	0.02		
C8H011	2.00	0.08	6.68	0.02		
C8H020	1.00	0.17	0.30	0.02	0.07	0.19
C8H026	10.00	0.00	1.00	0.02		

Appendix A Table 3. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q _{pmax}	Q _{pmin}	C _{pmax}	C _{pmin}	A	B
C9H021	10.00	0.10	1.00	0.02	0.05	0.25
D1H001	0.20	0.00	25.52	0.02		
D1H011	5.00	0.00	0.33	0.02	0.03	0.23
D3H015	0.05	0.00	0.65	0.02	0.08	0.25
E1H013	0.26	0.26	0.20	0.02	0.09	0.21
G1H036	1.00	0.03	4.67	0.02	0.67	0.18
G2H015	4.00	0.59	6.34	0.02		
G2H020	0.30	5.00	1.00	0.02		
G4H007	1.00	0.12	0.80	0.02	0.24	0.23
H1H003	3.00	0.01	2.20	0.02		
H2H006	3.50	0.05	3.62	0.02		
H3H011	0.50	0.11	3.23	0.02	0.46	0.10
H4H020	0.60	0.01	2.60	0.02	0.23	0.11
H5H002	2.00	1.92	1.24	0.02	0.15	0.22
H6H009	2.50	0.23	1.00	0.02		
H8H001	2.50	0.00	0.88	0.02	0.08	0.07
H9H005	0.60	0.00	0.37	0.02		
J1H018	0.10	0.00	0.10	0.02	0.15	0.30
J1H019	0.30	0.00	1.10	0.02	0.10	0.26
J4H002	0.70	0.00	1.65	0.02	0.08	0.28
K1H004	0.10	0.00	0.20	0.02	0.21	0.41
K1H005	0.15	0.02	0.45	0.02	0.09	0.25
N4H001	0.10	0.02	0.30	0.02	0.11	0.27
N4H003	1.50	0.25	2.90	0.02	0.28	0.19
P1H003	0.40	0.00	1.16	0.02	0.20	0.28
P3H001	0.02	0.00	15.51	0.00		
P4H001	0.04	0.00	3.39	0.00	0.93	0.27
Q3H004	0.40	0.00	3.82	0.02		
Q3H005	3.00	2.21	1.00	0.02	0.27	0.28
Q4H013	0.50	0.04	8.67	0.02		
Q6H003	1.50	0.00	1.65	0.00		

Appendix A Table 3. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
Q8H008	1.50	0.05	2.72	0.00	0.41	0.21
Q9H002	2.00	0.00	0.47	0.00		
Q9H012	6.00	1.60	3.12	0.00	0.40	0.21
Q9H018	10.00	1.57	2.67	0.00	0.23	0.21
R1H005	0.50	0.02	1.41	0.00	0.17	0.16
R1H015	4.00	0.00	1.50	0.02		
R2H027	3.20	0.01	2.41	0.02		
S3H004	1.00	0.00	1.20	0.00	0.19	0.27
S3H005	0.05	0.01	7.58	0.02		
S3H006	1.40	0.00	2.12	0.00		
S5H002	0.50	0.10	0.97	0.02	0.14	0.25
S5H004	0.50	0.01	0.54	0.02	0.07	0.21
S6H002	0.06	0.03	0.10	0.02	0.27	0.59
S7H001	0.10	0.01	8.52	0.02		
T1H001	1.50	0.20	0.47	0.02	0.07	0.17
T1H004	1.50	0.07	0.65	0.02		
T3H004	1.50	0.02	0.67	0.02	0.06	0.16
T4H001	3.00	0.69	0.72	0.02	0.14	0.29
T5H002	1.00	0.76	0.20	0.02	0.22	0.21
T5H004	3.00	0.10	0.40	0.02		
U1H006	2.00	1.19	0.40	0.02	0.07	0.22
U6H003	0.30	0.00	4.32	0.02	0.39	0.17
U8H003	0.50	0.00	1.17	0.02	0.32	0.24
V1H001	2.00	0.59	0.75	0.02	0.08	0.19
V1H010	3.00	0.01	0.81	0.02	0.05	0.20
V1H038	7.00	0.01	0.86	0.02	0.03	0.17
V1H041	6.00	0.25	0.34	0.02		
V1H058	5.00	0.35	0.34	0.02	0.03	0.25
V2H002	7.00	0.07	0.66	0.02	0.06	0.24
V2H004	5.00	0.02	0.80	0.02	0.07	0.24
V2H006	1.00	0.02	0.80	0.02	0.17	0.25

Appendix A Table 3. continued: Estimated parameters for a simple mechanistic model that distinguishes between point and diffuse Nitrate + Nitrite signatures, applied to DWA historical monitoring data

Station	Point Source Signature Parameters				Diffuse Source Signature Parameters	
	Q_{pmax}	Q_{pmin}	C_{pmax}	C_{pmin}	A	B
V3H010	5.00	0.15	6.28	0.02		
W1H009	2.00	0.41	0.60	0.02	0.10	0.19
W2H009	0.50	0.03	1.90	0.02		
W3H008	0.10	0.00	0.05	0.02	0.09	0.27
W3H015	0.50	0.00	1.29	0.02	0.33	0.26
W4H004	0.50	0.11	0.40	0.02	0.15	0.24
W5H005	1.00	0.01	0.40	0.02	0.08	0.22
W5H022	3.00	0.32	0.74	0.02	0.05	0.20
W5H024	4.00	0.08	0.63	0.02		
W5H025	1.00	0.03	0.64	0.02	0.04	0.28
W5H026	1.00	0.01	0.76	0.02	0.10	0.26
X1H001	3.00	0.63	0.96	0.02		
X1H016	0.25	0.25	0.05	0.02	0.08	0.44
X1H018	1.20	0.00	0.40	0.02		
X2H005	0.50	0.01	0.40	0.02	0.14	0.23
X2H006	6.00	1.64	2.91	0.02	0.19	0.12
X2H015	2.00	0.58	2.19	0.02		
X2H022	1.70	0.00	2.19	0.02	0.18	0.27
X2H031	0.50	0.04	0.30	0.02	0.14	0.34
X2H032	5.00	0.04	2.58	0.02	0.14	0.19
X3H004	0.60	0.00	1.91	0.02	0.33	0.24
X3H006	0.88	0.88	0.30	0.02	0.12	0.31
X3H008	1.20	0.01	0.20	0.02	0.05	0.27

Appendix A Table 4: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
A2H012	0.000	0.000	0.000	0.093	0.010	0.000	0.351	0.000	0.043	0.016	0.016	0.011	0.021	0.024	0.409	0.002	0.002
A2H014	0.000	0.000	0.000	0.186	0.008	0.000	0.406	0.000	0.039	0.030	0.005	0.011	0.011	0.021	0.275	0.003	0.006
A2H021	0.000	0.000	0.000	0.071	0.018	0.069	0.249	0.000	0.403	0.004	0.002	0.003	0.056	0.007	0.114	0.003	0.002
A2H048	0.000	0.000	0.000	0.150	0.043	0.002	0.269	0.000	0.144	0.014	0.009	0.008	0.085	0.015	0.253	0.005	0.001
A2H059	0.000	0.000	0.000	0.121	0.057	0.006	0.163	0.000	0.171	0.006	0.004	0.007	0.349	0.006	0.105	0.004	0.001
A2H060	0.000	0.000	0.000	0.100	0.042	0.028	0.193	0.000	0.264	0.005	0.003	0.006	0.241	0.006	0.107	0.003	0.002
A2H061	0.000	0.000	0.000	0.035	0.079	0.000	0.042	0.000	0.261	0.015	0.016	0.001	0.052	0.051	0.444	0.004	0.000
A2H083	0.000	0.000	0.000	0.157	0.013	0.000	0.301	0.000	0.101	0.016	0.011	0.008	0.088	0.016	0.282	0.006	0.001
A2H094	0.001	0.000	0.001	0.197	0.065	0.003	0.145	0.000	0.220	0.001	0.000	0.020	0.306	0.003	0.033	0.004	0.002
A2H106	0.000	0.000	0.000	0.083	0.016	0.055	0.257	0.000	0.384	0.005	0.002	0.003	0.058	0.008	0.123	0.003	0.003
A2H116	0.000	0.000	0.000	0.096	0.043	0.027	0.185	0.000	0.278	0.005	0.003	0.005	0.248	0.006	0.099	0.003	0.001
A4H002	0.000	0.000	0.000	0.288	0.016	0.000	0.100	0.000	0.317	0.001	0.000	0.000	0.275	0.000	0.001	0.002	0.000
A7H001	0.000	0.000	0.000	0.078	0.038	0.023	0.218	0.002	0.141	0.004	0.000	0.001	0.456	0.003	0.036	0.001	0.000
A9H001	0.000	0.121	0.002	0.012	0.000	0.069	0.008	0.000	0.019	0.113	0.000	0.000	0.647	0.000	0.008	0.002	0.000
A9H013	0.001	0.000	0.000	0.001	0.002	0.168	0.129	0.000	0.554	0.020	0.000	0.000	0.122	0.000	0.000	0.001	0.000
B1H005	0.000	0.000	0.000	0.403	0.002	0.000	0.530	0.000	0.000	0.006	0.002	0.041	0.001	0.001	0.006	0.006	0.002
B1H010	0.000	0.000	0.000	0.382	0.002	0.000	0.530	0.000	0.000	0.008	0.004	0.051	0.002	0.002	0.009	0.009	0.002
B1H012	0.000	0.000	0.000	0.416	0.006	0.000	0.459	0.000	0.000	0.027	0.000	0.071	0.001	0.002	0.005	0.008	0.004
B1H015	0.000	0.000	0.000	0.415	0.006	0.000	0.460	0.000	0.000	0.026	0.000	0.069	0.001	0.002	0.004	0.011	0.005
B1H020	0.000	0.000	0.000	0.437	0.002	0.000	0.537	0.000	0.000	0.004	0.000	0.010	0.001	0.001	0.002	0.004	0.001
B1H021	0.000	0.000	0.000	0.396	0.002	0.000	0.546	0.000	0.000	0.003	0.003	0.031	0.000	0.001	0.008	0.007	0.002

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
B2H003	0.000	0.000	0.000	0.461	0.006	0.000	0.466	0.000	0.000	0.018	0.001	0.005	0.005	0.002	0.023	0.006	0.007
B2H014	0.000	0.000	0.000	0.528	0.002	0.000	0.435	0.000	0.001	0.011	0.000	0.006	0.004	0.006	0.002	0.003	0.003
B2H015	0.000	0.000	0.000	0.426	0.004	0.000	0.506	0.000	0.005	0.018	0.000	0.006	0.011	0.004	0.012	0.004	0.004
B3H001	0.000	0.000	0.001	0.277	0.023	0.008	0.467	0.000	0.125	0.019	0.001	0.023	0.027	0.002	0.018	0.007	0.002
B3H021	0.000	0.000	0.001	0.240	0.034	0.067	0.218	0.001	0.365	0.004	0.000	0.001	0.030	0.001	0.039	0.001	0.000
B4H003	0.000	0.000	0.000	0.183	0.010	0.004	0.484	0.000	0.045	0.042	0.000	0.014	0.209	0.000	0.006	0.004	0.000
B4H010	0.000	0.000	0.000	0.101	0.016	0.000	0.696	0.000	0.000	0.057	0.000	0.000	0.111	0.001	0.016	0.002	0.000
B6H001	0.000	0.000	0.013	0.021	0.004	0.000	0.430	0.000	0.017	0.395	0.000	0.000	0.119	0.000	0.001	0.000	0.000
B6H004	0.000	0.000	0.003	0.015	0.055	0.015	0.344	0.000	0.021	0.119	0.000	0.000	0.421	0.000	0.004	0.002	0.000
B7H015	0.000	0.001	0.004	0.163	0.021	0.045	0.338	0.001	0.202	0.016	0.000	0.010	0.176	0.001	0.020	0.003	0.001
B7H019	0.000	0.000	0.051	0.003	0.000	0.070	0.095	0.000	0.578	0.000	0.000	0.012	0.169	0.001	0.020	0.001	0.000
B8H008	0.002	0.034	0.059	0.031	0.012	0.203	0.045	0.000	0.215	0.099	0.000	0.000	0.259	0.000	0.038	0.003	0.000
B8H009	0.000	0.102	0.048	0.004	0.012	0.092	0.072	0.000	0.071	0.331	0.000	0.000	0.232	0.001	0.028	0.006	0.000
B8H014	0.000	0.061	0.000	0.000	0.000	0.000	0.062	0.000	0.109	0.553	0.000	0.000	0.201	0.000	0.000	0.015	0.000
C1H002	0.000	0.000	0.000	0.138	0.001	0.000	0.839	0.001	0.000	0.003	0.000	0.000	0.011	0.000	0.001	0.001	0.005
C1H007	0.000	0.000	0.000	0.210	0.001	0.006	0.759	0.000	0.000	0.011	0.000	0.001	0.004	0.001	0.001	0.004	0.002
C1H008	0.000	0.000	0.000	0.430	0.003	0.000	0.556	0.000	0.000	0.003	0.000	0.000	0.001	0.000	0.001	0.003	0.003
C1H015	0.000	0.000	0.000	0.138	0.001	0.000	0.839	0.001	0.000	0.003	0.000	0.000	0.011	0.000	0.001	0.001	0.005
C2H001	0.000	0.000	0.000	0.272	0.007	0.001	0.628	0.000	0.007	0.010	0.000	0.027	0.011	0.000	0.030	0.003	0.004
C2H004	0.000	0.000	0.000	0.348	0.003	0.000	0.501	0.000	0.000	0.009	0.004	0.020	0.020	0.008	0.070	0.004	0.013
C2H005	0.000	0.000	0.000	0.463	0.009	0.000	0.359	0.000	0.004	0.005	0.000	0.014	0.009	0.017	0.118	0.001	0.000

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
C2H007	0.001	0.000	0.000	0.329	0.003	0.001	0.595	0.000	0.006	0.005	0.001	0.007	0.011	0.004	0.026	0.007	0.004
C2H008	0.001	0.000	0.000	0.320	0.002	0.001	0.606	0.000	0.000	0.005	0.001	0.006	0.010	0.005	0.029	0.009	0.004
C2H018	0.001	0.000	0.000	0.325	0.002	0.001	0.599	0.000	0.004	0.005	0.001	0.006	0.010	0.005	0.029	0.009	0.004
C2H021	0.000	0.000	0.000	0.108	0.001	0.000	0.421	0.000	0.004	0.007	0.013	0.060	0.028	0.059	0.275	0.005	0.018
C2H061	0.001	0.000	0.000	0.341	0.003	0.001	0.587	0.000	0.007	0.004	0.001	0.006	0.013	0.003	0.022	0.006	0.004
C2H069	0.000	0.000	0.000	0.258	0.010	0.000	0.558	0.000	0.001	0.015	0.001	0.070	0.008	0.001	0.077	0.001	0.001
C2H073	0.000	0.000	0.000	0.332	0.010	0.000	0.592	0.000	0.026	0.005	0.000	0.001	0.014	0.002	0.011	0.002	0.006
C2H085	0.000	0.000	0.000	0.267	0.008	0.001	0.621	0.000	0.009	0.008	0.000	0.019	0.023	0.002	0.036	0.003	0.003
C2H140	0.001	0.000	0.000	0.322	0.002	0.001	0.604	0.000	0.000	0.005	0.001	0.006	0.009	0.005	0.030	0.009	0.004
C3H003	0.000	0.000	0.000	0.406	0.006	0.035	0.429	0.000	0.005	0.008	0.000	0.002	0.094	0.000	0.006	0.002	0.008
C3H007	0.000	0.000	0.000	0.239	0.020	0.017	0.342	0.000	0.002	0.004	0.000	0.001	0.362	0.001	0.005	0.001	0.006
C3H016	0.000	0.000	0.000	0.122	0.008	0.000	0.511	0.000	0.000	0.001	0.000	0.001	0.330	0.002	0.009	0.003	0.012
C5H012	0.000	0.000	0.000	0.045	0.001	0.000	0.828	0.000	0.001	0.000	0.000	0.000	0.121	0.000	0.001	0.003	0.000
C5H014	0.000	0.000	0.000	0.130	0.008	0.000	0.529	0.000	0.000	0.001	0.000	0.001	0.302	0.002	0.010	0.004	0.013
C5H016	0.000	0.000	0.000	0.122	0.008	0.000	0.511	0.000	0.000	0.001	0.000	0.001	0.330	0.002	0.009	0.003	0.012
C5H018	0.000	0.000	0.000	0.204	0.004	0.001	0.514	0.000	0.000	0.001	0.000	0.001	0.233	0.003	0.017	0.003	0.018
C5H035	0.000	0.000	0.000	0.204	0.004	0.001	0.514	0.000	0.000	0.001	0.000	0.001	0.233	0.003	0.017	0.003	0.018
C5H048	0.000	0.000	0.000	0.118	0.009	0.000	0.503	0.000	0.000	0.001	0.000	0.001	0.343	0.002	0.009	0.003	0.012
C5H053	0.000	0.000	0.000	0.104	0.001	0.003	0.734	0.000	0.000	0.001	0.000	0.000	0.094	0.011	0.044	0.006	0.001
C6H001	0.000	0.000	0.000	0.360	0.001	0.000	0.621	0.000	0.000	0.001	0.000	0.000	0.002	0.002	0.007	0.003	0.003
C6H003	0.000	0.000	0.000	0.404	0.001	0.000	0.579	0.000	0.000	0.001	0.000	0.000	0.002	0.001	0.006	0.003	0.003

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
C6H007	0.001	0.000	0.000	0.360	0.001	0.000	0.625	0.000	0.000	0.001	0.000	0.000	0.002	0.000	0.005	0.003	0.002
C7H006	0.000	0.000	0.000	0.396	0.008	0.000	0.568	0.000	0.010	0.001	0.000	0.000	0.004	0.000	0.002	0.005	0.007
C8H001	0.004	0.000	0.000	0.361	0.001	0.001	0.596	0.000	0.000	0.004	0.000	0.000	0.013	0.000	0.009	0.006	0.004
C8H003	0.001	0.000	0.000	0.186	0.002	0.001	0.800	0.000	0.000	0.003	0.000	0.000	0.003	0.000	0.002	0.001	0.002
C8H004	0.006	0.001	0.000	0.578	0.000	0.000	0.388	0.000	0.000	0.002	0.000	0.000	0.007	0.000	0.006	0.004	0.007
C8H011	0.016	0.000	0.000	0.175	0.001	0.008	0.665	0.000	0.001	0.004	0.000	0.000	0.059	0.002	0.067	0.002	0.002
C8H020	0.006	0.001	0.000	0.575	0.001	0.000	0.390	0.000	0.000	0.002	0.000	0.000	0.007	0.000	0.006	0.004	0.007
C8H022	0.004	0.000	0.000	0.362	0.001	0.001	0.595	0.000	0.000	0.004	0.000	0.000	0.014	0.000	0.009	0.006	0.004
C8H026	0.005	0.001	0.000	0.541	0.000	0.000	0.431	0.000	0.000	0.002	0.000	0.000	0.006	0.000	0.006	0.003	0.006
C8H027	0.004	0.000	0.000	0.282	0.001	0.001	0.668	0.000	0.000	0.005	0.000	0.000	0.017	0.000	0.011	0.007	0.003
C8H028	0.005	0.000	0.000	0.263	0.001	0.002	0.669	0.000	0.000	0.006	0.000	0.000	0.024	0.000	0.015	0.010	0.003
C9H009	0.001	0.000	0.000	0.351	0.004	0.000	0.545	0.001	0.005	0.003	0.001	0.005	0.054	0.003	0.016	0.006	0.007
C9H010	0.001	0.000	0.000	0.314	0.007	0.003	0.490	0.001	0.004	0.003	0.000	0.004	0.145	0.002	0.014	0.005	0.007
C9H021	0.001	0.000	0.000	0.369	0.003	0.000	0.551	0.001	0.005	0.004	0.001	0.005	0.026	0.003	0.017	0.006	0.006
C9H024	0.001	0.000	0.000	0.306	0.007	0.003	0.478	0.001	0.004	0.003	0.000	0.004	0.166	0.002	0.013	0.005	0.007
D1H001	0.001	0.000	0.000	0.006	0.005	0.000	0.526	0.000	0.000	0.001	0.001	0.000	0.453	0.000	0.003	0.003	0.000
D1H011	0.013	0.000	0.000	0.049	0.007	0.000	0.899	0.001	0.000	0.001	0.002	0.000	0.025	0.000	0.001	0.001	0.001
D3H015	0.000	0.000	0.000	0.000	0.002	0.000	0.083	0.000	0.000	0.000	0.003	0.000	0.909	0.000	0.001	0.002	0.001
E1H013	0.000	0.000	0.081	0.011	0.089	0.000	0.005	0.000	0.000	0.003	0.000	0.000	0.802	0.000	0.001	0.005	0.002
E2H002	0.000	0.000	0.020	0.007	0.015	0.000	0.002	0.020	0.000	0.001	0.001	0.000	0.930	0.000	0.000	0.004	0.000
E2H003	0.000	0.000	0.006	0.026	0.007	0.000	0.001	0.033	0.000	0.000	0.000	0.000	0.924	0.000	0.000	0.002	0.000

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
G1H013	0.000	0.000	0.168	0.360	0.000	0.000	0.027	0.000	0.000	0.042	0.001	0.001	0.373	0.001	0.013	0.012	0.001
G1H031	0.000	0.000	0.128	0.498	0.000	0.000	0.020	0.000	0.000	0.031	0.001	0.001	0.296	0.001	0.012	0.010	0.001
G1H036	0.000	0.000	0.281	0.229	0.000	0.000	0.024	0.000	0.000	0.068	0.002	0.000	0.355	0.002	0.025	0.011	0.003
G2H015	0.000	0.000	0.562	0.000	0.029	0.000	0.000	0.000	0.000	0.097	0.003	0.001	0.240	0.004	0.046	0.018	0.000
G2H020	0.000	0.000	0.442	0.000	0.000	0.000	0.001	0.000	0.000	0.143	0.003	0.001	0.319	0.006	0.072	0.014	0.000
G4H007	0.000	0.000	0.293	0.000	0.000	0.000	0.002	0.000	0.000	0.121	0.000	0.000	0.557	0.001	0.005	0.022	0.000
H1H003	0.000	0.000	0.195	0.103	0.009	0.000	0.015	0.000	0.000	0.003	0.000	0.000	0.646	0.001	0.011	0.018	0.000
H1H006	0.000	0.000	0.170	0.089	0.007	0.000	0.013	0.000	0.000	0.003	0.000	0.000	0.692	0.000	0.010	0.016	0.000
H2H006	0.000	0.000	0.106	0.018	0.003	0.000	0.023	0.000	0.000	0.001	0.000	0.000	0.842	0.000	0.003	0.005	0.000
H3H011	0.000	0.000	0.071	0.069	0.003	0.000	0.018	0.000	0.001	0.000	0.001	0.000	0.831	0.000	0.004	0.003	0.000
H4H017	0.002	0.000	0.135	0.050	0.006	0.000	0.031	0.000	0.000	0.005	0.001	0.000	0.745	0.002	0.006	0.016	0.001
H4H020	0.000	0.000	0.102	0.139	0.002	0.000	0.041	0.000	0.000	0.001	0.000	0.000	0.709	0.000	0.000	0.006	0.000
H5H002	0.002	0.000	0.123	0.051	0.005	0.000	0.025	0.000	0.000	0.003	0.001	0.000	0.771	0.001	0.006	0.011	0.001
H5H004	0.002	0.000	0.123	0.050	0.005	0.000	0.025	0.000	0.000	0.003	0.001	0.000	0.771	0.001	0.006	0.011	0.001
H6H009	0.000	0.000	0.055	0.352	0.008	0.000	0.032	0.000	0.000	0.019	0.004	0.000	0.495	0.000	0.003	0.028	0.004
H7H006	0.001	0.000	0.105	0.157	0.006	0.000	0.025	0.000	0.000	0.006	0.001	0.000	0.677	0.001	0.005	0.014	0.001
H8H001	0.000	0.000	0.003	0.472	0.010	0.000	0.003	0.000	0.000	0.002	0.012	0.000	0.487	0.000	0.008	0.001	0.002
H9H005	0.000	0.000	0.000	0.190	0.071	0.000	0.007	0.000	0.000	0.025	0.023	0.000	0.651	0.000	0.000	0.004	0.029
J1H018	0.000	0.000	0.004	0.026	0.002	0.000	0.010	0.000	0.000	0.000	0.001	0.000	0.955	0.000	0.000	0.001	0.000
J1H019	0.000	0.000	0.004	0.014	0.006	0.000	0.008	0.000	0.000	0.000	0.001	0.000	0.964	0.000	0.001	0.001	0.000
J4H002	0.001	0.000	0.002	0.018	0.012	0.000	0.016	0.000	0.000	0.000	0.002	0.000	0.947	0.000	0.001	0.001	0.000

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
K1H004	0.000	0.000	0.000	0.164	0.035	0.000	0.019	0.000	0.000	0.045	0.022	0.000	0.714	0.000	0.000	0.000	0.000
K1H005	0.000	0.000	0.000	0.098	0.010	0.000	0.008	0.000	0.013	0.135	0.040	0.000	0.695	0.000	0.000	0.001	0.000
N4H001	0.000	0.000	0.000	0.000	0.015	0.000	0.099	0.000	0.002	0.000	0.002	0.000	0.880	0.000	0.001	0.003	0.000
N4H003	0.000	0.000	0.000	0.004	0.021	0.000	0.088	0.000	0.002	0.000	0.002	0.000	0.880	0.000	0.001	0.002	0.000
P1H003	0.000	0.000	0.000	0.001	0.003	0.002	0.069	0.000	0.003	0.002	0.000	0.000	0.919	0.000	0.001	0.001	0.000
P3H001	0.000	0.031	0.000	0.083	0.010	0.000	0.328	0.000	0.001	0.003	0.011	0.000	0.530	0.000	0.000	0.003	0.000
P4H001	0.000	0.052	0.000	0.055	0.011	0.002	0.272	0.000	0.004	0.009	0.002	0.000	0.567	0.001	0.022	0.001	0.000
Q1H002	0.000	0.000	0.000	0.000	0.015	0.000	0.134	0.000	0.000	0.000	0.010	0.000	0.839	0.000	0.000	0.001	0.000
Q1H012	0.000	0.000	0.000	0.000	0.025	0.000	0.357	0.000	0.000	0.000	0.003	0.000	0.612	0.000	0.001	0.001	0.000
Q1H013	0.000	0.000	0.000	0.000	0.016	0.000	0.141	0.000	0.000	0.000	0.003	0.000	0.836	0.000	0.003	0.001	0.000
Q3H004	0.000	0.000	0.000	0.000	0.007	0.000	0.173	0.000	0.000	0.000	0.012	0.000	0.807	0.000	0.000	0.000	0.000
Q3H005	0.000	0.000	0.000	0.000	0.020	0.000	0.170	0.000	0.000	0.000	0.005	0.000	0.801	0.000	0.001	0.002	0.002
Q4H013	0.000	0.000	0.000	0.002	0.011	0.000	0.279	0.001	0.000	0.000	0.002	0.000	0.701	0.000	0.001	0.002	0.001
Q6H003	0.000	0.000	0.000	0.001	0.002	0.000	0.660	0.000	0.000	0.000	0.000	0.000	0.337	0.000	0.000	0.000	0.000
Q7H005	0.000	0.000	0.000	0.000	0.027	0.000	0.148	0.000	0.088	0.000	0.002	0.000	0.733	0.000	0.002	0.001	0.000
Q8H008	0.000	0.000	0.000	0.000	0.023	0.000	0.274	0.000	0.092	0.001	0.003	0.000	0.603	0.000	0.003	0.001	0.000
Q9H002	0.000	0.000	0.000	0.000	0.023	0.007	0.709	0.000	0.012	0.002	0.001	0.000	0.243	0.000	0.001	0.001	0.000
Q9H012	0.000	0.000	0.000	0.000	0.026	0.000	0.205	0.000	0.017	0.000	0.003	0.000	0.745	0.000	0.001	0.001	0.001
Q9H018	0.000	0.000	0.001	0.000	0.022	0.002	0.214	0.000	0.022	0.002	0.002	0.000	0.730	0.000	0.002	0.001	0.001
Q9H029	0.000	0.000	0.018	0.001	0.002	0.020	0.301	0.000	0.068	0.038	0.000	0.000	0.547	0.000	0.003	0.002	0.000
R1H005	0.000	0.000	0.000	0.000	0.027	0.065	0.331	0.000	0.187	0.068	0.000	0.000	0.282	0.000	0.036	0.005	0.000

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
R1H015	0.000	0.000	0.001	0.000	0.008	0.071	0.393	0.000	0.058	0.029	0.000	0.000	0.390	0.000	0.046	0.003	0.000
R2H027	0.000	0.000	0.000	0.003	0.002	0.087	0.445	0.000	0.082	0.047	0.001	0.001	0.249	0.004	0.077	0.003	0.000
S3H004	0.000	0.000	0.000	0.001	0.003	0.008	0.839	0.021	0.001	0.001	0.002	0.000	0.106	0.000	0.016	0.001	0.000
S3H005	0.016	0.000	0.000	0.000	0.002	0.014	0.712	0.000	0.000	0.003	0.000	0.000	0.175	0.002	0.070	0.006	0.000
S3H006	0.006	0.000	0.000	0.006	0.008	0.002	0.747	0.014	0.000	0.001	0.002	0.000	0.212	0.000	0.001	0.001	0.001
S5H002	0.007	0.000	0.000	0.013	0.006	0.129	0.758	0.000	0.001	0.018	0.002	0.000	0.022	0.000	0.038	0.006	0.000
S5H004	0.009	0.000	0.000	0.017	0.006	0.104	0.783	0.001	0.000	0.022	0.003	0.000	0.026	0.000	0.022	0.007	0.000
S6H002	0.000	0.000	0.000	0.032	0.011	0.006	0.589	0.000	0.066	0.199	0.002	0.000	0.077	0.001	0.012	0.007	0.000
S7H001	0.000	0.000	0.000	0.000	0.000	0.263	0.542	0.000	0.000	0.019	0.001	0.000	0.075	0.001	0.095	0.004	0.000
S7H004	0.003	0.000	0.000	0.010	0.009	0.061	0.664	0.008	0.004	0.013	0.002	0.000	0.200	0.000	0.022	0.003	0.000
T1H001	0.002	0.000	0.000	0.067	0.001	0.087	0.763	0.001	0.010	0.029	0.000	0.000	0.031	0.000	0.005	0.001	0.005
T1H004	0.001	0.000	0.000	0.017	0.010	0.207	0.658	0.000	0.015	0.029	0.000	0.000	0.022	0.000	0.041	0.001	0.001
T3H004	0.000	0.000	0.000	0.096	0.050	0.003	0.786	0.000	0.000	0.018	0.011	0.000	0.016	0.000	0.004	0.004	0.011
T3H005	0.005	0.000	0.000	0.001	0.000	0.122	0.794	0.000	0.007	0.025	0.000	0.000	0.025	0.000	0.017	0.000	0.003
T3H006	0.006	0.000	0.000	0.035	0.000	0.121	0.749	0.001	0.002	0.046	0.000	0.000	0.013	0.000	0.021	0.001	0.005
T3H007	0.001	0.000	0.000	0.043	0.004	0.105	0.759	0.000	0.001	0.003	0.002	0.000	0.033	0.000	0.024	0.001	0.023
T3H008	0.001	0.000	0.000	0.099	0.012	0.042	0.783	0.000	0.000	0.002	0.004	0.000	0.014	0.000	0.008	0.003	0.031
T4H001	0.000	0.000	0.000	0.000	0.000	0.155	0.540	0.000	0.050	0.227	0.000	0.000	0.020	0.000	0.008	0.000	0.000
T5H002	0.000	0.000	0.000	0.000	0.000	0.106	0.570	0.000	0.056	0.204	0.000	0.000	0.037	0.000	0.027	0.000	0.000
T5H004	0.000	0.000	0.000	0.014	0.044	0.000	0.891	0.000	0.000	0.028	0.002	0.000	0.013	0.000	0.001	0.007	0.001
T5H007	0.001	0.000	0.000	0.017	0.047	0.076	0.728	0.000	0.016	0.074	0.003	0.000	0.019	0.000	0.010	0.004	0.004

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
U1H005	0.000	0.000	0.000	0.005	0.003	0.026	0.882	0.000	0.008	0.037	0.002	0.000	0.036	0.000	0.001	0.001	0.001
U1H006	0.000	0.000	0.004	0.009	0.025	0.048	0.604	0.000	0.011	0.124	0.004	0.000	0.169	0.000	0.001	0.002	0.000
U6H003	0.000	0.000	0.192	0.038	0.017	0.036	0.411	0.000	0.019	0.230	0.009	0.000	0.039	0.000	0.002	0.005	0.000
U8H003	0.000	0.000	0.073	0.004	0.000	0.105	0.372	0.000	0.007	0.086	0.000	0.000	0.351	0.000	0.000	0.000	0.000
V1H001	0.001	0.000	0.000	0.034	0.097	0.082	0.602	0.003	0.011	0.015	0.000	0.000	0.139	0.000	0.004	0.013	0.000
V1H010	0.000	0.000	0.000	0.010	0.153	0.101	0.640	0.003	0.016	0.036	0.000	0.000	0.028	0.000	0.010	0.003	0.000
V1H038	0.000	0.000	0.000	0.033	0.007	0.021	0.607	0.019	0.011	0.018	0.000	0.000	0.281	0.000	0.000	0.001	0.002
V1H041	0.001	0.000	0.000	0.000	0.006	0.054	0.752	0.001	0.011	0.007	0.000	0.000	0.164	0.000	0.000	0.000	0.004
V1H058	0.003	0.000	0.000	0.025	0.015	0.120	0.630	0.000	0.001	0.010	0.000	0.000	0.167	0.000	0.000	0.028	0.000
V2H002	0.000	0.000	0.000	0.059	0.119	0.000	0.753	0.000	0.003	0.031	0.002	0.000	0.016	0.000	0.002	0.012	0.003
V2H004	0.000	0.000	0.000	0.052	0.099	0.000	0.748	0.000	0.002	0.025	0.018	0.000	0.041	0.000	0.003	0.010	0.002
V2H006	0.000	0.000	0.000	0.086	0.079	0.000	0.739	0.000	0.008	0.034	0.002	0.000	0.028	0.000	0.000	0.017	0.007
V3H010	0.000	0.000	0.000	0.072	0.006	0.042	0.712	0.005	0.014	0.021	0.000	0.006	0.087	0.002	0.020	0.009	0.003
V5H002	0.000	0.000	0.002	0.038	0.024	0.071	0.608	0.007	0.013	0.019	0.003	0.001	0.197	0.001	0.008	0.005	0.001
V6H002	0.000	0.000	0.000	0.023	0.038	0.048	0.604	0.010	0.011	0.014	0.001	0.000	0.235	0.001	0.007	0.006	0.001
V6H004	0.000	0.000	0.000	0.016	0.006	0.031	0.576	0.017	0.029	0.011	0.000	0.001	0.307	0.000	0.001	0.004	0.000
W1H009	0.000	0.000	0.083	0.001	0.000	0.129	0.411	0.000	0.004	0.157	0.000	0.000	0.208	0.000	0.002	0.005	0.000
W2H005	0.000	0.000	0.000	0.035	0.003	0.102	0.700	0.018	0.005	0.053	0.000	0.001	0.073	0.001	0.008	0.002	0.000
W2H009	0.000	0.000	0.000	0.116	0.010	0.001	0.594	0.003	0.000	0.170	0.001	0.004	0.059	0.011	0.020	0.010	0.000
W3H008	0.000	0.003	0.008	0.015	0.002	0.082	0.427	0.002	0.329	0.051	0.000	0.004	0.076	0.000	0.000	0.001	0.000
W3H015	0.000	0.004	0.030	0.000	0.000	0.262	0.258	0.000	0.178	0.015	0.000	0.000	0.246	0.000	0.000	0.004	0.004

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
W4H004	0.000	0.000	0.000	0.119	0.001	0.000	0.690	0.000	0.001	0.178	0.000	0.003	0.007	0.000	0.000	0.001	0.000
W5H005	0.000	0.000	0.000	0.044	0.000	0.000	0.461	0.000	0.000	0.479	0.000	0.002	0.011	0.001	0.001	0.001	0.000
W5H022	0.000	0.000	0.000	0.090	0.002	0.024	0.648	0.000	0.000	0.203	0.000	0.002	0.005	0.001	0.006	0.021	0.000
W5H024	0.000	0.000	0.000	0.046	0.000	0.006	0.637	0.000	0.000	0.266	0.000	0.000	0.003	0.000	0.004	0.026	0.010
W5H025	0.000	0.000	0.000	0.057	0.000	0.000	0.642	0.000	0.000	0.282	0.000	0.000	0.005	0.000	0.001	0.012	0.001
W5H026	0.000	0.000	0.000	0.067	0.000	0.003	0.646	0.000	0.000	0.255	0.000	0.000	0.009	0.000	0.005	0.012	0.001
X1H001	0.000	0.000	0.000	0.097	0.014	0.007	0.694	0.000	0.000	0.126	0.000	0.001	0.050	0.000	0.004	0.006	0.001
X1H016	0.000	0.000	0.000	0.020	0.000	0.000	0.666	0.000	0.000	0.279	0.000	0.000	0.034	0.000	0.000	0.001	0.000
X1H018	0.000	0.000	0.000	0.189	0.002	0.000	0.751	0.000	0.000	0.032	0.000	0.001	0.012	0.000	0.003	0.008	0.002
X2H005	0.000	0.027	0.002	0.033	0.001	0.000	0.127	0.000	0.074	0.645	0.000	0.000	0.088	0.001	0.001	0.002	0.000
X2H006	0.000	0.011	0.004	0.034	0.033	0.000	0.369	0.000	0.031	0.301	0.000	0.000	0.206	0.001	0.005	0.003	0.000
X2H015	0.000	0.000	0.000	0.009	0.013	0.000	0.555	0.000	0.010	0.263	0.000	0.000	0.142	0.002	0.005	0.001	0.000
X2H016	0.000	0.007	0.015	0.028	0.024	0.007	0.227	0.000	0.246	0.190	0.000	0.000	0.242	0.001	0.009	0.002	0.000
X2H017	0.000	0.009	0.011	0.033	0.028	0.008	0.267	0.000	0.129	0.224	0.000	0.001	0.277	0.001	0.011	0.002	0.000
X2H022	0.000	0.010	0.003	0.041	0.033	0.000	0.294	0.000	0.051	0.275	0.000	0.000	0.282	0.001	0.006	0.002	0.000
X2H031	0.000	0.000	0.000	0.142	0.000	0.000	0.072	0.000	0.013	0.570	0.000	0.000	0.201	0.000	0.000	0.002	0.000
X2H032	0.000	0.014	0.004	0.033	0.032	0.000	0.353	0.000	0.035	0.286	0.000	0.000	0.232	0.001	0.007	0.003	0.000
X2H046	0.000	0.009	0.011	0.035	0.029	0.008	0.277	0.000	0.101	0.232	0.000	0.001	0.283	0.001	0.011	0.002	0.000
X3H004	0.002	0.027	0.075	0.004	0.057	0.000	0.093	0.000	0.000	0.342	0.000	0.000	0.373	0.000	0.022	0.008	0.000
X3H006	0.001	0.000	0.066	0.003	0.017	0.000	0.111	0.000	0.019	0.610	0.000	0.000	0.156	0.006	0.009	0.002	0.000
X3H008	0.001	0.000	0.006	0.000	0.000	0.117	0.469	0.000	0.111	0.036	0.000	0.000	0.157	0.000	0.101	0.002	0.000
X3H015	0.001	0.001	0.016	0.001	0.006	0.032	0.167	0.000	0.421	0.148	0.000	0.000	0.169	0.001	0.035	0.001	0.000

Appendix A Table 4 continued: Land cover fractions (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
*A6H009	0.000	0.003	0.000	0.081	0.008	0.106	0.173	0.000	0.227	0.000	0.000	0.001	0.381	0.000	0.017	0.001	0.001
*B8H033	0.002	0.000	0.010	0.595	0.031	0.090	0.035	0.000	0.206	0.026	0.000	0.000	0.002	0.000	0.002	0.000	0.000
*C4H017	0.477	0.000	0.000	0.403	0.006	0.000	0.006	0.008	0.063	0.011	0.000	0.000	0.000	0.000	0.011	0.014	0.001
*K4H001	0.000	0.000	0.000	0.000	0.166	0.000	0.000	0.000	0.003	0.422	0.028	0.000	0.330	0.002	0.000	0.050	0.000
*N2H007	0.000	0.000	0.000	0.000	0.017	0.000	0.117	0.000	0.000	0.000	0.002	0.000	0.861	0.000	0.001	0.002	0.000
*Q1H001	0.000	0.000	0.000	0.000	0.017	0.000	0.180	0.000	0.000	0.000	0.004	0.000	0.794	0.000	0.001	0.002	0.002
*T5H003	0.000	0.000	0.000	0.780	0.005	0.000	0.017	0.000	0.000	0.025	0.001	0.000	0.156	0.000	0.005	0.003	0.008
*U2H055	0.000	0.000	0.225	0.038	0.139	0.359	0.115	0.000	0.021	0.043	0.023	0.007	0.005	0.005	0.002	0.019	0.000

*- Land cover fractions from these stations were used as an independent data set to confirm the model in Chapter 5

Appendix A Table 5: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
A2H012	0.000	0.000	0.000	0.083	0.019	0.000	0.335	0.000	0.087	0.015	0.024	0.003	0.034	0.016	0.374	0.005	0.005
A2H014	0.000	0.000	0.000	0.194	0.027	0.000	0.418	0.000	0.122	0.042	0.017	0.006	0.003	0.005	0.136	0.013	0.018
A2H021	0.000	0.000	0.000	0.046	0.034	0.051	0.263	0.001	0.342	0.003	0.004	0.001	0.094	0.009	0.132	0.010	0.011
A2H048	0.000	0.000	0.000	0.155	0.067	0.000	0.234	0.000	0.164	0.012	0.013	0.002	0.086	0.011	0.236	0.017	0.003
A2H059	0.000	0.000	0.001	0.121	0.088	0.002	0.154	0.000	0.176	0.005	0.005	0.003	0.322	0.004	0.103	0.013	0.002
A2H060	0.000	0.000	0.000	0.092	0.069	0.019	0.192	0.000	0.242	0.004	0.005	0.002	0.241	0.006	0.111	0.011	0.005
A2H061	0.000	0.000	0.000	0.019	0.199	0.000	0.033	0.000	0.137	0.027	0.032	0.001	0.030	0.067	0.441	0.013	0.000
A2H083	0.000	0.000	0.000	0.171	0.019	0.000	0.270	0.000	0.116	0.014	0.015	0.002	0.094	0.010	0.266	0.019	0.003
A2H094	0.000	0.000	0.002	0.296	0.106	0.000	0.127	0.000	0.201	0.000	0.000	0.006	0.222	0.000	0.015	0.016	0.009
A2H106	0.000	0.000	0.000	0.053	0.034	0.035	0.272	0.001	0.348	0.004	0.005	0.001	0.078	0.011	0.135	0.011	0.013
A2H116	0.000	0.000	0.000	0.090	0.078	0.018	0.183	0.001	0.246	0.004	0.004	0.002	0.247	0.006	0.105	0.011	0.005
A4H002	0.000	0.000	0.000	0.461	0.031	0.000	0.086	0.000	0.213	0.002	0.000	0.000	0.202	0.000	0.000	0.006	0.000
A7H001	0.000	0.000	0.066	0.037	0.012	0.036	0.207	0.001	0.222	0.000	0.000	0.000	0.389	0.024	0.006	0.000	0.000
A9H001	0.000	0.200	0.002	0.006	0.001	0.088	0.009	0.000	0.002	0.093	0.000	0.000	0.581	0.000	0.015	0.005	0.000
A9H013	0.007	0.000	0.000	0.001	0.005	0.271	0.158	0.000	0.462	0.003	0.000	0.000	0.092	0.000	0.000	0.001	0.000
B1H005	0.000	0.000	0.000	0.286	0.004	0.000	0.633	0.000	0.000	0.003	0.001	0.053	0.003	0.001	0.009	0.007	0.000
B1H010	0.000	0.000	0.000	0.268	0.004	0.000	0.633	0.000	0.000	0.003	0.001	0.055	0.003	0.001	0.014	0.018	0.000
B1H012	0.000	0.000	0.000	0.284	0.010	0.000	0.569	0.000	0.000	0.009	0.000	0.118	0.001	0.000	0.000	0.009	0.000
B1H015	0.000	0.000	0.000	0.276	0.010	0.000	0.571	0.000	0.000	0.009	0.000	0.115	0.001	0.000	0.000	0.019	0.000
B1H020	0.000	0.000	0.000	0.322	0.002	0.000	0.635	0.000	0.000	0.004	0.001	0.028	0.000	0.002	0.004	0.002	0.001
B1H021	0.000	0.000	0.000	0.288	0.005	0.000	0.649	0.000	0.000	0.002	0.002	0.034	0.000	0.000	0.012	0.009	0.000

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
B2H003	0.000	0.000	0.000	0.367	0.007	0.000	0.553	0.000	0.000	0.009	0.000	0.004	0.003	0.002	0.032	0.017	0.006
B2H014	0.000	0.000	0.000	0.414	0.001	0.000	0.556	0.000	0.002	0.003	0.000	0.010	0.007	0.001	0.001	0.004	0.000
B2H015	0.000	0.000	0.000	0.325	0.004	0.000	0.602	0.000	0.002	0.007	0.000	0.005	0.023	0.002	0.019	0.009	0.003
B3H001	0.000	0.000	0.003	0.193	0.044	0.006	0.520	0.000	0.119	0.007	0.001	0.028	0.042	0.001	0.020	0.015	0.001
B3H021	0.000	0.000	0.000	0.282	0.041	0.069	0.227	0.000	0.304	0.002	0.000	0.000	0.038	0.000	0.031	0.005	0.000
B4H003	0.000	0.000	0.000	0.235	0.026	0.000	0.371	0.000	0.089	0.034	0.000	0.015	0.224	0.000	0.002	0.005	0.000
B4H010	0.000	0.000	0.000	0.155	0.041	0.000	0.708	0.000	0.000	0.038	0.000	0.000	0.037	0.001	0.016	0.004	0.000
B6H001	0.000	0.000	0.035	0.065	0.000	0.000	0.426	0.000	0.005	0.340	0.000	0.000	0.123	0.000	0.005	0.000	0.000
B6H004	0.000	0.000	0.011	0.020	0.128	0.002	0.342	0.000	0.007	0.114	0.000	0.000	0.367	0.000	0.002	0.006	0.000
B7H015	0.000	0.001	0.009	0.123	0.041	0.047	0.368	0.001	0.179	0.013	0.000	0.011	0.180	0.001	0.018	0.008	0.000
B7H019	0.000	0.000	0.121	0.002	0.000	0.089	0.087	0.000	0.453	0.000	0.000	0.014	0.217	0.002	0.014	0.001	0.000
B8H008	0.006	0.045	0.127	0.008	0.029	0.200	0.052	0.000	0.161	0.128	0.000	0.000	0.187	0.001	0.049	0.008	0.000
B8H009	0.000	0.095	0.068	0.001	0.031	0.111	0.090	0.000	0.074	0.315	0.000	0.000	0.158	0.002	0.039	0.016	0.000
B8H014	0.000	0.102	0.000	0.000	0.000	0.000	0.070	0.000	0.116	0.519	0.000	0.000	0.157	0.000	0.000	0.036	0.000
C1H002	0.000	0.000	0.000	0.110	0.003	0.000	0.856	0.001	0.000	0.004	0.000	0.000	0.008	0.000	0.001	0.000	0.018
C1H007	0.000	0.000	0.000	0.187	0.002	0.004	0.785	0.000	0.000	0.008	0.000	0.001	0.006	0.001	0.001	0.004	0.002
C1H008	0.000	0.000	0.000	0.356	0.006	0.000	0.623	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.002	0.004	0.006
C1H015	0.000	0.000	0.000	0.110	0.003	0.000	0.856	0.001	0.000	0.004	0.000	0.000	0.008	0.000	0.001	0.000	0.018
C2H001	0.000	0.000	0.000	0.223	0.011	0.002	0.630	0.000	0.006	0.020	0.001	0.027	0.007	0.000	0.050	0.012	0.010
C2H004	0.000	0.000	0.000	0.279	0.004	0.000	0.568	0.000	0.000	0.003	0.002	0.027	0.012	0.006	0.050	0.007	0.042
C2H005	0.000	0.000	0.000	0.423	0.006	0.000	0.432	0.000	0.007	0.006	0.000	0.023	0.007	0.002	0.091	0.003	0.000

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
C2H007	0.001	0.000	0.000	0.249	0.006	0.001	0.667	0.000	0.003	0.004	0.001	0.007	0.012	0.003	0.021	0.016	0.009
C2H008	0.002	0.000	0.000	0.252	0.003	0.001	0.669	0.000	0.000	0.004	0.001	0.006	0.009	0.004	0.022	0.018	0.010
C2H018	0.002	0.000	0.000	0.254	0.003	0.001	0.665	0.000	0.002	0.004	0.001	0.006	0.011	0.003	0.022	0.017	0.010
C2H021	0.000	0.000	0.000	0.123	0.000	0.000	0.435	0.000	0.000	0.010	0.011	0.064	0.021	0.039	0.200	0.014	0.083
C2H061	0.001	0.000	0.000	0.252	0.006	0.000	0.665	0.000	0.004	0.004	0.001	0.005	0.016	0.003	0.020	0.014	0.009
C2H069	0.000	0.000	0.000	0.167	0.011	0.000	0.609	0.000	0.001	0.035	0.002	0.056	0.013	0.000	0.104	0.001	0.001
C2H073	0.000	0.000	0.000	0.267	0.007	0.000	0.617	0.000	0.021	0.007	0.000	0.000	0.010	0.003	0.026	0.010	0.032
C2H085	0.000	0.000	0.000	0.241	0.017	0.001	0.622	0.000	0.004	0.014	0.002	0.018	0.006	0.001	0.053	0.014	0.007
C2H140	0.002	0.000	0.000	0.254	0.003	0.001	0.666	0.000	0.000	0.004	0.001	0.006	0.009	0.004	0.022	0.018	0.010
C3H003	0.000	0.000	0.000	0.214	0.011	0.013	0.541	0.000	0.001	0.011	0.000	0.000	0.181	0.001	0.011	0.012	0.005
C3H007	0.000	0.000	0.000	0.106	0.018	0.006	0.396	0.000	0.000	0.005	0.000	0.000	0.446	0.001	0.009	0.005	0.008
C3H016	0.000	0.000	0.000	0.079	0.019	0.004	0.323	0.000	0.000	0.004	0.000	0.000	0.540	0.001	0.007	0.009	0.014
C5H012	0.000	0.000	0.000	0.037	0.002	0.000	0.865	0.000	0.002	0.000	0.000	0.000	0.088	0.000	0.000	0.005	0.001
C5H014	0.000	0.000	0.000	0.052	0.019	0.001	0.713	0.000	0.000	0.001	0.000	0.000	0.179	0.004	0.012	0.013	0.003
C5H016	0.000	0.000	0.000	0.051	0.021	0.001	0.704	0.000	0.000	0.001	0.000	0.000	0.188	0.004	0.012	0.013	0.003
C5H018	0.000	0.000	0.000	0.085	0.015	0.002	0.678	0.000	0.000	0.002	0.001	0.000	0.165	0.009	0.024	0.014	0.006
C5H035	0.000	0.000	0.000	0.085	0.014	0.002	0.678	0.000	0.000	0.002	0.001	0.000	0.165	0.009	0.024	0.014	0.006
C5H048	0.000	0.000	0.000	0.050	0.023	0.001	0.696	0.000	0.000	0.001	0.000	0.000	0.195	0.004	0.012	0.013	0.003
C5H053	0.000	0.000	0.000	0.063	0.001	0.003	0.771	0.001	0.000	0.001	0.001	0.000	0.082	0.017	0.041	0.015	0.002
C6H001	0.000	0.000	0.000	0.265	0.003	0.000	0.708	0.000	0.000	0.000	0.000	0.000	0.003	0.002	0.008	0.006	0.005
C6H003	0.000	0.000	0.000	0.272	0.003	0.000	0.704	0.000	0.000	0.001	0.000	0.000	0.002	0.002	0.008	0.005	0.004

Appendix A

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
C6H007	0.001	0.000	0.000	0.287	0.003	0.000	0.686	0.000	0.000	0.001	0.000	0.000	0.004	0.000	0.010	0.006	0.002
C7H006	0.000	0.000	0.000	0.225	0.021	0.000	0.716	0.000	0.009	0.000	0.000	0.000	0.007	0.001	0.001	0.013	0.007
C8H001	0.005	0.000	0.000	0.283	0.002	0.000	0.664	0.000	0.000	0.003	0.000	0.000	0.015	0.001	0.011	0.009	0.005
C8H003	0.001	0.000	0.000	0.146	0.006	0.005	0.822	0.000	0.000	0.001	0.000	0.000	0.009	0.000	0.006	0.001	0.003
C8H004	0.008	0.002	0.000	0.456	0.001	0.000	0.496	0.001	0.000	0.001	0.000	0.000	0.013	0.000	0.005	0.009	0.010
C8H011	0.016	0.000	0.000	0.105	0.002	0.002	0.724	0.000	0.000	0.001	0.000	0.000	0.060	0.004	0.079	0.005	0.002
C8H020	0.008	0.002	0.000	0.456	0.002	0.000	0.496	0.001	0.000	0.001	0.000	0.000	0.012	0.000	0.005	0.009	0.010
C8H022	0.005	0.000	0.000	0.285	0.002	0.000	0.662	0.000	0.000	0.003	0.000	0.000	0.016	0.001	0.011	0.009	0.005
C8H026	0.006	0.001	0.000	0.426	0.001	0.000	0.534	0.001	0.000	0.001	0.000	0.000	0.010	0.000	0.004	0.007	0.008
C8H027	0.004	0.000	0.000	0.212	0.002	0.001	0.729	0.000	0.000	0.005	0.000	0.000	0.019	0.001	0.015	0.010	0.003
C8H028	0.005	0.000	0.000	0.210	0.002	0.001	0.712	0.000	0.000	0.006	0.000	0.000	0.024	0.001	0.020	0.013	0.004
C9H009	0.001	0.000	0.000	0.243	0.007	0.001	0.643	0.002	0.003	0.003	0.001	0.004	0.049	0.002	0.016	0.015	0.010
C9H010	0.001	0.000	0.000	0.219	0.009	0.001	0.596	0.002	0.002	0.004	0.001	0.004	0.120	0.002	0.015	0.014	0.010
C9H021	0.001	0.000	0.000	0.248	0.005	0.001	0.651	0.002	0.003	0.004	0.001	0.005	0.037	0.002	0.016	0.016	0.010
C9H024	0.001	0.000	0.000	0.215	0.009	0.001	0.588	0.002	0.002	0.003	0.001	0.004	0.132	0.002	0.015	0.014	0.011
D1H001	0.000	0.000	0.000	0.005	0.010	0.000	0.523	0.000	0.000	0.002	0.002	0.000	0.445	0.000	0.008	0.005	0.000
D1H011	0.016	0.000	0.000	0.048	0.019	0.000	0.880	0.001	0.000	0.002	0.005	0.000	0.024	0.000	0.002	0.001	0.002
D3H015	0.000	0.000	0.000	0.007	0.000	0.000	0.062	0.000	0.000	0.000	0.011	0.000	0.911	0.000	0.002	0.006	0.000
E1H013	0.000	0.000	0.178	0.022	0.119	0.000	0.009	0.000	0.000	0.006	0.000	0.000	0.652	0.000	0.002	0.007	0.006
E2H002	0.000	0.000	0.030	0.009	0.025	0.000	0.005	0.048	0.000	0.001	0.003	0.000	0.871	0.000	0.000	0.008	0.000
E2H003	0.001	0.000	0.009	0.024	0.016	0.000	0.002	0.065	0.000	0.000	0.001	0.000	0.878	0.000	0.000	0.003	0.000

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
G1H013	0.000	0.000	0.202	0.344	0.000	0.000	0.020	0.000	0.000	0.057	0.002	0.000	0.339	0.002	0.020	0.010	0.004
G1H031	0.000	0.001	0.151	0.499	0.000	0.000	0.014	0.000	0.000	0.041	0.002	0.000	0.260	0.001	0.017	0.009	0.003
G1H036	0.000	0.308	0.000	0.200	0.000	0.000	0.021	0.000	0.000	0.085	0.005	0.000	0.315	0.004	0.038	0.016	0.008
G2H015	0.000	0.000	0.465	0.000	0.007	0.000	0.001	0.000	0.000	0.104	0.003	0.000	0.328	0.007	0.070	0.016	0.000
G2H020	0.000	0.000	0.300	0.000	0.000	0.000	0.001	0.000	0.000	0.154	0.002	0.000	0.424	0.010	0.099	0.010	0.000
G4H007	0.000	0.000	0.355	0.000	0.000	0.000	0.000	0.000	0.000	0.114	0.000	0.000	0.490	0.000	0.005	0.037	0.000
H1H003	0.000	0.000	0.326	0.058	0.007	0.000	0.017	0.000	0.000	0.003	0.000	0.000	0.535	0.002	0.029	0.024	0.000
H1H006	0.000	0.000	0.260	0.046	0.006	0.000	0.013	0.000	0.000	0.002	0.000	0.000	0.629	0.002	0.023	0.019	0.000
H2H006	0.000	0.000	0.205	0.025	0.004	0.000	0.017	0.000	0.000	0.002	0.000	0.000	0.735	0.000	0.005	0.008	0.000
H3H011	0.000	0.000	0.161	0.044	0.002	0.000	0.008	0.000	0.000	0.001	0.001	0.000	0.770	0.000	0.008	0.005	0.000
H4H017	0.002	0.001	0.225	0.037	0.007	0.000	0.037	0.000	0.000	0.003	0.000	0.000	0.664	0.003	0.007	0.011	0.003
H4H020	0.000	0.000	0.173	0.105	0.002	0.000	0.019	0.000	0.000	0.000	0.002	0.000	0.687	0.000	0.000	0.011	0.000
H5H002	0.003	0.001	0.220	0.036	0.006	0.000	0.027	0.000	0.000	0.002	0.000	0.000	0.683	0.002	0.008	0.010	0.002
H5H004	0.003	0.001	0.221	0.036	0.006	0.000	0.027	0.000	0.000	0.002	0.000	0.000	0.683	0.002	0.008	0.010	0.002
H6H009	0.000	0.000	0.080	0.300	0.021	0.000	0.029	0.000	0.000	0.011	0.008	0.000	0.475	0.000	0.007	0.060	0.009
H7H006	0.002	0.000	0.187	0.140	0.010	0.000	0.025	0.000	0.000	0.004	0.002	0.000	0.598	0.001	0.007	0.020	0.003
H8H001	0.000	0.000	0.009	0.462	0.015	0.000	0.006	0.000	0.000	0.002	0.029	0.000	0.446	0.000	0.022	0.004	0.005
H9H005	0.000	0.000	0.000	0.133	0.140	0.000	0.000	0.000	0.000	0.025	0.026	0.000	0.598	0.000	0.000	0.007	0.070
J1H018	0.000	0.000	0.013	0.040	0.005	0.000	0.010	0.000	0.000	0.000	0.003	0.000	0.925	0.000	0.001	0.002	0.000

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
J1H019	0.000	0.000	0.011	0.022	0.013	0.000	0.009	0.000	0.000	0.001	0.004	0.000	0.936	0.000	0.001	0.003	0.000
J4H002	0.001	0.000	0.005	0.017	0.030	0.000	0.021	0.000	0.000	0.000	0.005	0.000	0.916	0.000	0.002	0.002	0.000
K1H004	0.000	0.000	0.000	0.133	0.063	0.000	0.000	0.000	0.000	0.000	0.015	0.000	0.788	0.000	0.000	0.001	0.000
K1H005	0.000	0.000	0.000	0.011	0.010	0.000	0.005	0.000	0.022	0.150	0.048	0.000	0.754	0.000	0.000	0.001	0.000
N4H001	0.000	0.000	0.000	0.000	0.039	0.000	0.076	0.000	0.002	0.000	0.004	0.000	0.869	0.000	0.002	0.006	0.000
N4H003	0.000	0.000	0.000	0.004	0.052	0.000	0.068	0.000	0.002	0.001	0.004	0.000	0.861	0.000	0.002	0.005	0.000
P1H003	0.000	0.000	0.000	0.001	0.005	0.004	0.049	0.000	0.002	0.003	0.000	0.000	0.932	0.000	0.002	0.001	0.000
P3H001	0.000	0.021	0.000	0.063	0.018	0.000	0.238	0.000	0.000	0.002	0.011	0.000	0.641	0.000	0.000	0.005	0.000
P4H001	0.000	0.025	0.000	0.028	0.023	0.006	0.167	0.000	0.004	0.005	0.003	0.000	0.714	0.002	0.024	0.001	0.000
Q1H002	0.000	0.000	0.000	0.000	0.039	0.000	0.089	0.000	0.000	0.000	0.026	0.000	0.845	0.000	0.000	0.001	0.000
Q1H012	0.000	0.000	0.000	0.000	0.026	0.000	0.329	0.000	0.000	0.000	0.006	0.000	0.630	0.000	0.007	0.002	0.000
Q1H013	0.000	0.000	0.000	0.000	0.069	0.000	0.093	0.000	0.000	0.000	0.007	0.000	0.818	0.000	0.011	0.002	0.000
Q3H004	0.000	0.000	0.000	0.000	0.016	0.000	0.109	0.000	0.000	0.000	0.026	0.000	0.849	0.000	0.000	0.000	0.000
Q3H005	0.000	0.000	0.000	0.000	0.055	0.000	0.135	0.000	0.000	0.000	0.015	0.000	0.786	0.000	0.003	0.004	0.001
Q4H013	0.000	0.000	0.000	0.000	0.036	0.000	0.305	0.002	0.000	0.000	0.005	0.000	0.641	0.000	0.001	0.004	0.002
Q6H003	0.000	0.000	0.000	0.000	0.004	0.000	0.631	0.000	0.000	0.000	0.001	0.000	0.361	0.000	0.000	0.000	0.000
Q7H005	0.000	0.000	0.000	0.000	0.067	0.000	0.120	0.000	0.055	0.001	0.004	0.000	0.750	0.000	0.001	0.002	0.000
Q8H008	0.000	0.000	0.000	0.000	0.052	0.000	0.203	0.000	0.064	0.002	0.006	0.000	0.670	0.000	0.002	0.001	0.000
Q9H002	0.000	0.000	0.000	0.000	0.058	0.017	0.642	0.000	0.004	0.005	0.002	0.000	0.270	0.000	0.002	0.001	0.000
Q9H012	0.000	0.000	0.000	0.000	0.070	0.000	0.179	0.000	0.013	0.000	0.007	0.000	0.722	0.000	0.002	0.003	0.001
Q9H018	0.000	0.000	0.003	0.000	0.057	0.004	0.191	0.000	0.016	0.002	0.006	0.000	0.714	0.000	0.004	0.003	0.001

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
Q9H029	0.000	0.000	0.060	0.000	0.005	0.057	0.230	0.000	0.052	0.025	0.000	0.000	0.562	0.000	0.003	0.007	0.000
R1H005	0.000	0.000	0.000	0.000	0.075	0.069	0.326	0.000	0.133	0.062	0.000	0.000	0.265	0.000	0.055	0.014	0.000
R1H015	0.000	0.000	0.002	0.000	0.021	0.068	0.411	0.000	0.040	0.022	0.000	0.000	0.374	0.001	0.053	0.007	0.000
R2H027	0.000	0.000	0.000	0.000	0.005	0.119	0.388	0.000	0.074	0.015	0.000	0.001	0.307	0.007	0.072	0.007	0.000
S3H004	0.000	0.000	0.000	0.000	0.012	0.015	0.851	0.009	0.005	0.001	0.004	0.000	0.071	0.000	0.030	0.002	0.000
S3H005	0.001	0.000	0.000	0.000	0.007	0.003	0.766	0.000	0.000	0.000	0.000	0.000	0.108	0.003	0.093	0.018	0.000
S3H006	0.003	0.001	0.000	0.000	0.027	0.009	0.753	0.013	0.000	0.001	0.005	0.000	0.175	0.000	0.003	0.002	0.000
S5H002	0.003	0.000	0.000	0.000	0.012	0.160	0.723	0.000	0.000	0.014	0.004	0.000	0.021	0.000	0.051	0.000	0.000
S5H004	0.004	0.000	0.000	0.000	0.012	0.136	0.744	0.000	0.001	0.018	0.006	0.000	0.026	0.000	0.022	0.016	0.000
S6H002	0.000	0.000	0.000	0.000	0.031	0.014	0.676	0.000	0.024	0.133	0.000	0.000	0.086	0.000	0.007	0.018	0.000
S7H001	0.000	0.000	0.000	0.000	0.000	0.356	0.397	0.000	0.000	0.020	0.002	0.000	0.112	0.000	0.103	0.010	0.000
S7H004	0.002	0.000	0.000	0.000	0.020	0.079	0.610	0.007	0.002	0.011	0.003	0.000	0.227	0.000	0.022	0.007	0.000
T1H001	0.003	0.000	0.000	0.000	0.001	0.146	0.700	0.003	0.012	0.017	0.000	0.000	0.054	0.000	0.008	0.002	0.002
T1H004	0.001	0.000	0.000	0.000	0.007	0.248	0.643	0.001	0.009	0.019	0.000	0.000	0.034	0.000	0.025	0.001	0.000
T3H004	0.000	0.000	0.000	0.000	0.082	0.008	0.718	0.000	0.000	0.009	0.007	0.000	0.019	0.001	0.006	0.005	0.036
T3H005	0.004	0.000	0.000	0.000	0.000	0.152	0.796	0.000	0.000	0.008	0.000	0.000	0.021	0.000	0.012	0.000	0.006
T3H006	0.004	0.000	0.034	0.000	0.122	0.000	0.207	0.000	0.042	0.000	0.000	0.000	0.572	0.012	0.001	0.006	0.000
T3H007	0.001	0.000	0.000	0.000	0.004	0.132	0.716	0.000	0.002	0.003	0.001	0.000	0.042	0.000	0.014	0.003	0.054
T3H008	0.000	0.000	0.000	0.000	0.013	0.059	0.751	0.000	0.000	0.002	0.002	0.000	0.019	0.000	0.008	0.006	0.064
T4H001	0.000	0.000	0.000	0.000	0.000	0.247	0.573	0.000	0.023	0.122	0.000	0.000	0.027	0.000	0.008	0.000	0.000
T5H002	0.001	0.000	0.000	0.000	0.000	0.193	0.523	0.000	0.042	0.189	0.000	0.000	0.037	0.000	0.015	0.000	0.000

Appendix A

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
T5H004	0.000	0.000	0.000	0.029	0.099	0.000	0.821	0.000	0.000	0.017	0.003	0.000	0.026	0.000	0.003	0.003	0.000
T5H007	0.001	0.000	0.000	0.016	0.060	0.101	0.712	0.001	0.011	0.044	0.004	0.000	0.022	0.000	0.012	0.005	0.011
U1H005	0.000	0.000	0.000	0.005	0.006	0.029	0.878	0.000	0.004	0.026	0.002	0.000	0.049	0.000	0.000	0.000	0.002
U1H006	0.000	0.000	0.000	0.009	0.038	0.066	0.561	0.000	0.004	0.085	0.005	0.000	0.228	0.000	0.000	0.002	0.001
U6H003	0.000	0.000	0.173	0.039	0.035	0.068	0.415	0.000	0.013	0.201	0.008	0.000	0.030	0.001	0.006	0.010	0.000
U8H003	0.000	0.000	0.068	0.000	0.000	0.147	0.226	0.000	0.017	0.063	0.000	0.000	0.479	0.000	0.000	0.000	0.000
V1H001	0.001	0.000	0.000	0.029	0.131	0.093	0.542	0.002	0.004	0.016	0.000	0.000	0.139	0.000	0.004	0.039	0.000
V1H010	0.000	0.000	0.000	0.024	0.260	0.150	0.479	0.000	0.008	0.047	0.000	0.000	0.022	0.000	0.007	0.002	0.000
V1H038	0.000	0.000	0.000	0.023	0.004	0.026	0.565	0.012	0.014	0.007	0.000	0.000	0.342	0.000	0.000	0.002	0.005
V1H041	0.001	0.000	0.000	0.000	0.015	0.049	0.727	0.001	0.016	0.013	0.000	0.000	0.174	0.000	0.000	0.000	0.003
V1H058	0.002	0.000	0.000	0.028	0.027	0.114	0.540	0.000	0.001	0.007	0.000	0.000	0.197	0.000	0.001	0.084	0.000
V2H002	0.000	0.000	0.000	0.062	0.137	0.000	0.730	0.000	0.006	0.027	0.001	0.000	0.021	0.000	0.003	0.009	0.003
V2H004	0.000	0.000	0.000	0.065	0.115	0.000	0.734	0.000	0.004	0.022	0.024	0.000	0.019	0.001	0.005	0.008	0.002
V2H006	0.000	0.000	0.000	0.078	0.095	0.000	0.729	0.000	0.013	0.028	0.000	0.000	0.035	0.000	0.000	0.015	0.008
V3H010	0.000	0.000	0.000	0.086	0.014	0.041	0.668	0.002	0.014	0.014	0.001	0.009	0.095	0.002	0.016	0.028	0.009
V5H002	0.000	0.000	0.003	0.037	0.036	0.087	0.552	0.005	0.009	0.015	0.005	0.002	0.223	0.001	0.009	0.013	0.003
V6H002	0.000	0.000	0.000	0.021	0.053	0.060	0.551	0.008	0.008	0.010	0.003	0.001	0.257	0.001	0.011	0.015	0.001
V6H004	0.000	0.000	0.000	0.025	0.019	0.014	0.589	0.012	0.022	0.009	0.000	0.001	0.293	0.000	0.003	0.013	0.000
W1H009	0.000	0.000	0.122	0.000	0.000	0.089	0.388	0.000	0.008	0.140	0.000	0.001	0.240	0.000	0.002	0.010	0.000
W2H005	0.000	0.000	0.000	0.026	0.004	0.119	0.717	0.009	0.000	0.039	0.000	0.001	0.077	0.000	0.003	0.005	0.000
W2H009	0.000	0.000	0.000	0.104	0.017	0.000	0.690	0.000	0.000	0.110	0.001	0.000	0.035	0.000	0.012	0.032	0.000

Appendix A

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

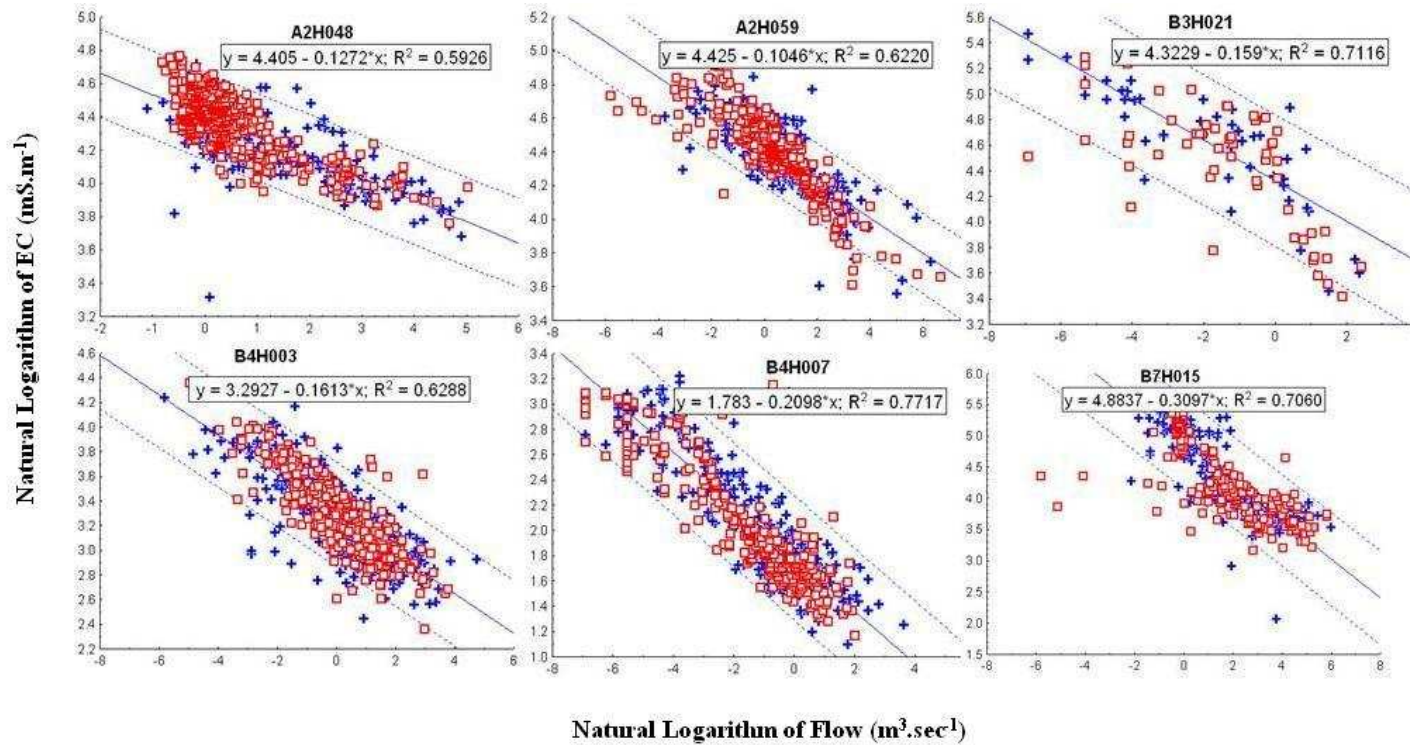
DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
W3H008	0.000	0.000	0.018	0.020	0.009	0.058	0.336	0.002	0.443	0.039	0.000	0.003	0.070	0.000	0.001	0.002	0.000
W3H015	0.000	0.011	0.050	0.000	0.000	0.231	0.208	0.000	0.193	0.004	0.000	0.000	0.287	0.000	0.000	0.009	0.008
W4H004	0.000	0.000	0.000	0.129	0.002	0.000	0.720	0.000	0.000	0.136	0.000	0.002	0.011	0.000	0.000	0.000	0.000
W5H005	0.000	0.000	0.000	0.050	0.000	0.000	0.539	0.000	0.000	0.400	0.000	0.005	0.006	0.000	0.000	0.000	0.000
W5H022	0.000	0.000	0.000	0.067	0.000	0.005	0.704	0.000	0.000	0.165	0.000	0.003	0.001	0.001	0.000	0.053	0.000
W5H024	0.000	0.000	0.000	0.038	0.001	0.010	0.628	0.000	0.000	0.307	0.000	0.000	0.003	0.001	0.005	0.006	0.001
W5H025	0.000	0.000	0.000	0.037	0.001	0.000	0.699	0.000	0.000	0.231	0.000	0.000	0.005	0.000	0.001	0.024	0.002
W5H026	0.000	0.000	0.000	0.061	0.000	0.006	0.676	0.000	0.000	0.203	0.000	0.000	0.005	0.001	0.012	0.034	0.002
X1H001	0.000	0.000	0.000	0.073	0.027	0.011	0.706	0.000	0.000	0.103	0.000	0.001	0.063	0.000	0.004	0.011	0.000
X1H016	0.000	0.000	0.000	0.041	0.000	0.000	0.739	0.000	0.000	0.195	0.000	0.000	0.023	0.000	0.001	0.000	0.000
X1H018	0.000	0.000	0.000	0.136	0.002	0.000	0.799	0.000	0.000	0.019	0.000	0.002	0.028	0.000	0.000	0.014	0.000
X2H005	0.000	0.050	0.003	0.041	0.000	0.000	0.142	0.000	0.082	0.587	0.000	0.000	0.087	0.001	0.001	0.006	0.000
X2H006	0.000	0.020	0.011	0.040	0.065	0.000	0.299	0.000	0.040	0.287	0.000	0.000	0.221	0.002	0.007	0.008	0.000
X2H015	0.000	0.000	0.000	0.019	0.052	0.000	0.489	0.000	0.000	0.208	0.000	0.000	0.205	0.003	0.020	0.004	0.000
X2H016	0.000	0.015	0.022	0.035	0.049	0.008	0.188	0.000	0.264	0.188	0.000	0.001	0.216	0.001	0.010	0.005	0.000
X2H017	0.000	0.018	0.014	0.041	0.057	0.009	0.221	0.000	0.155	0.221	0.000	0.001	0.244	0.001	0.012	0.005	0.000
X2H022	0.000	0.020	0.009	0.049	0.067	0.000	0.238	0.000	0.059	0.268	0.000	0.001	0.273	0.002	0.006	0.006	0.000
X2H031	0.000	0.000	0.000	0.177	0.000	0.000	0.059	0.000	0.000	0.566	0.000	0.000	0.195	0.000	0.000	0.003	0.000
X2H032	0.000	0.025	0.011	0.037	0.061	0.000	0.283	0.000	0.043	0.272	0.000	0.000	0.248	0.002	0.008	0.007	0.000
X2H046	0.000	0.017	0.014	0.042	0.060	0.009	0.229	0.000	0.126	0.229	0.000	0.001	0.252	0.001	0.013	0.005	0.000
X3H004	0.003	0.033	0.013	0.000	0.071	0.000	0.068	0.000	0.000	0.408	0.000	0.000	0.391	0.000	0.000	0.013	0.000
X3H006	0.001	0.000	0.026	0.000	0.041	0.000	0.091	0.000	0.018	0.599	0.000	0.000	0.192	0.014	0.019	0.000	0.000
X3H008	0.003	0.000	0.010	0.000	0.000	0.123	0.391	0.000	0.113	0.051	0.000	0.000	0.214	0.000	0.092	0.003	0.000
X3H015	0.003	0.002	0.013	0.000	0.015	0.028	0.162	0.000	0.339	0.174	0.000	0.000	0.229	0.002	0.033	0.001	0.000

Appendix A Table 5 continued: Land cover fractions for 1 km riparian zone (codes taken from Table 5.1) for all DWA monitoring sites investigated

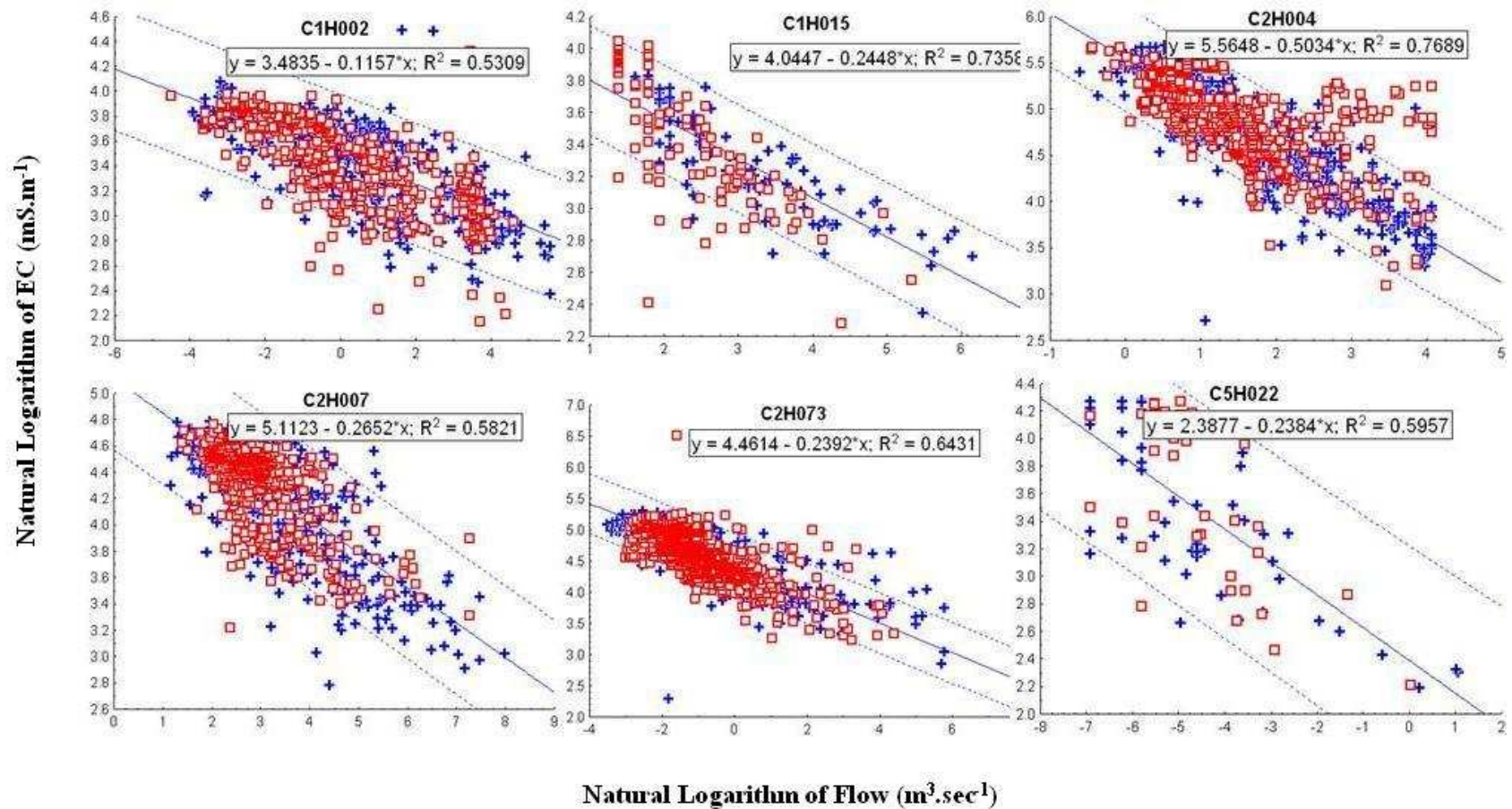
DWA station	BR	C:PCD	C:PCI	C:TCD	C:TCI	C:TCSD	DNA	DSES	UFNA	FP	IG	MQ	UB	U:CI	U:R	WB	W
*A6H009	0.000	0.004	0.000	0.096	0.014	0.126	0.188	0.000	0.266	0.001	0.000	0.001	0.266	0.001	0.025	0.006	0.004
*B8H033	0.006	0.009	0.002	0.015	0.169	0.187	0.036	0.000	0.006	0.008	0.000	0.000	0.535	0.000	0.018	0.009	0.000
*C4H017	0.001	0.000	0.000	0.266	0.002	0.000	0.606	0.021	0.001	0.000	0.000	0.003	0.077	0.001	0.006	0.009	0.007
*K4H001	0.000	0.000	0.000	0.000	0.016	0.000	0.000	0.000	0.260	0.250	0.017	0.000	0.452	0.004	0.000	0.002	0.000
*N2H007	0.000	0.000	0.000	0.000	0.045	0.000	0.092	0.000	0.000	0.000	0.006	0.000	0.850	0.000	0.003	0.004	0.000
*Q1H001	0.000	0.000	0.000	0.000	0.049	0.000	0.148	0.000	0.000	0.000	0.013	0.000	0.779	0.000	0.004	0.006	0.002
*T5H003	0.000	0.000	0.000	0.022	0.119	0.000	0.789	0.000	0.000	0.016	0.006	0.000	0.009	0.000	0.000	0.032	0.006
*U2H055	0.000	0.000	0.059	0.049	0.020	0.056	0.347	0.000	0.018	0.198	0.025	0.000	0.160	0.005	0.036	0.026	0.001

*- Land cover fractions from these stations were used as an independent data set to confirm the model in Chapter 5

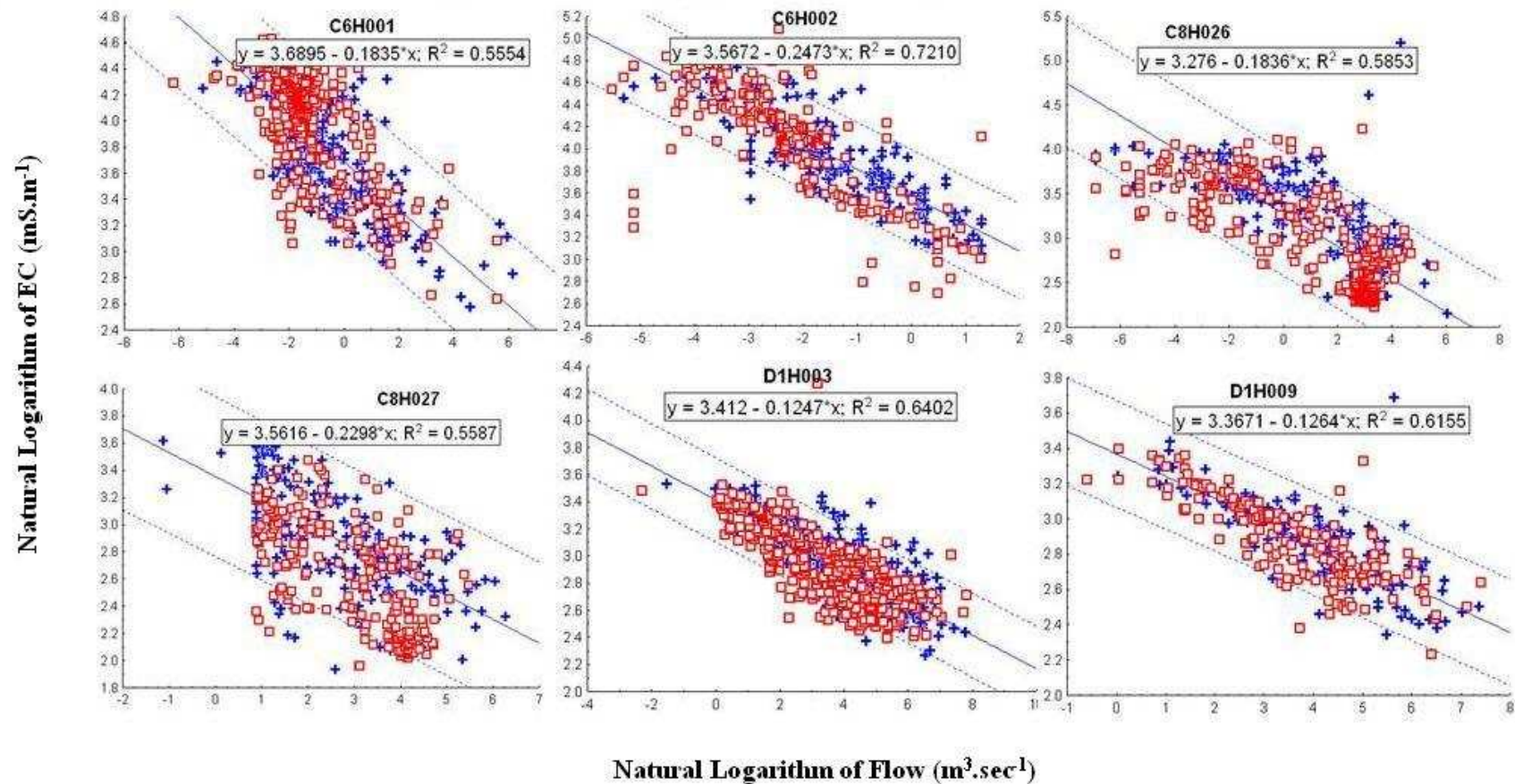
Appendix B



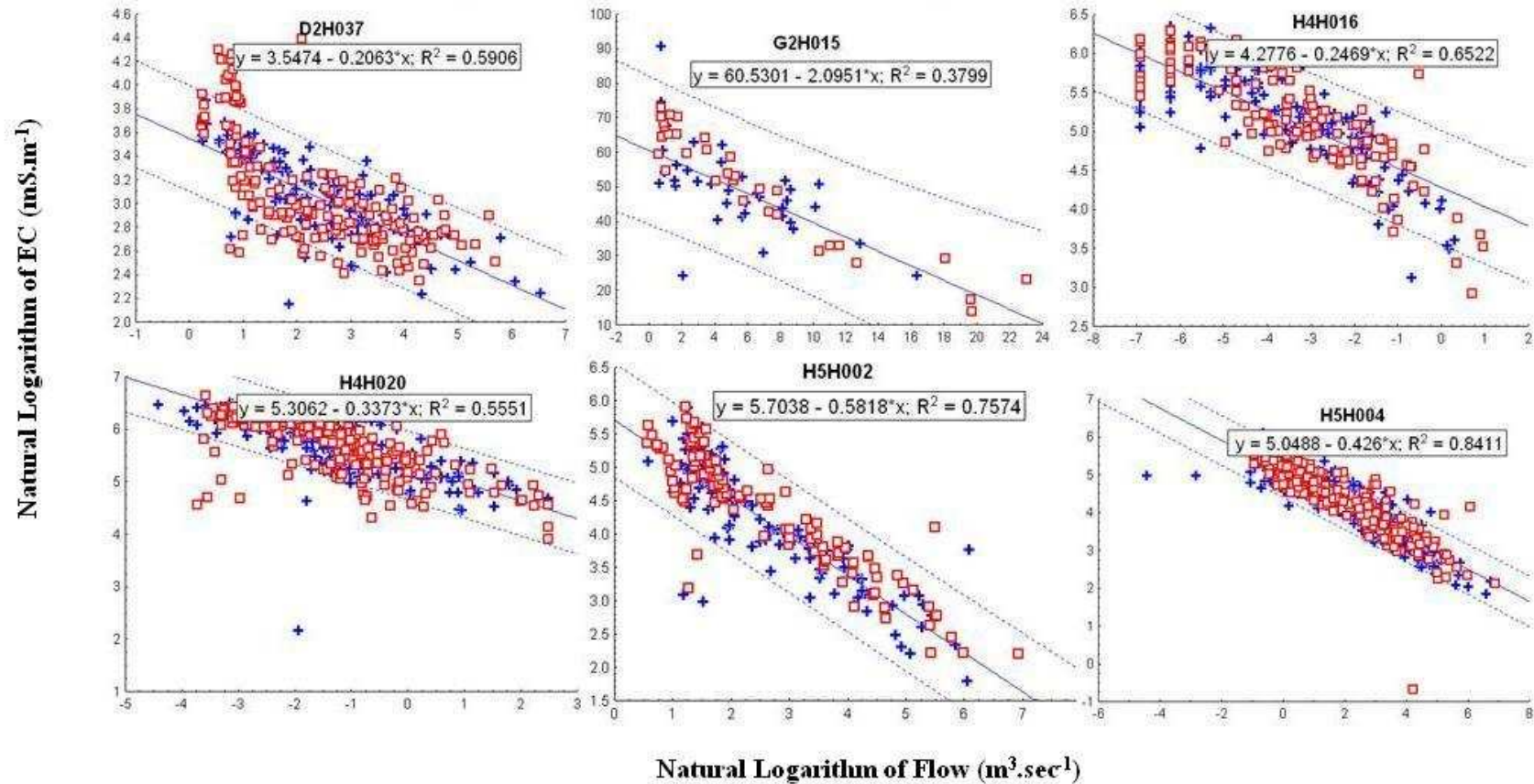
Appendix B Figure 1: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



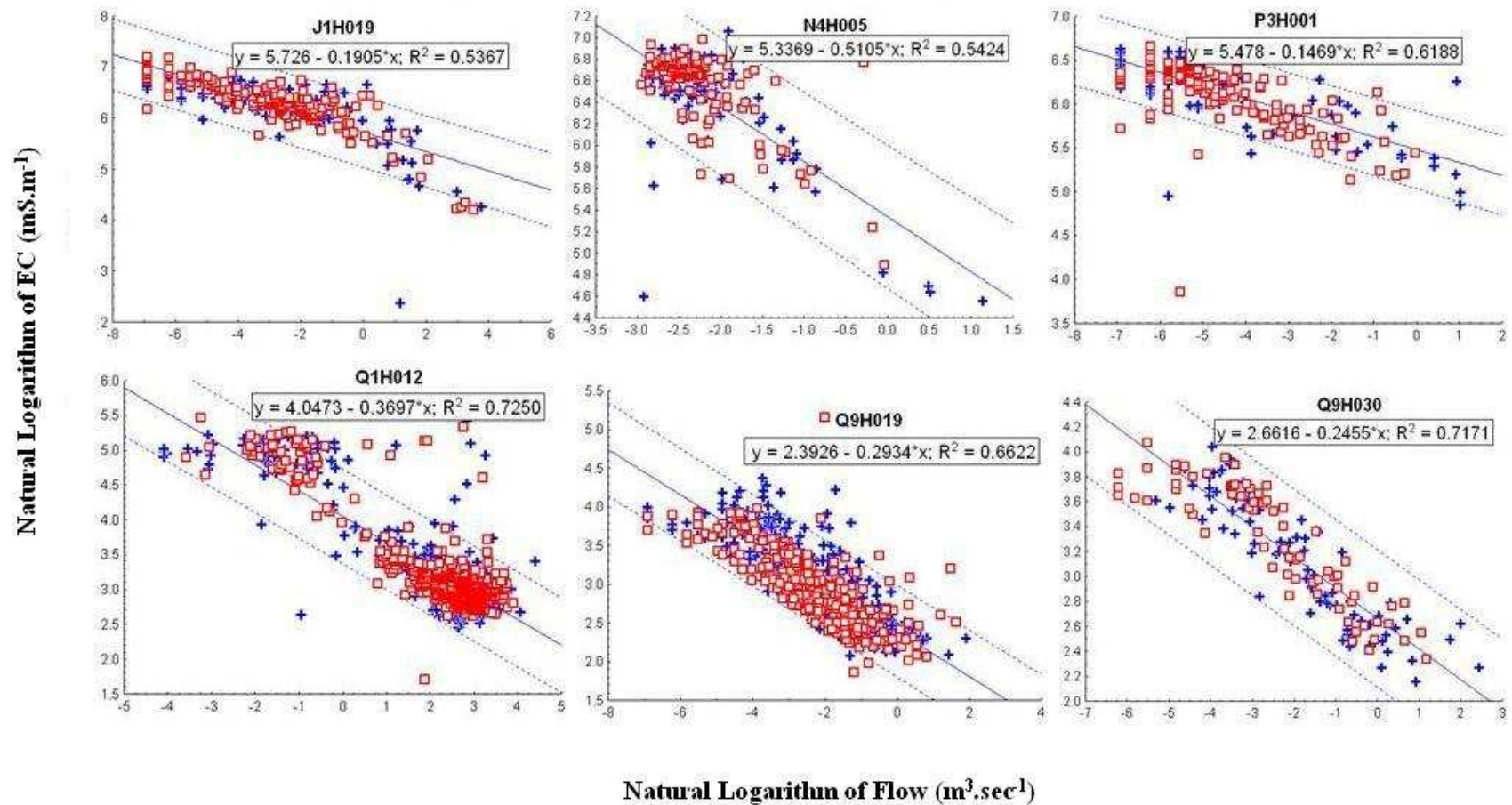
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R² given for calibration data set.



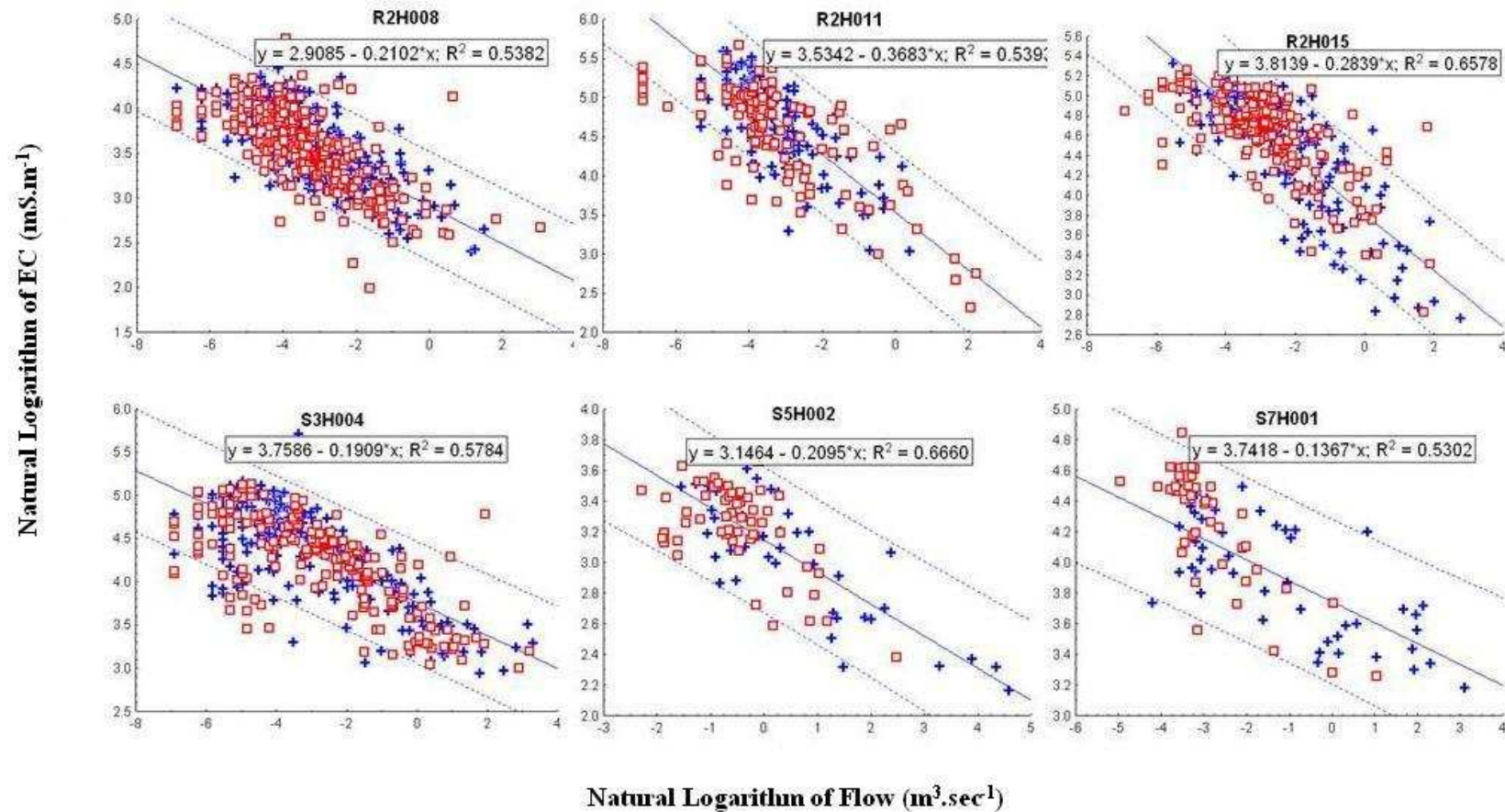
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R² given for calibration data set.



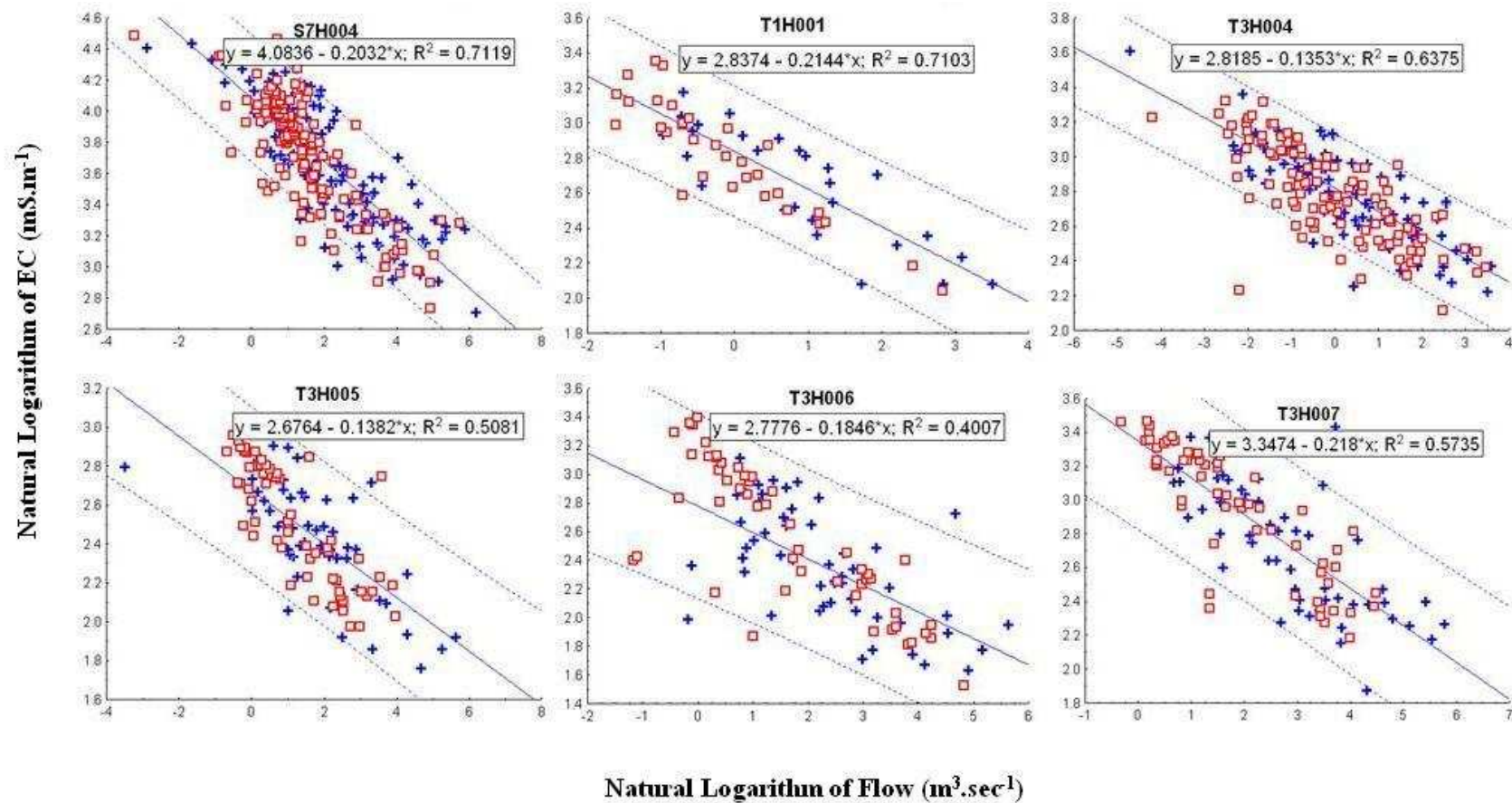
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R² given for calibration data set.



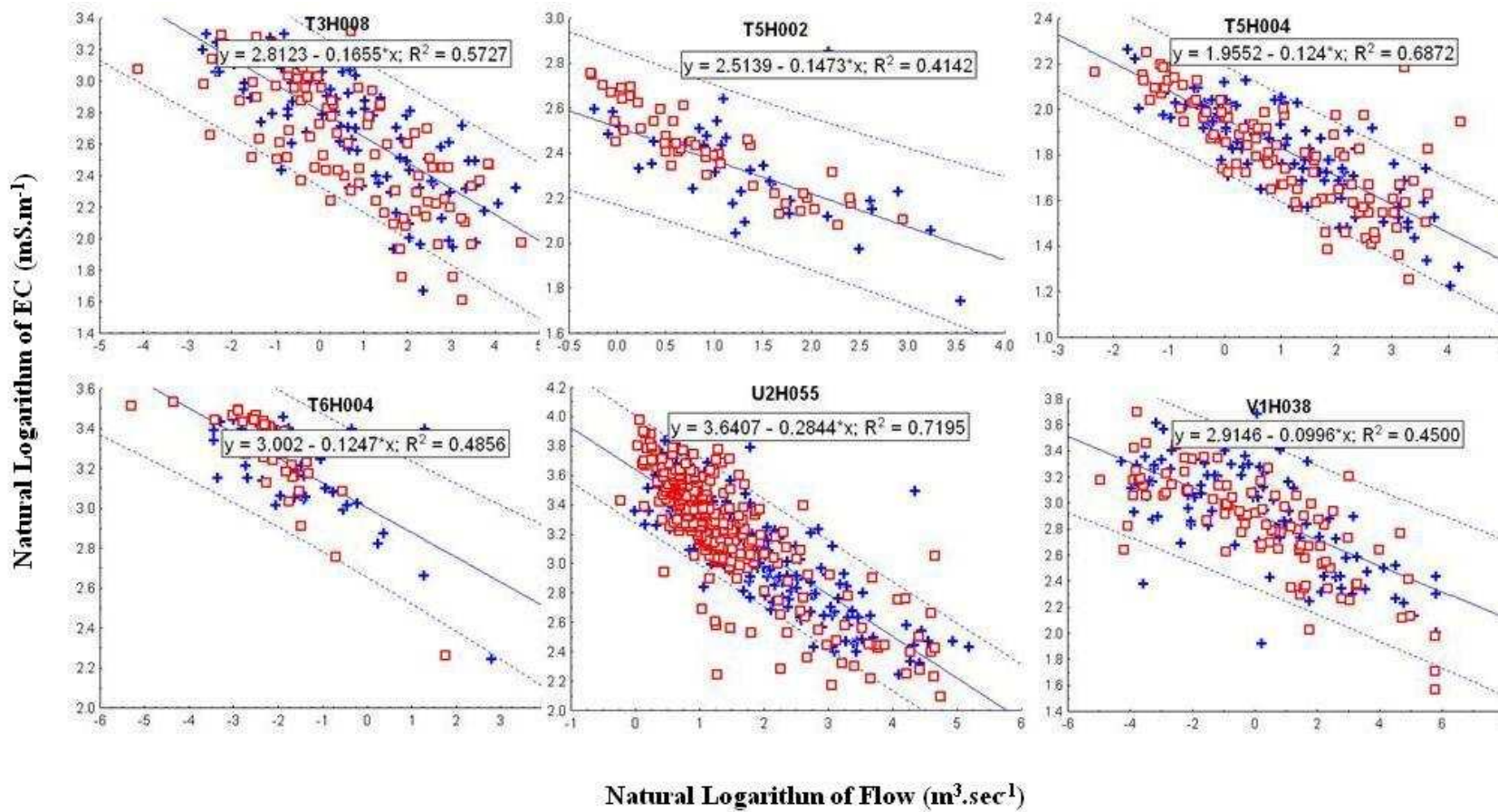
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R² given for calibration data set.



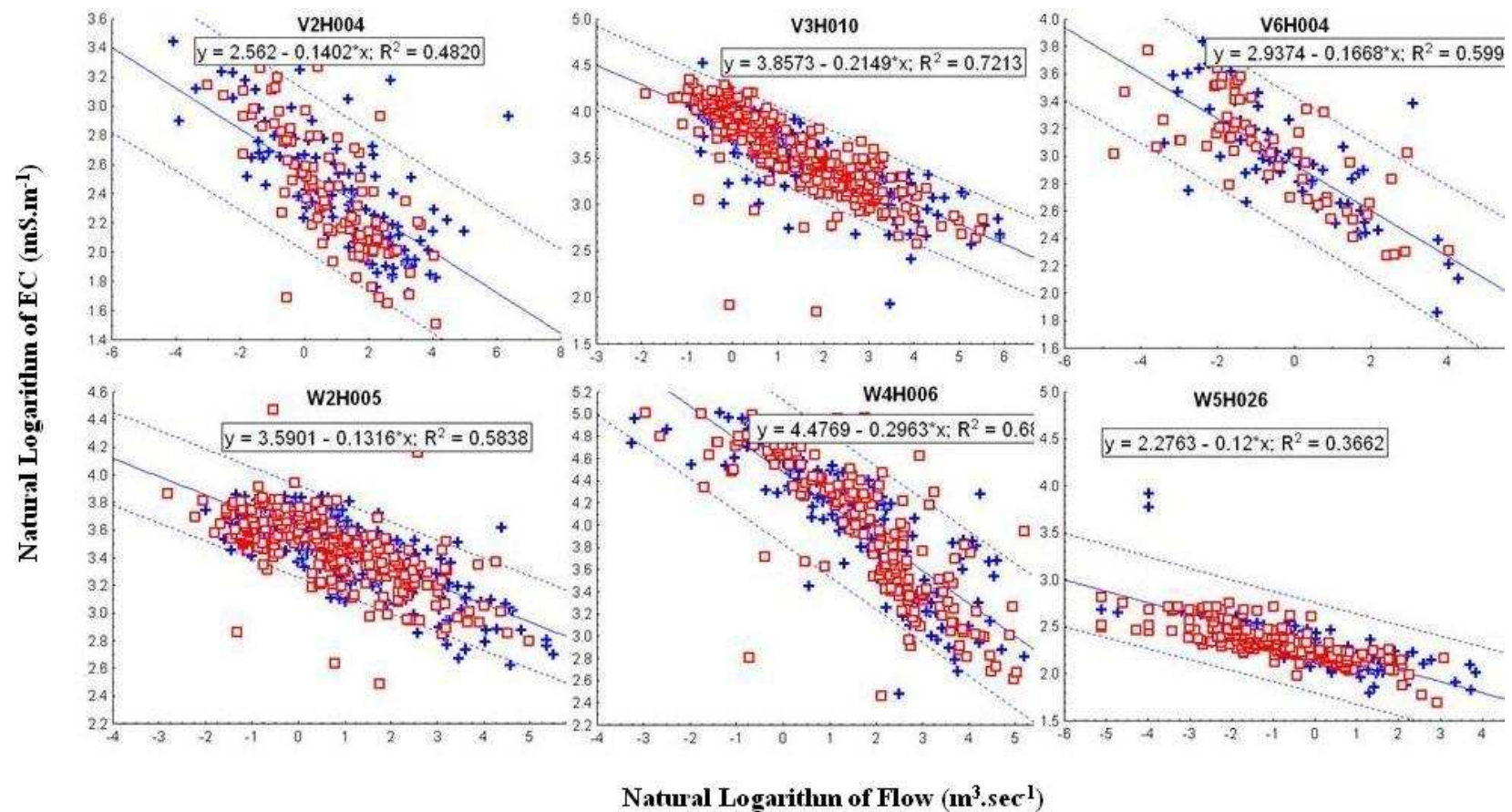
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



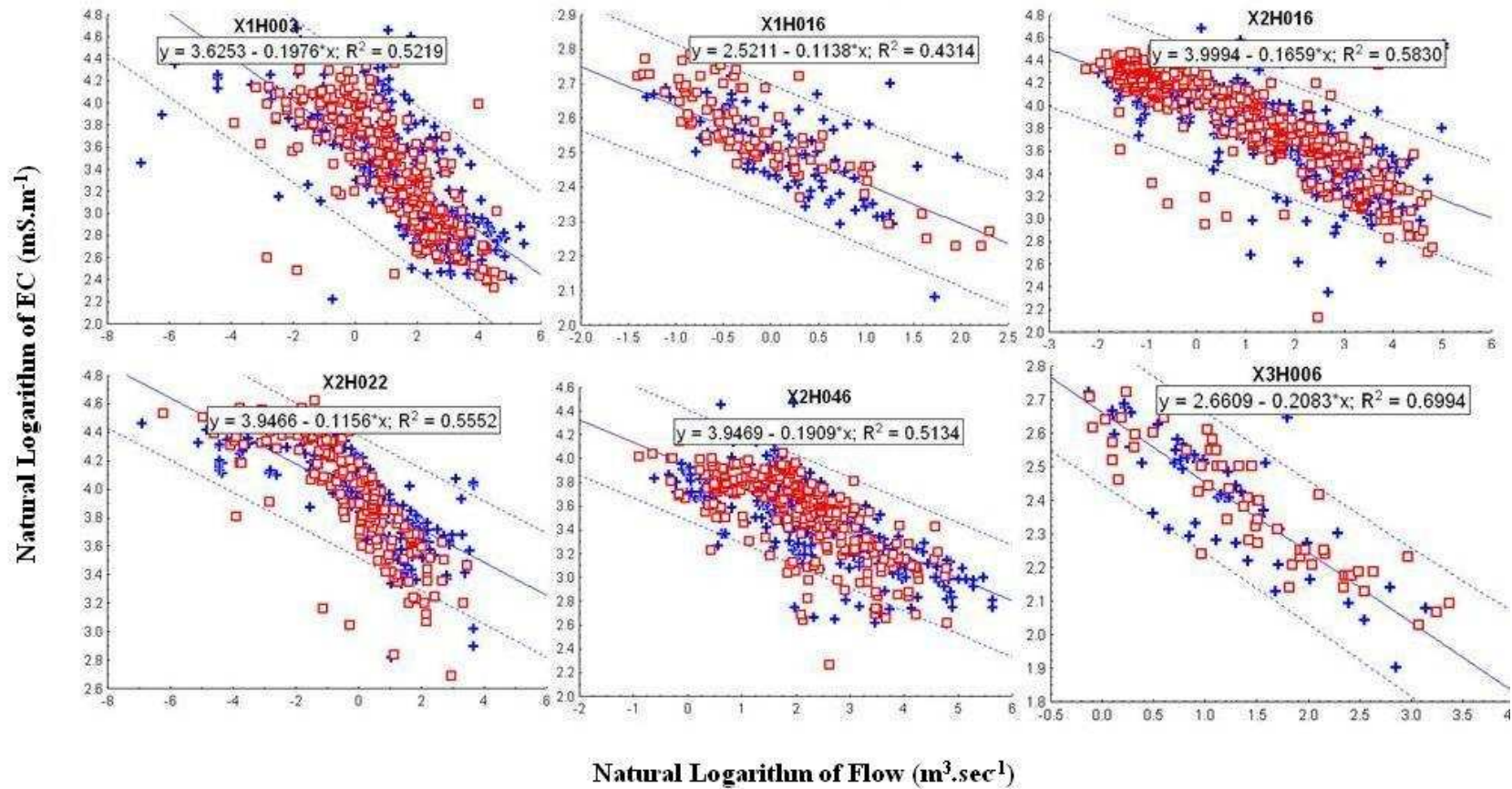
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



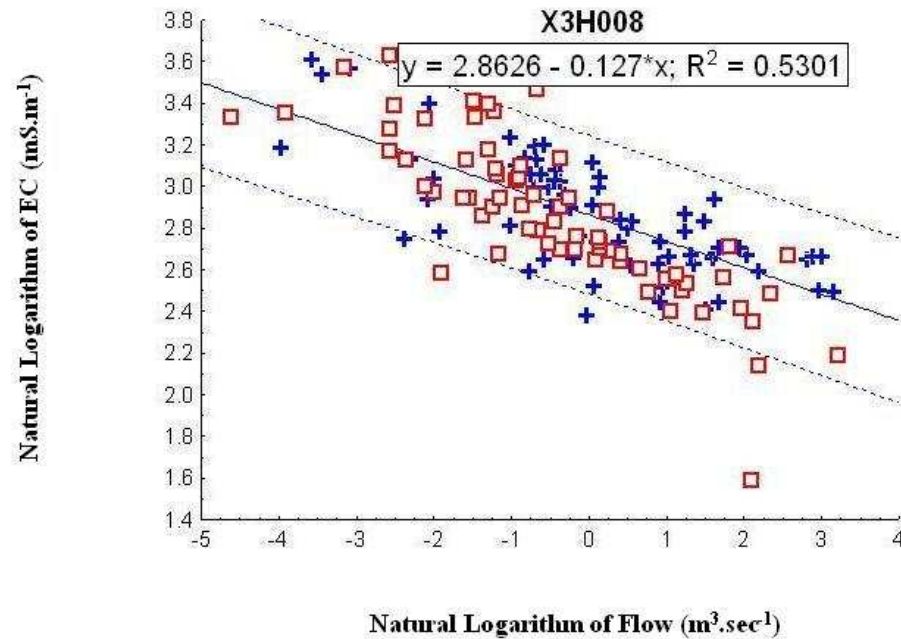
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



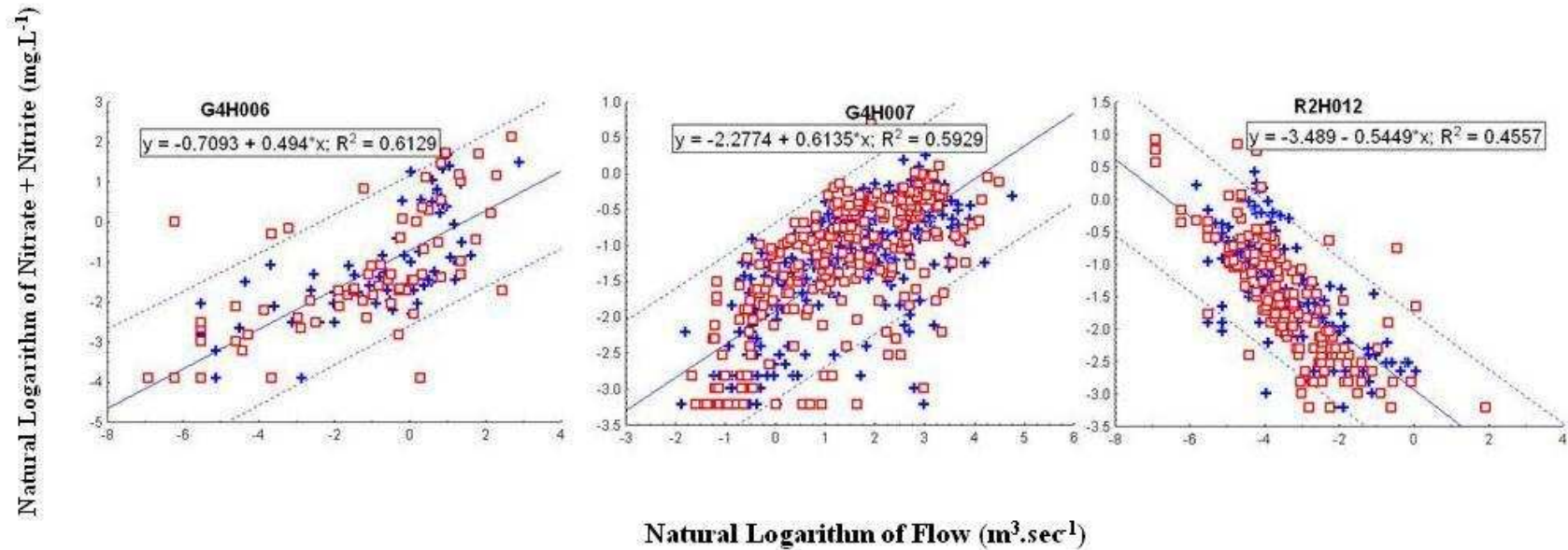
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



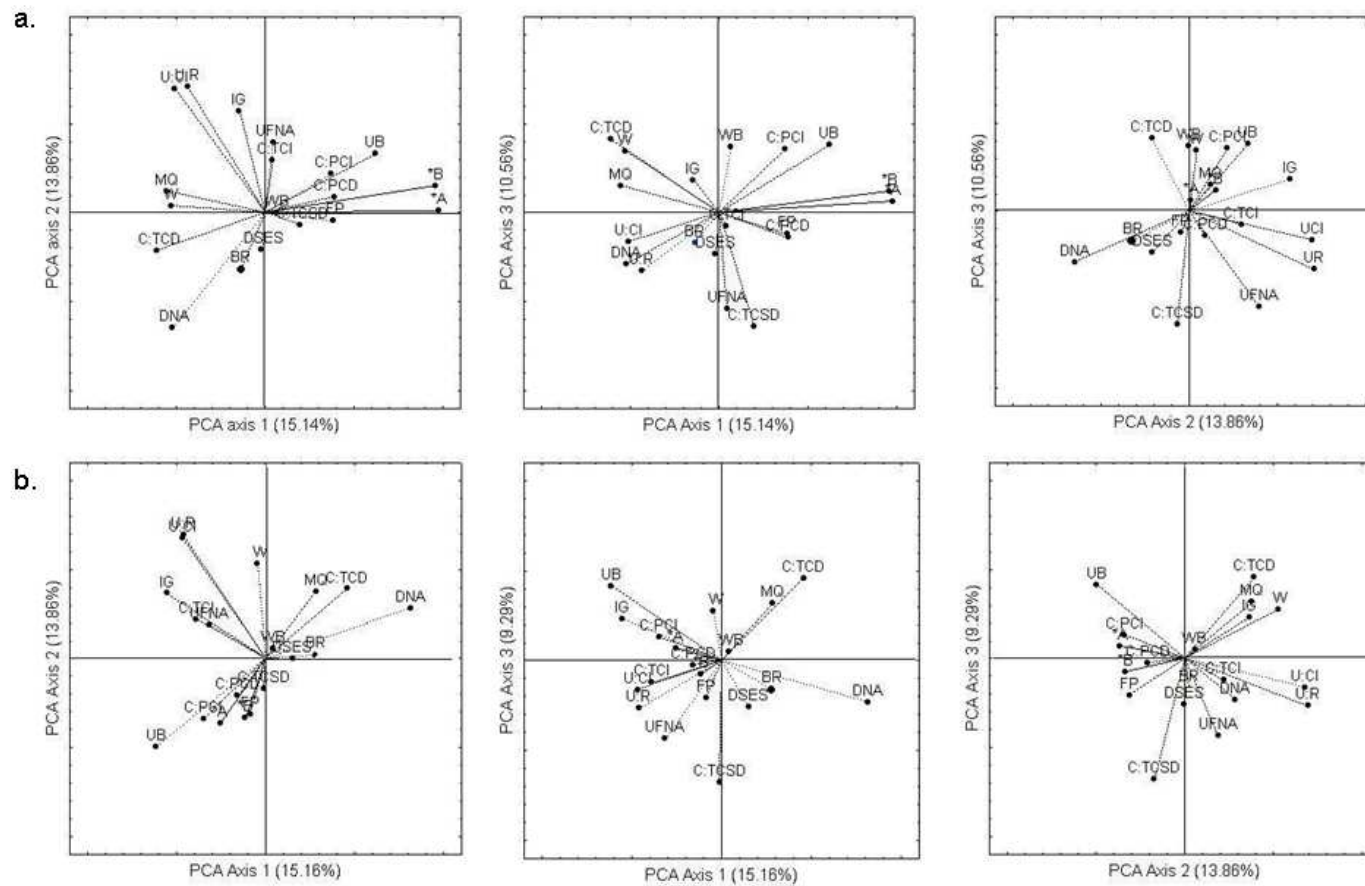
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R² given for calibration data set.



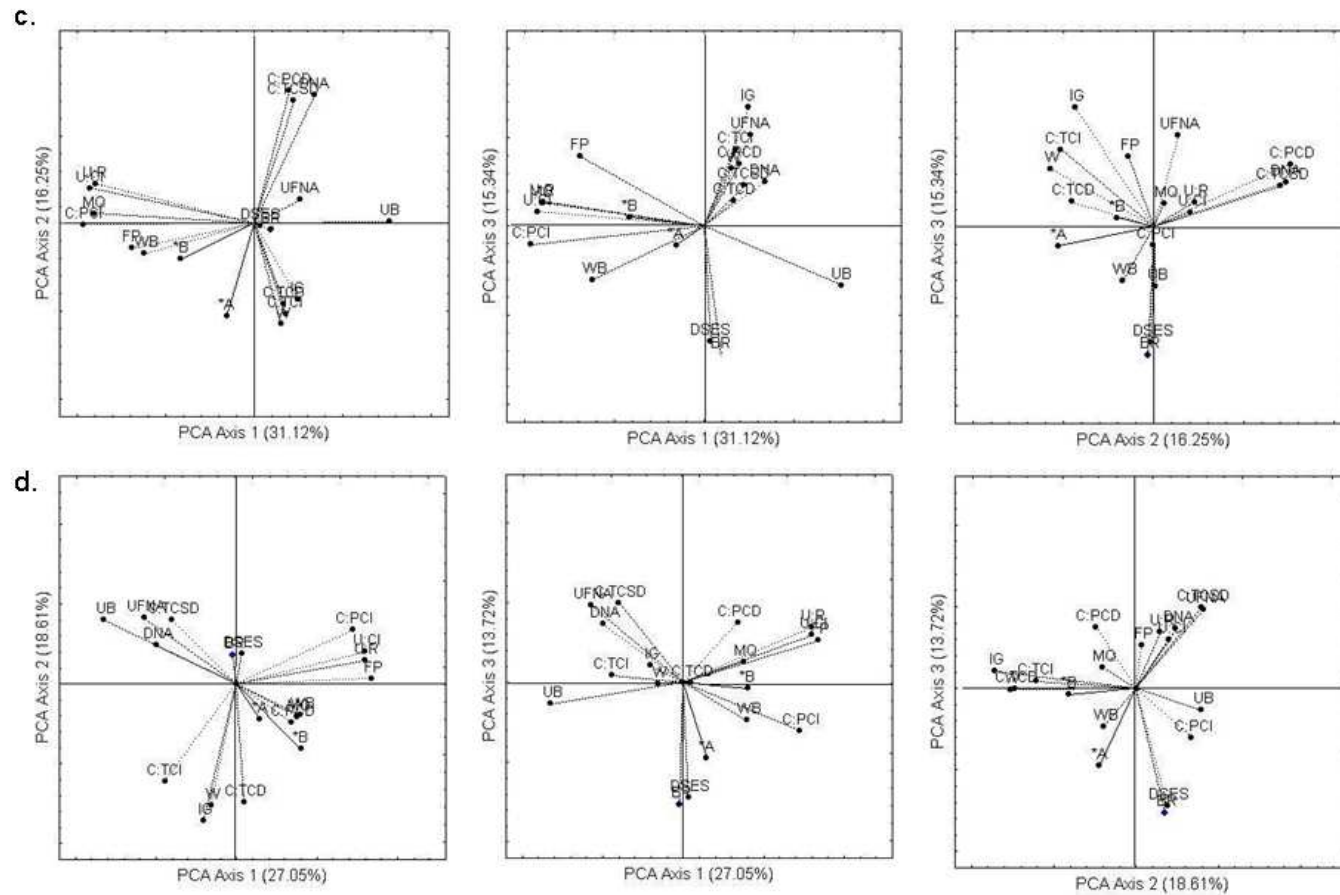
Appendix B Figure 1. continued: Linear regressions of flow versus electrical conductivity for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



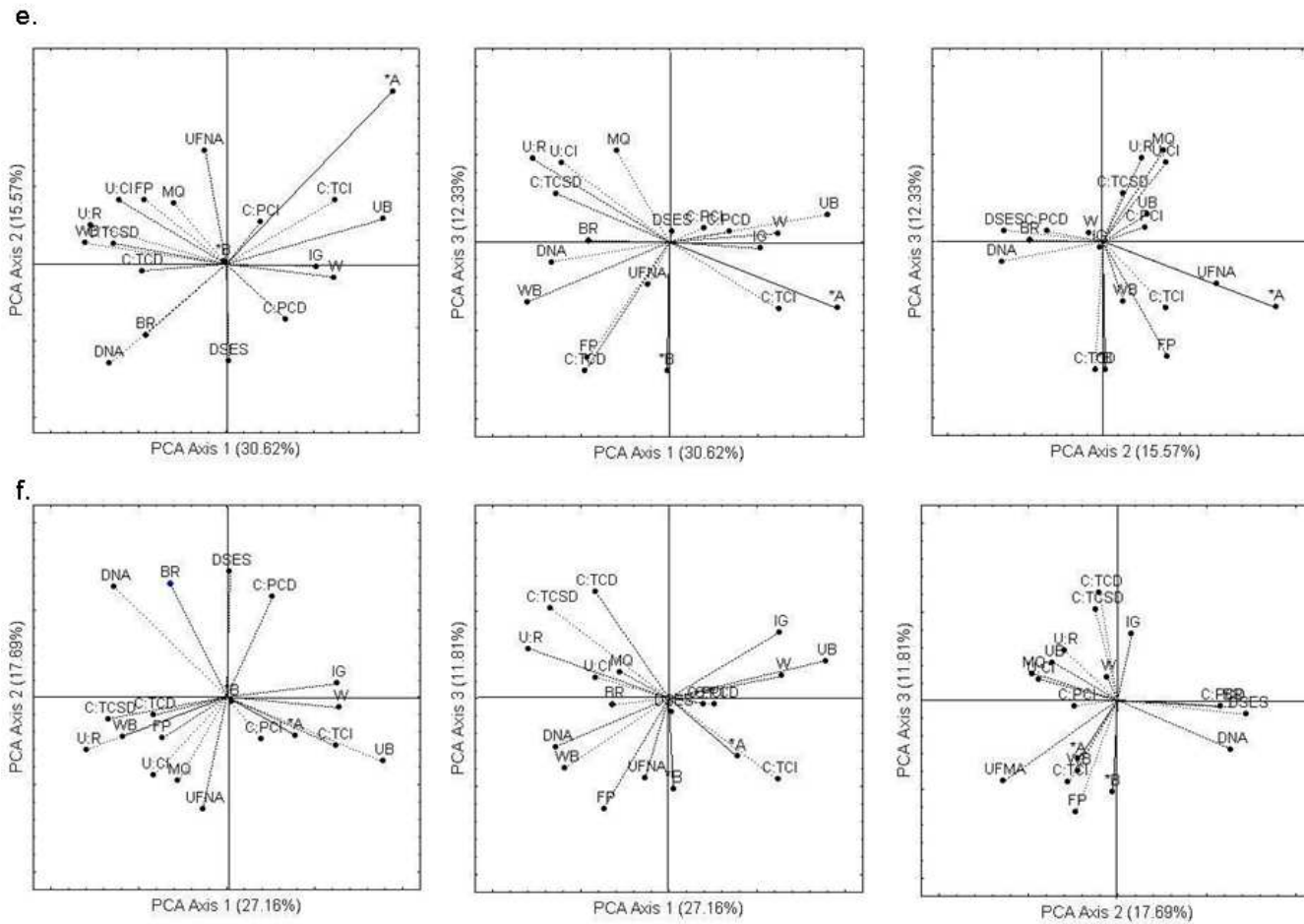
Appendix B Figure 2: Linear regressions of flow versus nitrite + nitrate for various Department of Water Affairs (DWA) monitoring sites. Calibration data set: cross data points with 95 % prediction limits (dotted lines). Confirmation data set: Square data points. Regression equation and R^2 given for calibration data set.



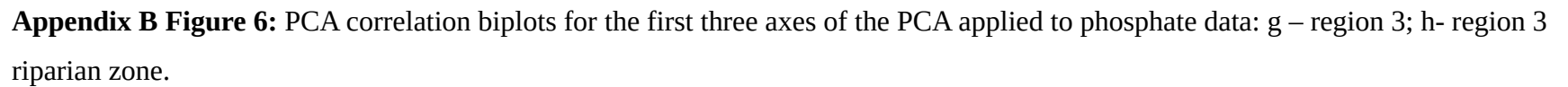
Appendix B Figure 3: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: a – all regions; b- all regions riparian zone.

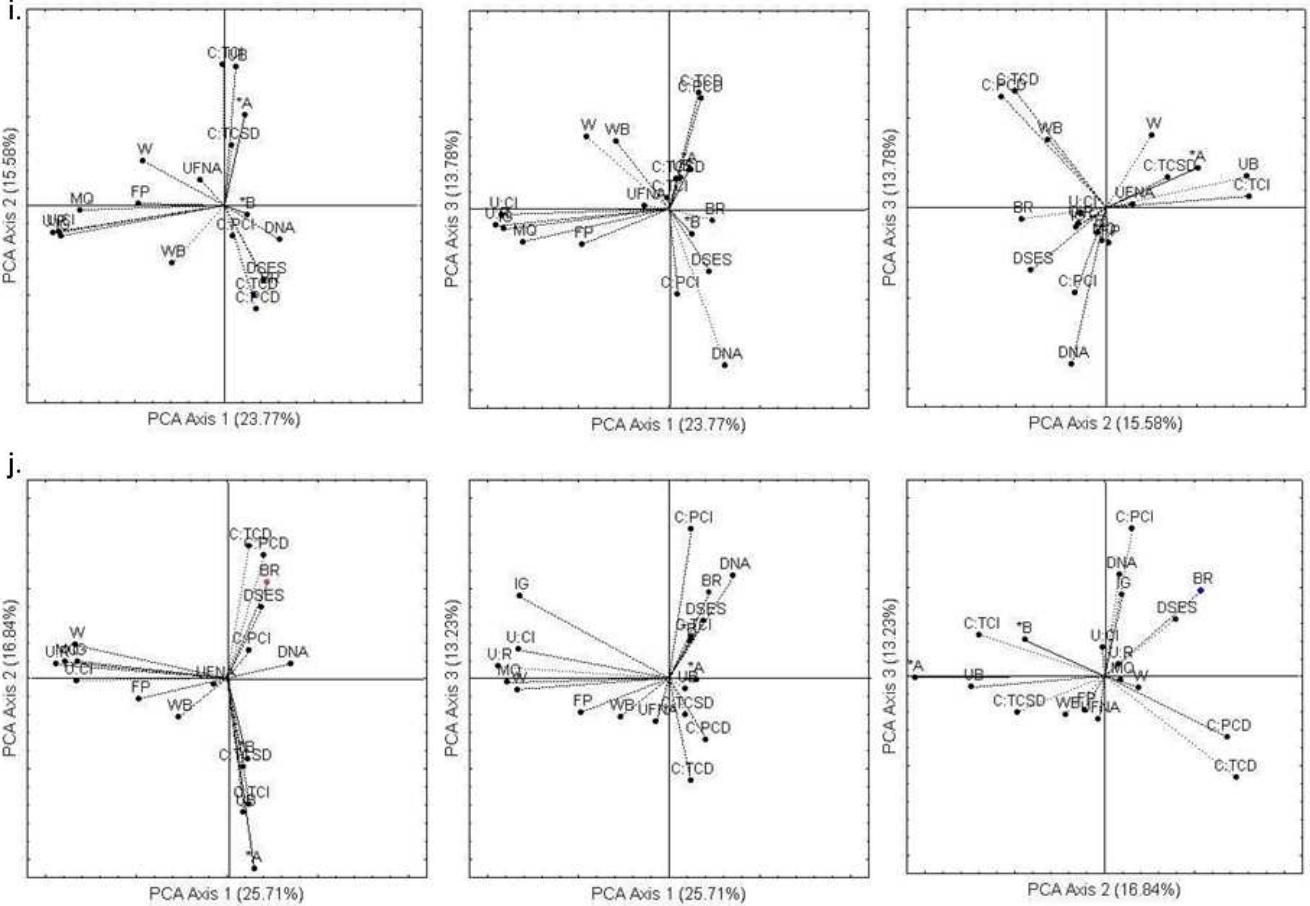


Appendix B Figure 4: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: c – region 1; d- region 1 riparian zone.

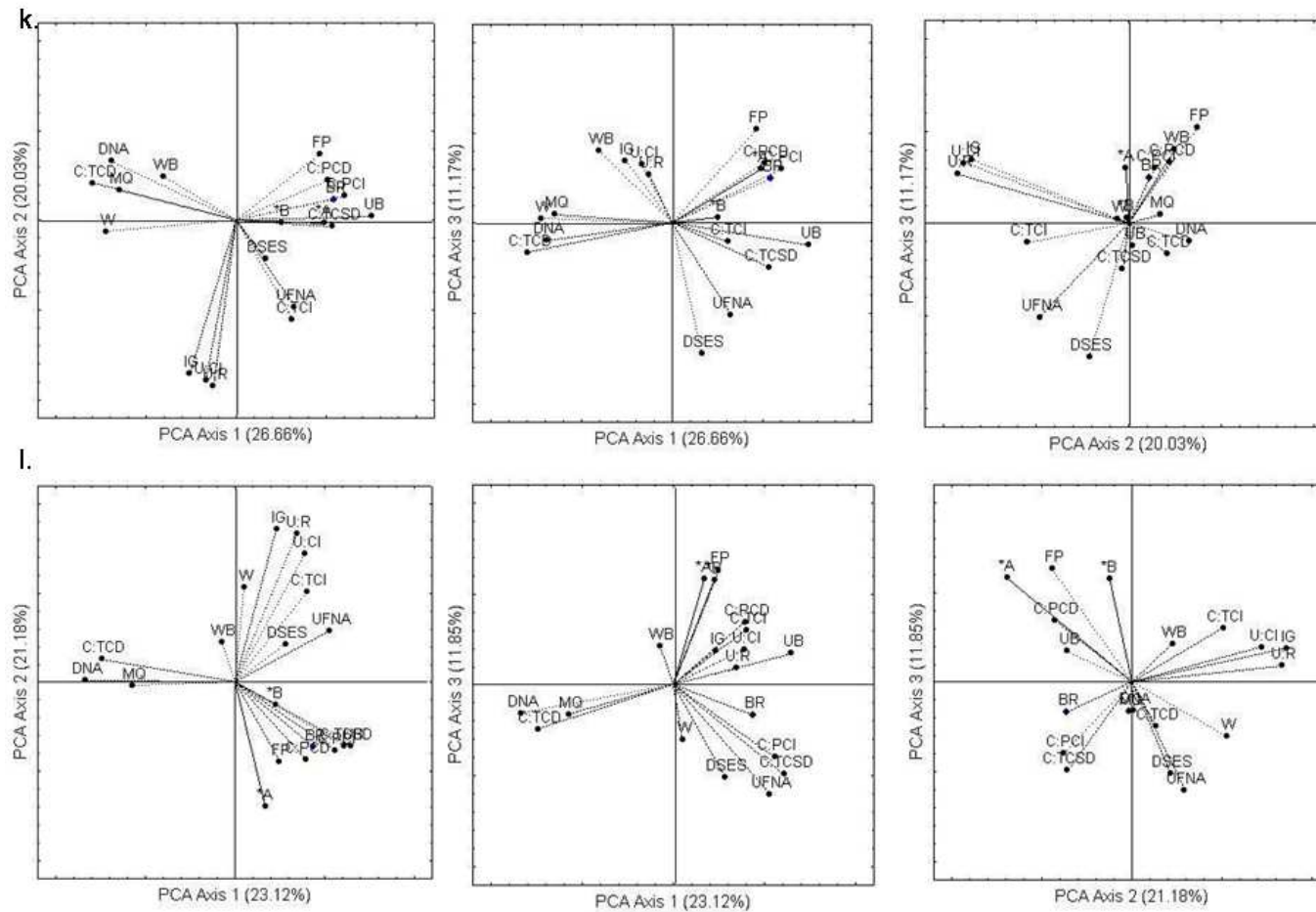


Appendix B Figure 5: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: e – region 2b; f- region 2b riparian zone.

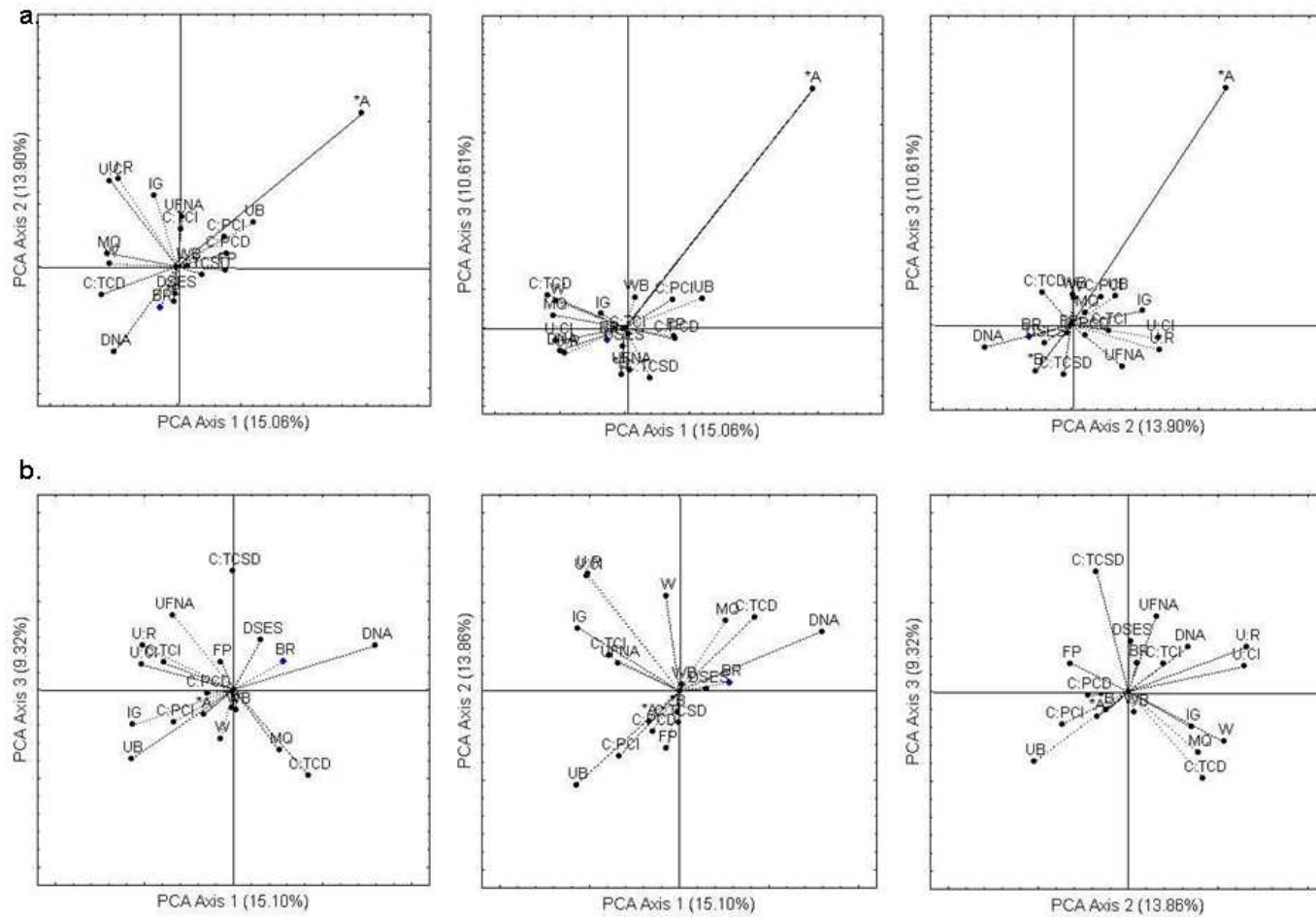




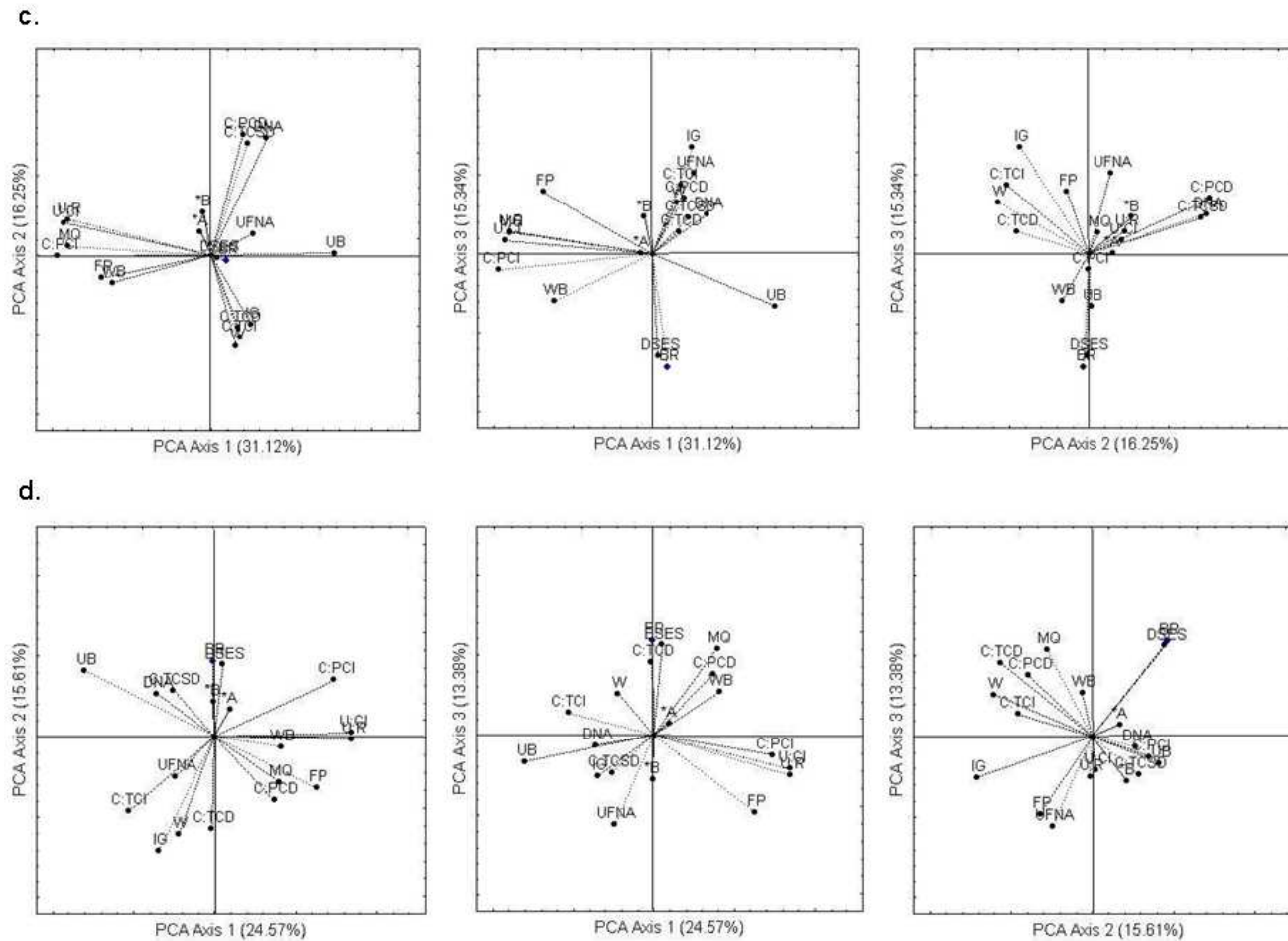
Appendix B Figure 7: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: i – region 4; j- region 4 riparian zone.



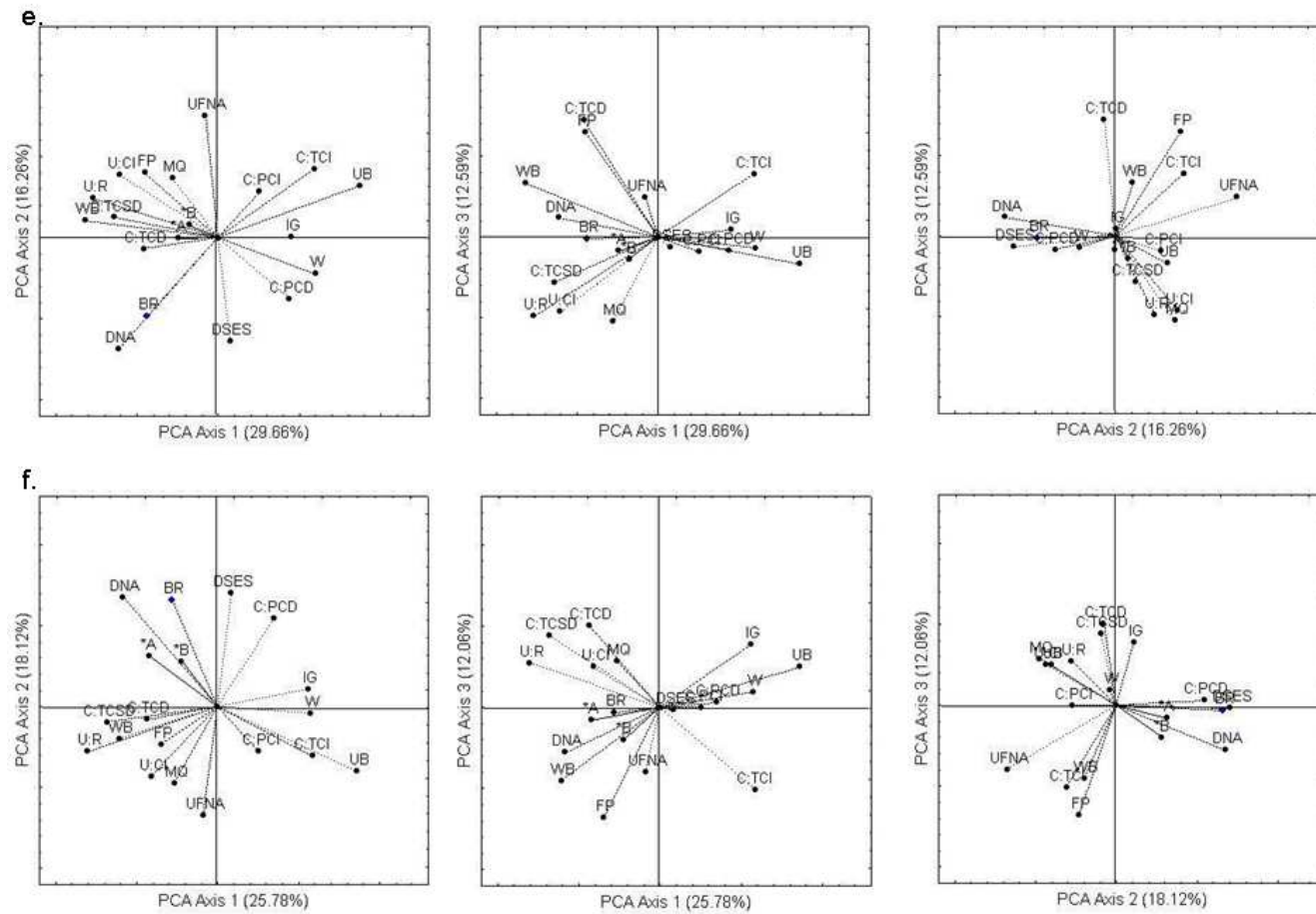
Appendix B Figure 8: PCA correlation biplots for the first three axes of the PCA applied to phosphate data: k- region 5; l- region 5 riparian zone.



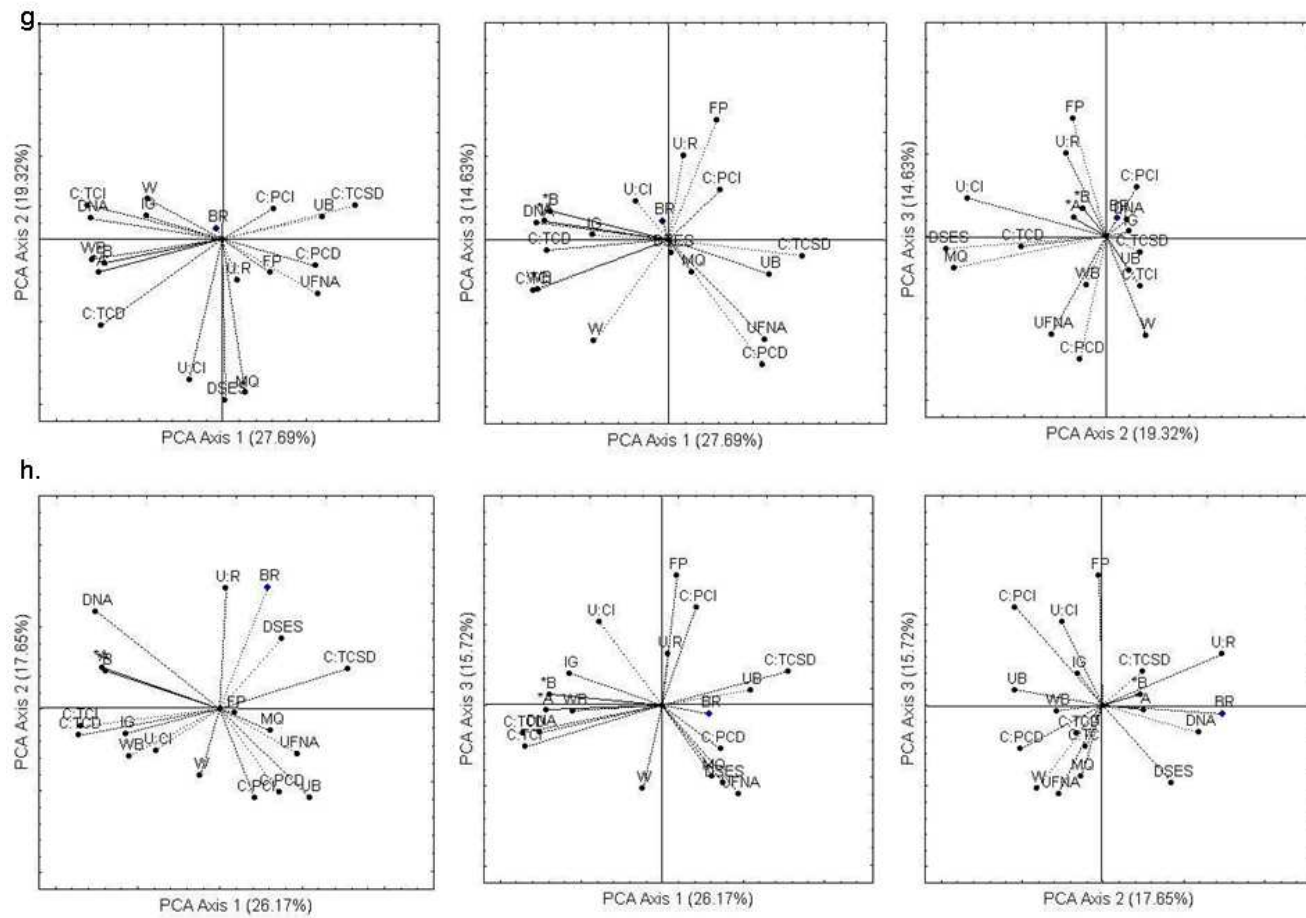
Appendix B Figure 9: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: a – all regions; b- all regions riparian zone.



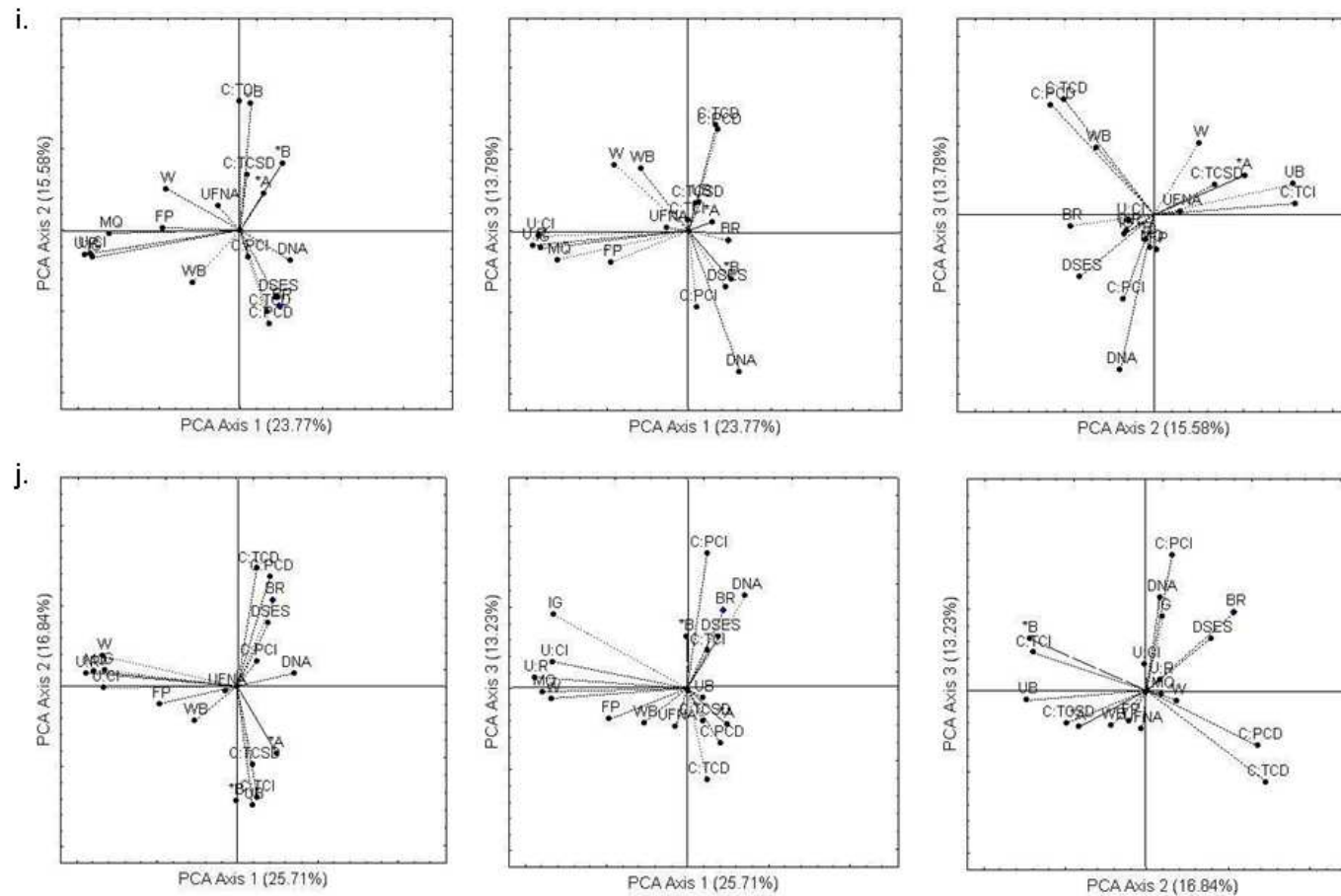
Appendix B Figure 10: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: c- region 1; d- region 1 riparian zone.



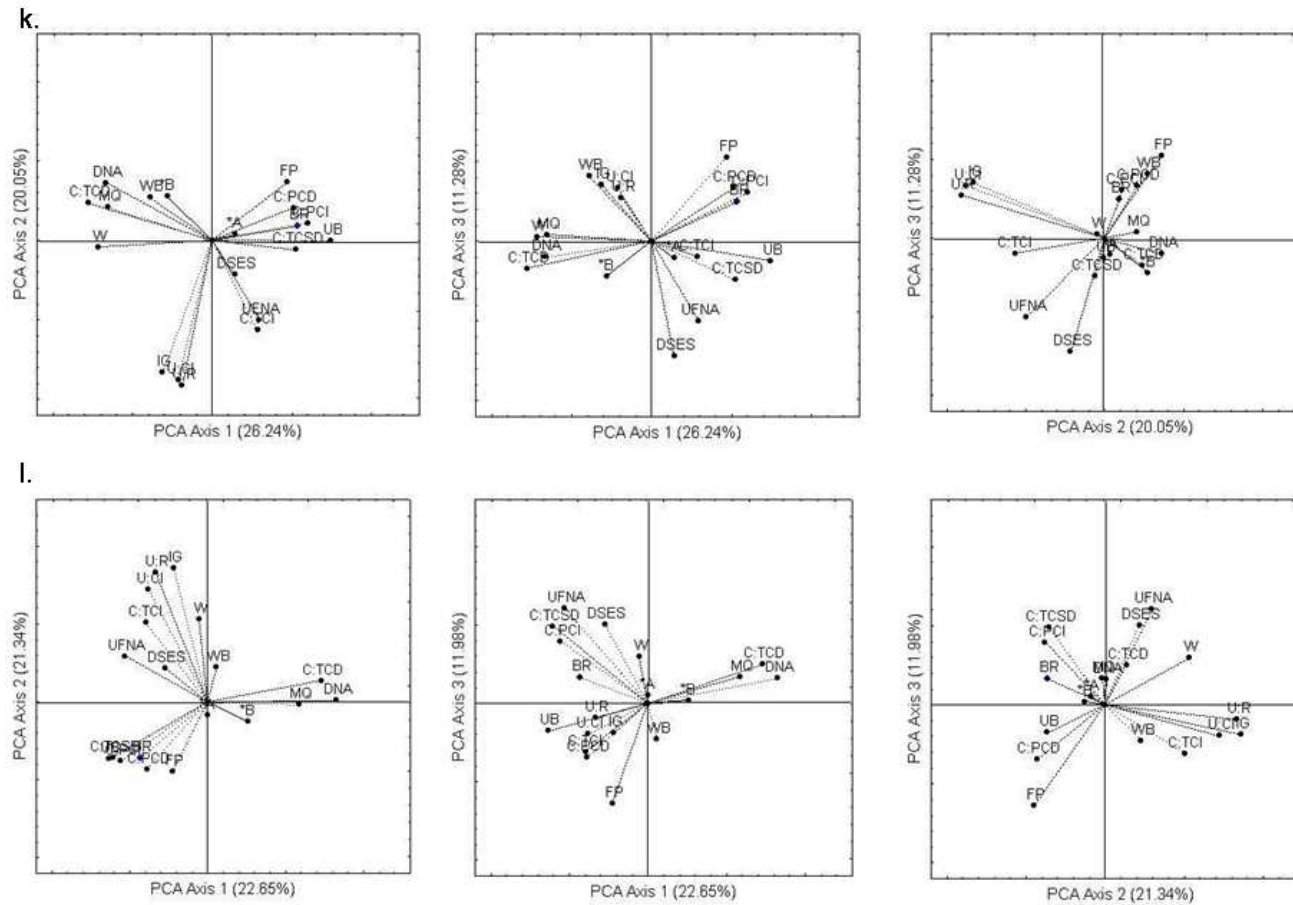
Appendix B Figure 11: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: e – region 2b; f- region 2b riparian zone.



Appendix B Figure 12: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: g- region 3; h- region 3 riparian zone.



Appendix B Figure 13: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: i – region 4; j- region 4 riparian zone.



Appendix B Figure 14: PCA correlation biplots for the first three axes of the PCA applied to nitrogen data: k- region 5; l- region 5 riparian zone.

References

(APHA) American Public Health Association (1992). Standard methods for the examination of water and wastewater. 18th ed. APHA, Washington, DC.

(APHA) American Public Health Association, American Water Works Association, and Water Pollution Control Federation (1971). Standard Methods for the Examination of Water and Wastewater. 13th ed. American Public health Association, Washington, DC.

Anderson, A., Karar, E., and Farolfi, S. (2008). Synthesis: IWRM lessons for implementation. *Water SA*, 34(6). 665 – 670.

Anonymous (2009). The state of water in South Africa – Are we heading for a crisis? *The Water Wheel*, 8(5). 31-33.

ANZECC (1992). *Australian Water Quality Guidelines*. Australian and New Zealand Environmental and Conservation Council, Melbourne, Australia.

Arnold, J.G., Srinivasan, R., Muttiah, R.S., and Williams, J.R. (1998). Large Area Hydrologic Modeling and Assessment Part I: Model Development. *Journal of American Water Resources Association*, 34. 73- 89.

Arnold, J. G. and Williams, J. R. (1995). The EPIC model. In Singh,V. P. (ed.), Computer Models of Watershed Hydrology. Water Resources Publications, Highlands Ranch (CO): 847–908.

Arthington, A.L., King, J.M., O’Keefe, J.H., Bunn, S.E., Day, J.A., Pusey, B.J., Bludhorn, D.R., and Tharme, R.E. (1992). Development of an holistic approach for assessing environmental water requirements of riverine ecosystems. In Pigram JJ. Hooper, B.P.

(Eds), Water allocation for the environment – Proceedings of an International Seminar and Workshop Armingdale, Australia (pp. 69 – 76). Armidale, Australia: The Centre for Water Policy Research.

Avila, A., Neal, C. and Terradas, J. (1996). Climate change implications for streamflow and streamwater chemistry in a Mediterranean catchment. *Journal of Hydrology*, 177. 99 – 116.

Azzellino, A., Salvetti, R., Vismara, R., Bonomo, L. (2006). Combined use of the EPA-QUAL2E simulation model and factor analysis to assess the source apportionment of point and non point loads of nutrients to surface waters. *Science of the Total Environment*, 371. 214 – 222.

Beck, M.B. (1981). Hard of Soft Environmental Systems. *Ecological Modelling*, 11. 233 – 251.

Beck, M.B., (1987). Water quality modelling: a review of the analysis of uncertainty. *Water Resources Research*, 23. 1393 - 1442.

Behrendt, H. and Opitz, D. (2000). Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologia*, 410. 111 – 122.

Berka, C., Schreier, H. and Hall, K. (2001). Linking Water Quality with Agricultural Intensification in a Rural Watershed. *Water, Air, and Pollution*, 127. 389 – 401.

Bevan, K.J. and Binley, A.M. (1992). The future of distributed models; model calibration and predictive uncertainty. *Hydrological Processes*, 6. 279 – 298.

Bevan, K., and Freer, J. (2001). Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE

References

methodology. *Journal of Hydrology*, 249. 11 – 29.

Biswas, A.K. (2008). Integrated Water Resources Management: Is It Working? *Water Resources Development*, 24(1). 5 – 22.

Bowes, M.J., Smith, J.T., Jarvie, H.P. and Neal, C. (2008). Modelling of phosphorus inputs to rivers from diffuse and point sources. *Science of the Total Environment*, 395. 125 – 138.

Bowie, G.L., Mills, W.B., Porcella, D.B., Campbell, C.L., Pagenkopf, J.R., Rupp, G.L., Johnson, K.M., Chan, P.W.H. and Gherini, S.A. (1985) Rates, constants, and kinetics formulations in surface water quality modelling (second edition). EPA report No: EPA/600/3-85/040.

Brisbin, P.E. (1995). Agricultural Nutrient Management in the Lower Fraser Valley. Report 4. DOE-FRAP, Environment Canada, 81pp.

Britton, D.L., Day, J.A. and Henshall-Howard, M-P. (1993). Hydrological response during storm events in a South African mountain catchment: the influence of antecedent conditions. *Hydrobiologia*, 250. 143 – 157.

Braune, E. and Xu, Y. (2008). Groundwater management issues in Southern Africa- An IWRM perspective. *Water SA*, 34(6). 699 – 706.

Cambray, J (2010). *Personal Communication*. Makana Biodiversity Centre, Albany Museum, Somerset Street, Grahamstown, South Africa.

Chapra, S. (1997). Surface water-quality modelling. The McGraw-Hill Companies, Inc.

Chapra, S.C. (2003). Engineering Water Quality Models and TMDLs. *Journal of Water*

Resources Planning and Management, July/August. 247 – 257.

Chung, S.W. (2004) Application of an unsteady river water quality model for the analysis of reservoir flushing effect on downstream water quality. *Journal of KWWA*, 37(10). 857 – 868.

Chung, S.W., Hwan Ko, I. and Kyung Kim, Y. (2008). Effect of reservoir flushing on downstream river water quality. *Journal of Environmental Management*, 86. 139 – 147.

Cole, T.M. and Buchak, E.M., (1995). CE-QUAL-W2: A Two-dimensional, Laterally Averaged, Hydrodynamic and Water Quality Model, Version 2.0. User Manual. Instruction Report EL-95, U.S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MI.

Connolly, J.P. and Coffin, R.B. (1995). Model of carbon cycling in planktonic food webs. *Journal of Environmental Engineering*, 121(10). 682-690.

Costanza, R., d'Arge, R., de Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., O'Neill, R.V., Paruelo, J., Raskin, R.G., Sutton, P., van den Belt, M. (1987). The Value of the World's Ecosystem Services and Natural Capital. *Nature*, 387. 253 – 260.

Daily, G.C., (1999). Developing a scientific basis for managing Earth's life-support systems. *Conservation Ecology*, 3(2), 14. [online] URL: <http://www.consecol.org/vol3/iss2/art14/>

Davies, B. R., Day, J.A. (1998). *Vanishing Waters*. University of Cape Town Press, Cape Town, South Africa.

Day, J.A. and King, J.M. (1995). Geographic patterns, and their origins, in the dominance

References

of major ions in South African rivers. *South African Journal of Science*, 91. 299 – 305.

Day, J.A. (1993). The major ion chemistry of some southern African saline systems. *Hydrobiologia*, 267. 37 – 59.

Day, J.A., Dallas, H.F. and Wackernagel, A. (1998). Delineation of management regions for South African rivers based on water chemistry. *Aquatic Ecosystem Health and Management*, 1. 183 – 197.

Di Toro, D.M., and Fitzpatrick, J.F. (1993). Chesapeake Bay sediment flux model. Contract Rep. EL-93-2. Prepared by HydroQual, Inc. for U.S. Army Corps of Engineers, Vicksburg, Mississippi.

Di Toro, D.M., O'Connor, D.J. and Thomann, R.V., 1971. A dynamic model of the phytoplankton population in the Sacramento-San Joaquin delta. *Advances in Chemistry*, 106. 131–180.

Di Toro, D.M., Paquin, P.R., Subburamu, K. and Gruber, D.A. (1990). Sediment oxygen demand model: methane and ammonia oxidation. *Journal of Environmental Engineering*, 116(5). 945 – 986.

Donigian, A.S., Bicknell, B.R., Patwardhan, A.S., Linker, L.C., Alegre, D.Y., Chang, C-H., Reynolds, R. (1991). Watershed model application to calculate Bay nutrient loadings: Final findings and recommendations. Prepared by Aqua Terra Consultants, Comp. Sci. Corp. for Chesapeake Bay Program Office, U.S. EPA, Annapolis, Md.

(DWA) Department of Water Affairs and Forestry (1986). Management of the Water Resources of the Republic of South Africa. Pretoria, South Africa.

(DWA) Department of Water Affairs and Forestry (1991). Water quality management

References

policies and strategies in the RSA. Department of Water Affairs and Forestry, Private Bag x313, Pretoria, South Africa.

(DWA) Department of Water Affairs (1996). South African Water Quality Guidelines. Volume 7: Aquatic Ecosystems. Pretoria, South Africa.

(DWA) Department of Water Affairs and Forestry (2008). Methods for determining the Water Quality component of the Ecological Reserve. Prepared by Scherman Consulting. Pretoria, South Africa.

(DWA) Department of Water Affairs (2009). Comp-RHAM: Computational support for the Rapid Assessment Method, Birkhead, A.L. Produced for Water for Africa (Aquatic Ecology) as part of the Development and Pilot Implementation of a Framework to Operationalise the Reserve. DWA Project no. WP8888. Pretoria, South Africa.

(DWA) Department of Water Affairs (2010). National Groundwater Database. <http://WWTW3.dwa.gov.za/NGANET>.

Eekhout, S., Brown, C.A. and King, J.M. (1996). National Biomonitoring Programme for Riverine Ecosystems: Technical considerations and protocol for the selection of reference and monitoring sites. NBP Report Series No 3. Institute for Water Quality Studies, Department of Water Affairs and Forestry, Pretoria, South Africa.

Eiger, S.M, Billen, G., Bacq, N., Thery, S., Ruelland, D., Garnier, J., Cugier, P., Poulin, M., Blane, S., Lamy, F. and Paffoni, C. (2007). New tools for modelling water quality of hydrosystems: An application in the Seine River basin in the frame of the Water Framework Directive. *Science of the Total Environment*, 375. 274 – 291.

Fan, C., Ko, C., Wang, W. (2009). An innovative modeling approach using QUAL2K and HEC-RAS integration to assess the impact of tidal effect in river water quality

simulation. *Journal of Environmental Management*, 90. 1824 – 1832.

Flugel, W-A. and Kienzie, S. (1989) Hydrology and salinity dynamics of the Breede River, Western Cape Province, republic of South Africa. Proceeds of the International Association of Hydrological Sciences (IAHS), Baltimore, USA, May 1989.

Fortin, J.-P., Moussa, R., Bocquillon, C. and Villeneuve, J-P.(1995). HYDROTEL, un Modèle Hydrologique Distribué Pouvant Bénéficier des Données Fournies par la Télédétection et les Systèmes d'Information Géographique. *Revue des Sciences de l'Eau* , 8. 97–124.

Froelich, P.N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. *Limnology and Oceanography* , 33. 49–668.

Garcia, L.E. (2008). Integrated Water Resources Management: A 'Small' Step for Conceptualists, a Giant Step for Practitioners. *Water Resources Development*, 24(1). 23-36.

Gibbons, H.L. (1981). Phytoplankton production and regulating factors in Liberty Lake, Washington with possible implications of restoration activities. Ph.D. Dissertation, College of Engineering, Washington Sate University, Pullman, WA.

Glaser, D. and Bridges, T.S. (2007). Separating the Wheat from the Chaff: The Effective Use of Mathematical Models as Decision Tools. *Integrated Environmental Assessment and Management*, 3(3). 442 – 449.

GLOBAL WATER PARTNERSHIP (2000). Integrated Water Resources Management. GWP Catalyzing Change Series.

References

Gordon, A.K., Muller, W.J., Gysman, N., Marshall, S.J., Sparman, C.J., O'Connor, S.M. and Whelan, M.J. (2009). Effect of laundry activities on in-stream concentrations of linear alkylbenzene sulfonate in a small rural South African river. *Science of the Total Environment*, 407. 4465 – 4471.

Görgens, A.H.M. and de Clercq, W.P. (2006) Research on Berg River Water Management - Summary of Water Quality Information System and Soil Quality Studies. Water Research Commission Report No: TT252/06, Pretoria, South Africa.

Gorgens, A.H.M., Jonker, V. and Buester, H. (2001). The DISA Hydrosalinity Model. Water Research Commission Report No: 369/1/01.

Gosselain V., Viroux L. and Descy J.-P. (1998). Can a community of small-bodied grazers control phytoplankton in rivers? *Freshwater Biology*, 39. 9 – 24.

Gowda, P.H., Dalzell, B.J., Mulla, D.J. (2007). Model based nitrate TMDLs for two agricultural watersheds of southeastern Minnesota. *Journal of the American Water* , 43(1). 254 - 262.

Grobler, D.C. and Silberbauer, M.J. (1985). The combined effect of geology, phosphate sources and runoff on phosphate export from drainage basins. *Water Research*, 19(8). 975 – 981.

GWP (2000). Integrated Water Resources Management, TAC background Paper No. 4 (Stockholm: Global Water Partnership. Technical Advisory Committee (TAC)).

Hendricks, D.W. (1979). Application of water quality models. In *Modelling of rivers* edited by Hsieh Wen Shen. John Wiley, New York.

Herold, C.E. and van Eeden, P.H. (2001). The feasibility of low cost modelling

References

techniques to relate river water quality and diffuse loads to a range of land uses. Water Research Commission (WRC) Report No. 796/1/01, Pretoria, South Africa.

Herold, C.E. and le Roux, P.J. (2004). WQ2000: Development of an interactive surface water quality information and evaluation system for South Africa. Water Research Commission Report No: 950/1/04, Pretoria, South Africa.

Hosking, S.G. and du Preez, M. (2002) Valuing water gains in the Eastern Cape's Working for Water Programme. *Water SA*, 28(1). 23- 28.

Heydorn, A.E.F and Grindley, J.R. (1982). Estuaries of the Cape. Report No. 10: Kowie (CSE10). CSIR research report 409, Stellenbosch, South Africa.

Hughes, D.A. (2004). Incorporating ground water recharge and discharge functions into an existing monthly rainfall-runoff model. *Hydrological Research and Applications*, 21. 899 – 908.

Hughes, D.A. (2008). Simulating the hydrology and total dissolved solids (TDS) of an ephemeral river in South Africa for environmental water requirement determinations. *River Research and applications*, 24. 1 - 11

Hughes, D.A. (2010). *Personal Communication*. Institute for Water Research, Rhodes University, Grahamstown, South Africa.

Hughes, D.A. and Sami, K. (1994). A semi-distributed, variable time interval model of catchment hydrology – structure and parameter estimation procedures. *Journal of Hydrology*, 155. 265 – 291.

Hughes, D.A. and van Ginkel, C. (1994). Nutrient loads from developing urban areas, a

simulation approach and identification of information requirements. *Water SA*, 20(2). 139 – 149.

Hunter, H.M. and Walton, R.S. (2008). Land - use effects on fluxes of suspended sediment, nitrogen and phosphorus from a river catchment of the Great Barrier Reef, Australia *Journal of Hydrology*, 356. 131 – 146.

Hydroscience, Inc. (1971) Simplified Mathematical Modelling Of Water Quality. Report No: CandEE;88.

James, W.F. and Larson, C.E. (2008). Phosphorus dynamics and loading in the turbid Minnesota River (USA): controls and recycling potential. *Biogeochemistry*, 90. 75 – 92.

Jarvie, H.P., Neal, C., Withers, P.J.A., Wescott, C. and Acornley, R.M. (2005). Nutrient hydrochemistry for a groundwater-dominated catchment: The Hampshire Avon, UK *Science of the Total Environment*, 344. 143 – 158.

Jarvie, H.P., Wade, A.J., Butterfield, D., Whitehead, P.G., Tindall, C.I., Virtue, W.A., Dryburgh, W., McGraw, A. (2002). Modelling nitrogen dynamics and distributions in the River Tweed, Scotland: an application of the INCA model. *Hydrology and Earth Sciences*, 6(3). 433 – 453.

Jewitt, G.. (2002). Can Integrated Water Resources Management sustain the provision of ecosystem goods and services? *Physics and Chemistry of the Earth*, 27. 887 – 895.

Jonker, L. (2007). Integrated water resources management: The theory-praxis-nexus, a South African perspective. *Physics and Chemistry of the Earth*, 32. 1257 – 1263.

Jordan, P., Arnscheidt, A., McGrogan, H. and McCormick, S. (2007). Characterising phosphorus transfers in rural catchments using a continuous bank-side analyzer.

References

Hydrological Earth System Science, 11(1). 372 – 381.

Jordan, T.E., Correll, D.L. and Weller, D.E. (1997a). Effects of Agriculture on Discharges of Nutrients from Coastal Plain Watersheds of Chesapeake Bay. *Journal of Environmental Quality*, 26. 836 – 848.

Jordan, T.E., Correll, D.L. and Weller, D.E. (1997b). Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research*, 33(11). 2579 – 2590.

Kato, T. (2005). Development of a water quality tank model classified by land use for nitrogen load reduction scenarios. *Paddy and Water Environment*, 3. 21 – 27.

Kefford, B.J., Papas, P.J., Crowther, D. and Nuggeoda, D. (2002). Are salts toxicants? *Australasian Journal of Ecotoxicology*, 8. 63 – 68

Kefford, B.J., Zalizniak, L., and Nuggeoda, D. (2006). Growth of the damselfly *Ischnura heterostricta* is better in saline water than freshwater. *Environmental Pollution*, 141. 409 – 419.

Khalili, M.I. and Weyhenmeyer, G.A. (2009). Growing season variability of nitrate along a trophic gradient - contrasting patterns between lakes and streams. *Aquatic Science*, 71. 25 – 33.

King J.M., and Louw, M.D. (1998) Instream flow assessments for regulated rivers in South Africa using the Building Block Methodology. *Aquatic Ecosystem Health and Management*, 1. 109-124.

King, J.M, Tharme, R.E., and de Villiers, M.S. (2000). Environmental Flow Assessments for Rivers: Manual for the Building Block Methodology. WRC Report No. TT 131/00.

Water Research Commission, Pretoria, South Africa.

Kienzle, S.W., Lorentz, S.A. and Schultze, R.E. (1997). Hydrology and Water Quality of the Mgeni Catchment. Water Research Commission Report (WRC) Report No. TT87/97. Pretoria, South Africa.

Kirchner, J., Moolman, J.H., du Plessis, H.M., Reynders, A.G. (1997) Causes and management of salinity in the Breede River Valley, South Africa. *Hydrogeology*, 5(1). 98 – 108.

Kleynhans, C.J., and Hill, L. (1999). Preliminary ecoregion classification system for South Africa. pp R1/2-R1/18 in (MacKay, H., Ed.) Resource directed measures for protection of water resources. Volume 3; River ecosystems. Version 1.0, DWAF, Pretoria.

Leenderste, K., Mitchell, S., and Harlin, J. (2008). IWRM and the environment: A view on their interaction and examples where IWRM led to better environmental management in developing countries. *Water SA*, 34(6). 691 – 698.

Leonard, R.A., Knisel, W.G., and Still, D.A. (1987). GLEAMS: Groundwater Loading Effects of Agricultural Management Systems. *Transactions of ASAE*, 30(5). 1403 – 1418.

Lindenschmidt, K.E. (2006). The effect of complexity on parameter sensitivity and model uncertainty in river water quality modelling. *Ecological Modelling*, 190. 72 – 86.

Liu, Y., Gupta, H., Springer, E., Wagner, T. (2008). Linking science with environmental decision making: Experiences from an integrated modelling approach to supporting sustainable water resources management. *Environmental Modelling and Software*, 23. 846 – 858.

Lottig, N.H. and Stanley, E.H. (2007). Benthic sediment influence on dissolved

- phosphorus concentrations in a headwater stream. *Biogeochemistry*, 84. 297 – 309.
- Mahamah, D.S. (1984). Numerical methods for assessing water quality in lakes and reservoirs. Ph.D. Dissertation, Washington State University, Pullman, WA, 122 pp.
- Mahamah, D.S. (1998). Simplifying assumptions in water quality modelling. *Ecological Modelling*, 109. 295 – 300.
- Malan, H.L. and Day, J.A. (2002a) Development of Numerical Methods for Predicting Relationships Between Stream Flow, Water Quality and Biotic Response in Rivers. Water Research Commission (WRC) Report no. 956/1/02, Pretoria, South Africa.
- Malan, H.L. and Day, J.A. (2002b) Linking Discharge, Water Quality and Biotic Response in Rivers: A Literature Review. Water Research Commission (WRC) Report no. 956/2/02, Pretoria, South Africa.
- McDiffet, W.F., Beidler, A.W., Dominick, T.F. and McCrea, K.D. (1989). Nutrient Concentration - Stream discharge relationships during storm events in a first - order stream. *Hydrobiologia*, 179. 97 – 102.
- McDonnel, R.A. (2008). Challenges for Integrated Water Resources Management: How Do We Provide the Knowledge to Support Truly Integrated Thinking? *Water Resources Development*, 24(1). 131 – 143.
- McIntyre, N.R., Wagner, T., Wheeler, H.S., Si Yu, Z. (2003). Uncertainty and risk in water quality modelling and management. *Journal of Hydroinformatics*, 5(4). 259 – 274.
- Meals, D.W., Cassel, E.A., Hugwell, D., Wood, L., Jokela, W.E. and Parsons, R. (2008). Dynamic spatially explicit mass-balance modelling for targeted watershed phosphorus management II. Model application. *Agriculture, Ecosystems and Environment*, 127. 223 –

233.

Merrey, D.J. (2008). Is normative integrated water resources management implementable? Charting a practical course with lessons from Southern Africa. *Physics and Chemistry of the Earth*, 33. 899 – 905.

Middleton, B.J., Bailey, A.K. (2005). Water resources of South Africa, 2005 STUDY (WR2005), Water Research Commission (WRC) Report No K5/1491, Pretoria, South Africa.

Midgley, D.C., Pitman, W.V., Middleton, B.J. (1994). Surface water resources of South Africa 1990: user's manual, Water Research Commission (WRC) Report No 298/1/94, Pretoria, South Africa.

O'Conner, D.J., Mueller, J.A., and Farley, K.J. (1983). Distribution of kepone in the James River estuary. *Journal of Environmental Engineering*, 109(2). 396 – 413.

O'Connor, D.J. (1988). Models of sorptive toxic substances in fresh water systems, I: Basic equations. *Journal of Environmental Engineering*, 114(3). 507 – 532.

O'Connor, D.J. and W.E. Dobbins (1958). Mechanism of Reaeration in Natural Streams. *ASCE Transactions*. Paper N_ 2934.

O'Keefe, J.H., van Ginkel, C.E., Hughes, D.A., Hill, T.R., Ashton, P.J. (1996). A situation analysis of water quality in the catchment of the Buffalo River, Eastern Cape, with special emphasis on the impacts of low cost, high-density urban development on water quality. Water Research Commission Report 405/1/96, Pretoria, South Africa.

O'Keefe, J. (2000) Environmental flow assessments within the South African integrated planning process for water resources. In King, J.M., de Villiers, M. and Tharme, R.E.

References

(Eds.) Flow Assessments for rivers: manual for the Building Block Methodology. Water Research Commission Report No. TT 131/00, Pretoria.

O'Keefe, J.H., Palmer, R.W., Byren, B.A. and Davies, B.R. (1990). The effects of impoundment on the physicochemistry of two contrasting southern African river systems. *Regulated Rivers: Research and Management*, 5. 97 – 110.

Oreskes, N., K. Shrader-Frechette, and K. Belitz. (1994). Verification, validation, and confirmation of numerical models in the earth sciences. *Science*, 263. 641–646.

Palmer, C.H., Berold, R., Muller, W.J. and Schermann, P.A. (2002). *Some, For All, Forever*. Water Ecosystems and People. Water Research Commission report TT176/02. Water Research Commission, Pretoria, South Africa.

Palmer, R.W. and O'Keefe, J.H. (1989). Temperature characteristics of an impounded river. *Archives of Hydrobiology*, 116(4). 471 – 485.

Parsons, R., Wentzel, J., (2006) Groundwater Resource Directed Measures (GRDM) manual. Water Research Commission (WRC) Report no. K5/1427, Pretoria, South Africa.

Pegram, G.C. and Gorgens, A.H.M. (2001). A guide to non-point source assessment to support water quality management of surface water resources in South Africa. Water Research Commission (WRC) Report no. TT 142/01, Pretoria, South Africa.

Pelletier, G.J., Chapra, S.C., Tao, H. (2006). QUAL2Kw - A framework for modeling water quality in streams and rivers using a genetic algorithm for calibration. *Environmental Modelling and Software*, 21. 419 – 425.

Pionke, H.B., Gburek, W.J., Schnabel, R.R., Sharpley, A.N. and Elwinger, G.F. (1999). Seasonal flow, nutrient concentrations and loading patterns in stream flow draining an

agricultural hill-land watershed. *Journal of Hydrology*, 220. 62 – 73.

Pollard, S. and du Toit, D. (2008). Integrated water resources management in complex systems: How the catchment management strategies seek to achieve sustainability and equity in water resources in South Africa. *Water SA*, 34(6). 671 – 680.

Popper, K.R. (1968). *The Logic of Scientific Discovery*. Hutchinson, London, United Kingdom.

Reckhow, K.H. (1983). Confirmation of water quality models. *Ecological Modelling*, 20. 113 – 133.

Reckhow, K.H. (1990). Bayesian inference in non-replicated ecological studies. *Ecology*, 71. 2053 - 2059.

Reckhow, K.H. (1994). Water quality simulation modeling and uncertainty analysis for risk assessment and decision making. *Ecological Modelling*, 72. 1 – 20.

Reckhow, K.H. and Chapra, S.C. (1999). Modelling excessive nutrient loading in the environment. *Environmental Pollution*, 100. 197 – 207.

Rossouw, J.N., Quibell, G. (1993). Simulation of nutrient and algal growth dynamics in the middle Vaal River. Proceedings of the Sixth South African National Hydrological Symposium, Pietermaritzburg, South Africa. 8 – 10 September.

Rouch, W., Henze, M., Koncsos, L., Reichert, P., Shanahan, P., Somlyódy, L. and Vanrolleghem, P (1998). River Water Quality Modelling: I. State of the Art. Proceedings of the IAWQ Biennial International Conference. Vancouver, British Columbia, Canada. 21 - 26 June 1998.

Rousseau, A.N., Mailhot, A., Turcotte, R., Duchemin, M., Blanchette, C., Roux, M., Etong, N., Dupont, J. and Villeneuve, J.P. (2000). GIBSI - An integrated modelling system prototype for river basin management. *Hydrobiologia*, 422/423. 456 – 475.

Ruggiero, A., Solimini, A.G., Anello, M., Romano, A., de Cicco, M. and Carchini, G. (2006). Nitrogen and phosphorus retention in a human altered stream. *Chemistry and Ecology*, 9(22). S1 – S13.

Santhi, C., Srinivasan, R., Arnold, J.G. and Williams, J.R. (2006). A modeling approach to evaluate the impacts of water quality management plans implemented in a watershed in Texas. *Environmental Modelling and Software*, 21. 1141- 1157.

Schulz, R. (2001). Rainfall-induced sediment and pesticide input from orchards into the Lourens River, Western Cape, South Africa: Importance of a single event. *Water Research*, 35(8). 1869 – 1876.

Simpson, D.E. and Stone, V.C. (1988). A case study of urban runoff pollution: 1. Data collection, runoff quality and loads. *Water SA*, 14(2). 229 – 237.

Sivapalan, M., Takeuchi, K., Franks, S.W., Gupta, V.K., Karambiri, H., Lakshmi, V., Liang, X., McDonnel, J.J., Mendiando, E.M., O’Connel, P.E., Oki, T., Pomeroy, J.W., Schertzer, D., Uhlenbrook, S., Zehe, E. (2003). IAHS Decade on Predictions in Ungauged Basins (PUB), 2003 – 2012: Shaping an exciting future for the hydrological sciences. *Hydrological Sciences*, 48(6). 857 – 880.

Shanahan, P., Henze, M., Koncsos, L., Rauch, W., Reichert, P., Somlyody, L. and Vanrolleghem, P. (1998). River water quality modelling: II. Problems of the Art. Proceedings of the IAWQ Biennial International Conference. Vancouver, British Columbia, Canada. 21 - 26 June 1998.

References

Simpson, D.E. (1991). Quantification of the effects of land-use on runoff water quality in selected catchments in Natal. Water Research Commission (WRC) Report No: 237/1/91, Pretoria, South Africa.

Skaggs, R.W. (1982). Field Evaluation of a Water Management Simulation Model. *Transactions of ASAE*, 25(3). 66 – 674.

Snaddon, B.R. Davies and M.J. Wishart (1999), A Global Overview of Inter-basin Water Transfer Schemes, with an Appraisal of their Ecological, Socio-economic and Socio-political Implications, and Recommendations for their Management. Water Research Commission Report No: TT 120/00, Pretoria (1999).

Spear, R.C., Hornberger, G.M., (1980). Eutrophication in Peel Inlet, II. Identification of critical uncertainties via generalized sensitivity analysis. *Water Resources Research*, 14. 43-49.

Stalnaker, C.B., Lamb, B.L., Henriksen, J., Bovee, K.D. and Bartholow, J. (1994). The Instream Flow Incremental Methodology: a primer for IFIM. National Ecology Research Center, internal publication. Fort Collins, CO, USA.

StatSoft, Inc. (2007). STATISTICA (data analysis software system), version 8. WWW.statsoft.com.

Strahler, A.N. (1952). Hypsometric (area altitude) analysis of erosional topology. *Geological. Society of America Bulletin*, 63. 1117–1142.

Stéphanie, E., Poulin, M., Garnier, J., Billen, G., Servais, P., Chesterikoff, E. and Coste, M. (1998). River ecosystem modelling: application of the PROSE model to the Seine river (France). *Hydrobiologia*, 373/374. 27 – 45.

Streeter W.H. and Phelps E.B. (1925). A study of the pollution and natural purification of the Ohio River. Public Health Bulletin Report No: 146, U.S. Public Health Service, Washington D.C.

Stutter, M.I. and Lumsdon, D.G. (2008). Interactions of land use and dynamic river conditions on sorption equilibria between benthic sediments and river soluble reactive phosphorus concentrations. *Water Research*, 42. 4249 – 4260.

Tarboton, K.C. and Schulze, R.E. (1991). The ACRU modelling system for large catchment water resources management. In: Van de Ven, F.H.M., Gutknecht, D., Loucks, D.P. and Salewicz, K.A. *Hydrology for the Water Management of Large River Basins*. IAHS Publ. (201) 219 – 232.

Thomann, R.V. (1998). The Future "Golden Age" of Predictive models for Surface Water Quality and Ecosystem management. *Journal of Environmental Engineering*, 2. 94 – 103.

Thomann, R.V., and Di Toro, D.M. (1983). Physico chemical model of toxic substances in the Great Lakes. *Journal of Great Lakes Research*, 9(4). 474 – 496.

Tong, S.T.Y., and Chen, W. (2002). Modeling the relationship between land use and surface water quality. *Journal of Environmental Management*, 66. 377 – 393.

Tu, J. and Xia, Z.G. (2008). Examining spatially varying relationships between land use and water quality using geographically weighted regression I: Model design and evaluation. *Science of the Total Environment*, 407(1). 358-378.

Van der Keur, P., Henriksen, H.J., Refsgaard, J.C., Brugnach, M., Pahl-Wostl, C., Dewulf, A., Buiteveld, H. (2008). Identification of Major Sources of Uncertainty in Current IWRM Practice. Illustrated for the Rhine Basin. *Water Resource Management*, 22. 1677 – 1708.

References

Van Nieuwenhuysen, E.E. (2007). Response of summer chlorophyll concentration to reduced total phosphorus concentration in the Rhine River (Netherlands) and the Sacramento - San Joaquin delta (California, USA). *Canadian Journal of Fisheries and Aquatic Science*, 64. 1529 – 1542.

Van Wyk, E., van Wilgen, B.W. (2002). The cost of water hyacinth control in South Africa: a case study of three options. *African Journal of Aquatic Science*, 27. 141 – 149.

Velghe, N., and Claeys, A. (1983). Rapid Spectrophotometric Determination of Nitrate with Phenol. *Analyst*, 108. 1018 – 1022.

Venter, S.N., Steynberg, M.C., de Wet, C.M.E., Hohls, D., du Plessis, G. and Kfir, R. (1997). A situational analysis of the microbial water quality in a peri-urban catchment in South Africa. *Water Science and Technology*, 35 (11-12). 119 – 124.

Wade, A.J., Durand, P., Beaujouan, V., Wessel, W.W., Raat, K.J., Whitehead, P.G., Butterfield, D., Rankinen, K and Lepisto, A. (2002). A nitrogen model of European catchments: INCA, new model structure and equations. *Hydrology and Earth System Sciences*, 6(3). 559 – 582.

Walmsley, R.D., Walmsley J J, Silberbauer M. (1999). National State of the Environment – South Africa: Freshwater Systems and Resources: Overview. Report prepared by Mzuri Consultants for the Department of Water Affairs: <http://WWTW.environment.gov.za/Enviro-Info/sote/nsoer/issues/water/index.htm>.

Wang, X. and Yin, Z.Y. (1997). Using GIS to assess the relationship between land use and water quality at a watershed level. *Environmental International*, 23(1). 103 – 114.

Whitehead, P.G., Wilson, E.J. and Butterfield, D. (1998). A semi-distributed Integrated

References

Nitrogen model for multiple source assessment in Catchments (INCA): Part I – model structure and process equations. *The Science of the Total Environment*, 210/211. 547 – 558.

Williams, J. R. (1995). The EPIC model. In Singh, V. P. (ed.), *Computer Models of Watershed Hydrology*. Water Resources Publications, Highlands Ranch (CO): 909–1000.

Williams, W.D. (2001). Anthropogenic salinization of inland waters. *Hydrobiologia*, 466. 329 – 337.

Wimberley, F. and Coleman, T (2005). *Water Quality Modelling for Planning*. Department of Water Affairs Report No: 7028-6631-1-E, Pretoria, South Africa.

Wischmeier, W. H. and Smith, D. D. (1978). Predicting Rainfall Erosion Losses – A Guide to Conservation Planning. Agricultural Handbook No. 537, U.S. Department of Agriculture, Washington, DC, 58 pp.

Withers, P.J.A. and Jarvie, H.P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of the Total Environment*, 400. 379 - 395.

Wood, F.L., Heathwaite, A.L. and Haygarth, P.M. (2005). Evaluation diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. *Journal of Hydrology*, 304. 118 – 138.

Yalin, Y. S. (1963). An Expression for Bed-Load Transportation. *Journal of Hydraulic Division*, 89. 221–250.

Young, P., Parkinson, S., Lees, M. (1996). Simplicity out of complexity in environmental modelling: Occam's razor revisited. *Journal of Applied Statistics*, 23(2 and 3). 165 – 210.

References

Zuma, B. (2010). Microbial ecology of the Buffalo River in response to water quality changes. M.Sc. Thesis. Rhodes University, Grahamstown, South Africa.

References
