MODELLING WATER QUALITY: COMPLEXITY VERSUS SIMPLICITY

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ABSTRACT

Water quality management makes use of water quality models as decision making tools. Water quality management decisions need to be informed by information that is as reliable as possible. There are many situations where observational data are limited and therefore models or simulation methods have a significant role to play in providing some information that can be used to guide management decisions. Water quality modelling is the use of mathematical equations and statistics to represent the processes affecting water quality in the natural environment. Water quality data are expensive and difficult to obtain. Nutrient sampling requires a technician to obtain 'grab samples' which need to be kept at low temperatures and analysed in a laboratory. The laboratory analyses of nutrients is expensive and time consuming. The data required by water quality models are seldom available as complete datasets of sufficient length. This is especially true for ungauged regions, either in small rural catchments or even major rivers in developing countries. Water quality modelling requires simulated or observed water quantity data as water quality is affected by water quantity. Both the water quality modelling and water quantity modelling require data to simulate the required processes. Data are necessary for both model structure as well as model set up for calibration and validation. This study aimed to investigate the simulation of water quality in a low order stream with limited observed data using a relatively complex as well as a much simpler water quality model, represented by QUAL2K and an in-house developed Mass Balance Nutrient (MBN) model, respectively. The two models differ greatly in the approach adopted for water quality modelling, with QUAL2K being an instream water quality fate model and the MBN model being a catchment scale model that links water quantity and quality. The MBN model uses hydrological routines to simulate those components of the hydrological cycle that are expected to differ with respect to their water quality signatures (low flows, high flows, etc.). Incremental flows are broken down into flow fractions, and nutrient signatures are assigned to fractions to represent catchment nutrient load input. A linear regression linked to an urban runoff model was used to simulate water quality entering the river system from failing municipal infrastructure, which was found to be a highly variable source of nutrients within the system. A simple algal model was adapted from CE-QUAL-W2 to simulate nutrient assimilation by benthic algae. QUAL2K, an instream water quality fate model, proved unsuitable for modelling diffuse sources for a wide range

of conditions and was data intensive when compared to the data requirements of the MBN model. QUAL2K did not simulate water quality accurately over a wide range of flow conditions and was found to be more suitable to simulating point sources. The MBN model did not provide accurate results in terms of the simulation of individual daily water quality values; however, the general trends and frequency characteristics of the simulations were satisfactory. Despite some uncertainties, the MBN model remains useful for extending data for catchments with limited observed water quality data. The MBN model was found to be more suitable for South African conditions than QUAL2K, given the data requirements of each model and water quality and flow data available from the Department of Water and Sanitation. The MBN model was found to be particularly useful by providing frequency distributions of water quality loads or concentrations using minimal data that can be related to the risks of exceeding management thresholds.

Table of Contents

List of Tables

List of Figures

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1. INTRODUCTION

1.1 Water Quality

There is increasing pressure on global water resources with increases in the human population size, improvements in service delivery and increasing affluence, as water finds application in nearly every aspect of society and is necessary to sustain life. History shows many examples of human abuse of water resources, both in terms of over-consumption and pollution. Globally, fresh water is currently experiencing a deterioration of water quality (Smith, 2003).

Water quality is described as the physical, chemical and biological characteristics of water, and is characterised by the requirements of the water user, for example, human consumption. Water quality is affected by both natural and anthropogenic sources. Natural sources affecting water quality include weathering of rocks containing minerals, animal wastes and atmospheric deposition (Dabrowski and de Klerk 2013). Anthropogenic sources of water pollution include industrial effluent, agricultural runoff, enhanced erosion, waste water treatment effluent and urban runoff (Pegram and Gorgens, 2001). Water pollution is classified into broad classes, including organic pollution, inorganic pollution and thermal pollution.

Eutrophication of lakes and rivers has become a widespread problem (Hilton *et al.*, 2006). Eutrophication is defined as the excess of nutrients in water, which promotes the increased growth rate of phytoplankton and algae. The nutrients that result in eutrophication include inorganic and organic phosphorus, nitrogen and iron. The depletion of dissolved oxygen, increased turbidity, increased presence of toxic blue-green algae and the death of aquatic fauna are some of the problems associated with the increase of algae and phytoplankton (Hilton *et al.*, 2006). Eutrophication increases the cost of water purification and results in a loss of biodiversity in aquatic systems. Nutrient pollution and associated eutrophication is the most wide spread water quality problem globally, as human activities typically result in the release of nutrients into water resources; therefore, this thesis has focused on the simulation of nutrients in water resources.

Sources of pollution can generally be classified as point and non-point sources. Point sources are defined as easily identifiable points, such as a pipe outlet or a ditch (Huang and Xia, 2001). With the increase in urbanisation, there has been an increase in human waste inputs from point sources, thereby increasing the stress placed on natural systems to assimilate pollutants of anthropogenic origin. Non-point sources are defined as sources of pollution that have a diffuse entry into water systems, such as runoff from agricultural areas. Point and non-point sources show different characteristics when associated with stream-flow and runoff. Point sources generally have the highest impact on the water resource during low flows, as concentrations are diluted at high flows, assuming that the point source is not directly influenced by rainfall. However, waste water treatment works (WWTWs) do overflow during high rainfall events, contributing to the input of untreated sewage into water drainage systems. Diffuse sources have the greatest impact at times of surface runoff, as surface runoff is required to transport pollutants from the soil surface to the water resource. However, agricultural diffuse sources can impact water quality at low flows when irrigation is inefficiently applied (Bowes *et al.*, 2008). Over-irrigation results in return flow which transports soluble nutrients in solution to the water resource.

As we become more aware of the human dependence on water and water availability becomes more limited, an emphasis has been placed on decreasing consumption as well as minimising anthropogenic impacts on natural water systems (Horn *et al.*, 2004). On a global level, more emphasis is being placed on environmental protection through increasing knowledge of the link between human well-being and the health of the environment (Watkins, 2009). It is understood that human health is directly related to the health of the surrounding environment (Watkins, 2009). Water of sub-standard quality is the greatest factor contributing to the high infant mortality rate worldwide. Cases of child mortality exceeding 1.8 million have been attributed to a lack of sanitation and access to safe drinking water (Watkins, 2009). Poor sanitation or a lack thereof results in cholera and diarrhea, which lead to mortalities, especially in infants. The treatment of waste water is arguably the first barrier of defence against deteriorating water resources.

1.2 Water quality management

Because of the relationship between environmental health, human population health and water quality, it is imperative to manage water quality. Water quality management involves the monitoring and control of diffuse and point source impacts on a water resource. However, natural water resources have the ability to assimilate a certain level of nutrient pollution. Water quality management ensures that the level of pollution in the system does not exceed the assimilative capacity of the resource over the short- and long-term. However, water quality management also needs to ensure that water quality guidelines that are set by water resource governing bodies are met.

Two legal documents guiding water management in South Africa exist. In 1997, the Water Services Act (WSA: No. 108 of 1997) was promulgated, and the National Water Act (NWA: No. 36 of 1998) was passed in 1998. The WSA focuses on the provision of water whereas the NWA is focused on the management of water resources. The principles adopted within the NWA adhere to an Integrated Water Resource Management (IWRM) approach in that the NWA attempts to achieve sustainable and equitable use of water resources by integrating natural processes and the needs of society, industry and agriculture. One accepted definition of IWRM is that stated by the Global Water Partnership (GWP, 2000): 'a process which promotes the coordinated development and management of water, land and related resources, in order to maximise the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems'.

The NWA stipulates an ecological Reserve, which is the quantity and quality of water required to sustain aquatic ecosystems, as well as a human Reserve, which is a specific volume of water allocated per person within the catchment. The ecological and human reserves must be met before water can be allocated to agriculture and industry. Resource Directed Measures (RDMs) are goals set for the ecological state of each catchment, set as ecological categories (A–F, with 'A' indicating pristine, and 'F' indicating severe human impact). Resource Quality Objectives (RQOs) are guidelines for specific water quantity or quality variables, required to achieve the RDM. Source Directed Controls (SDCs) stipulate the control of effluent released from industries and agriculture to achieve RQOs.

1.3 Water Quality Modelling

Water quality modelling involves the use of mathematical algorithms and statistical relationships to predict the pollutant and natural water quality dynamics in water bodies (Mahama, 1998). The focus for this study is on river water quality modelling. River water quality models differ from reservoir and estuarine models, as river models generally operate in one dimension (longitudinally), whereas reservoir and estuarine models are required to operate in multiple dimensions (vertical, horizontal and longitudinal) and simulate stratification. Policies have been implemented to maintain the quality of water in rivers in many regions globally, such as in the European Union in 2000, South Africa in 1998 and in the United States of America in 1994 (Horn *et al.*, 2004). Water quality modelling is used to determine the effect of pollutant loadings, the assimilative capacity of the river system, the assessment of management decisions and changes in management practices, the prediction of future conditions within the river and the extension of current data (Loucks *et al.*, 2005). Although modelling is a tool that aids management decisions, water quality models do not provide the complete answer to a problem. Nutrient dynamics in river systems are influenced by a large number of variables, and the process of modelling the complete system is therefore very complicated. However, many processes are relatively insignificant, and a system can be simulated 'accurately' by only modelling the major processes affecting water quality. By simplifying the model, the number of required parameters decreases, resulting in simpler and more cost-effective data collection. Financial restraints limit both data and time available for modelling (Mahama, 1998). However, the complexity of the model should be related to the problem (Loucks *et al.*, 2005).

There is an increasing drive to implement transdisciplinarity in water resource management, and move from management to governance through transdisciplinarity, i.e., 'a process of joint production of knowledge and joint definition of the underlying norms and interpretive patterns of knowledge' (Rist *et al.*, 2007). This paradigm shift is due to the recognition of the complexity and inter-connectivity of water resources and many other systems. The paradigm of transdisciplinarity recognises that an integrated approach is required for the management of complex systems, rather than a scientific reductionist approach, which has traditionally been used (Janssen and Goldsworthy, 1995). However, some degree of reductionism is inevitable. Stirzaker *et al.* (2010) introduces the concept of 'requisite simplicity' as 'there is a requisite level of simplicity behind the complexity (of a system), that if identified, can lead to an understanding that is rigorously developed but can be communicated lucidly'. Even with the drive towards transdisciplinarity, there is acceptance that simple models can be more useful than complex models, as complex models are prone to equifinality, which is the process of arriving at the same conclusion, through different processes. However, it is important that the shortcomings of the model are communicated effectively and transparently (Stirzaker *et al.*, 2010).

1.4 Aims

The modelling of water quality is a useful tool in the management of water resources. However, the process of simulating water quality faces many challenges. Modelling requires experienced modellers, time and data, all of which cost money (Loucks *et al.*, 2005). In addition, complex models are not necessarily more useful than simple models. To facilitate more efficient modelling of water quality, the use of simpler models may be more appealing (Loucks *et al.*, 2005). In the past, more complex models were preferred; however, there is a push in ecological modelling towards simpler models (Evans *et al.*, 2013). Therefore, the aim of the project is to test two water quality models in terms of their ability to simulate water quality variations in the Bloukrans River, a small river that is impacted by several point and diffuse inputs. The two models are at opposite ends of the complexity scale: one complex in structure, whereas the other model was created to be as simple as possible. QUAL2K was selected to represent a complicated water quality model. The model was used successfully on the Bloukrans River by Slaughter (2011). QUAL2K is the updated version of QUAL2E. The United States Environmental Protection Agency developed the QUAL2E river water quality model, which has become one of the preferred models for water quality modelling in Europe and the USA. Here, a mass balance nutrient model similar to the HBV-NP model (Anderson *et al.*, 2005), which was developed in-house, was used to represent a simple modelling approach, which we called the Mass Balance Nutrient Model (MBN MODEL).

Water quality modelling can be a highly complicated process due to the number of variables influencing each nutrient. Complex models have the following disadvantages:

- Data intensive.
- Require the estimation of parameters which are difficult to measure and cannot be accurately represented in the laboratory.
- Potentially suffer from equifinality.

However, when modelling nutrients, it is argued that one can simplify a model to a certain extent by focusing on the processes that most affect water quality (requisite simplicity), as well as focus on the water quality variables of concern. This project aims to test this hypothesis. Equifinality refers to the situation where multiple parameter value sets will provide the same or similar model outcome (Bevan, 2006). This phenomenon becomes more prevalent as model parameters increase, and acceptable model calibration to historical observed data may be a statistical artefact because of the large number of parameters used, rather than a realistic representation of the system processes. Incorrect calibration of a model because of equifinality may lead to inaccurate modelling of future scenarios (Oreskes *et al.*, 1994).

During the modelling process, a suitable complex model should be simplified to the point where the accuracy of the simulation remains acceptable (Lindenschmidt, 2006), similar to the concept of Occam`s Razor (Young *et al.*, 1996). However the complexity of the problem requires acceptable complexity of the model (Loucks *et al.*, 2005). Both developing and many developed countries have sparse or even non-existent water quality data. In the past, the adopted simpler models tended to represent statistical relationships; however, a recent trend has been the move towards using more mechanistic models. Simple models have the following advantages over complex models:

- Lower data demand.
- Easier to calibrate.
- Fewer parameters and less chance of equifinality.
- Lower modelling time required.
- Site specific.
- More likely to provide modelling output that is useful from a management perspective.

However, the disadvantages of simpler models are that some processes are not taken into account; therefore, these models cannot be used for testing scientific hypotheses. If simpler water quality models can achieve an acceptable degree of accuracy for the purposes of management, they could find widespread use in water management due to their decreased cost, time and data requirements.

The specific questions that were raised by this study are:

1. Can a simple model provide realistic results?
2. Can a complex model provide realistic results with limited data?
3. Given similar data constraints, can a simple model perform adequately as compared to a complex model?

2. LITERATURE REVIEW

This chapter reviews the available literature covering important nutrients, sources of nutrients to rivers, and instream processes affecting nutrients. In addition, the literature representation of the aforementioned within water quality modelling is discussed.

2.1 Important nutrient water quality variables

Nutrients can be described as non-conservative water quality variables, i.e., the chemical form of nutrients can change over time (Malan and Day, 2002). Plants require nutrients for growth and reproduction. Nitrogen and phosphorus are the main nutrients required by plants; however, other nutrients are required in small quantities for plant growth, such as selenium and silica (Garnier *et al.*, 1995). The processes controlling the fate of nutrients are termed biogeochemical processes, as biological, geomorphologic and chemical processes all affect the fate of nutrients. Figure 2.1 illustrates the chemical fate of nutrients in a river system that can be referred to throughout this chapter. Biogeochemical processes in rivers are controlled through oxidation-reduction reactions by biota to gain energy, fix nutrients and synthesise tissue (Triska and Higler, 2010). Excess levels of nutrients are the main contributors to eutrophication (Tao *et al.*, 2010), leading to promoted growth of phytoplankton, algae and macrophytes.

2.1.1 Nitrates and nitrites

The most common form of nitrogen in waters under natural conditions is the nitrate ion (NO_3^-), with concentrations generally below 0.1 mg ℓ^{-1} globally (Dallas and Day, 2004). Nitrate undergoes denitrification under anaerobic conditions and is reduced to nitrite (NO_2^-) or ammonium (NH_4^+) (See Figure 2.1), whereas the opposite occurs under aerobic conditions, called nitrification (Chapra, 1997). The process of nitrification is represented in Equations (2.1) and (2.2). Nitrite concentrations are generally low in freshwater systems. High levels of NO_2 indicate the presence of industrial effluent and are associated with poor microbial activity (Dallas and Day, 2004). Anthropogenic additions from industry, agriculture, WWTWs and landfills increase the level of nitrates in natural waters. The use of inorganic nitrate fertilisers can contribute significant amounts of nitrates to water bodies. Certain land-use practises increase the rate of nitrate leaching, with the highest leaching rates occurring from arable agriculture, although this is dependent on seasonal factors and the degree of disturbance of the soil (Ferrier *et al.*, 1995).

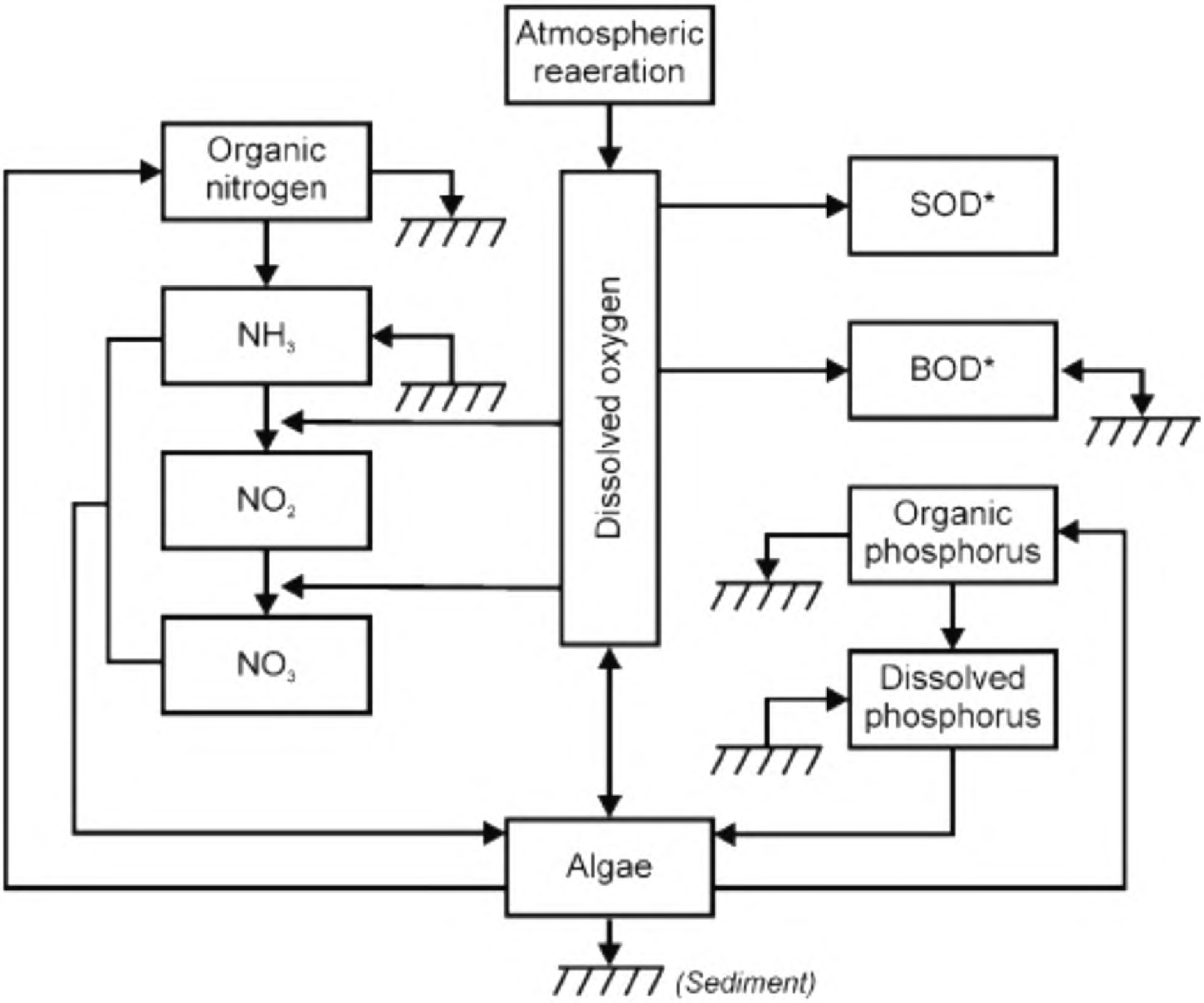

Figure 2.1: A conceptual depiction of the biogeochemical processes occurring within in a river system (taken from Horn *et al*., 2004).

NO_3^- concentrations > 5mg ℓ$^{-1}$ indicate animal and human faecal contamination or fertiliser runoff (Dallas and Day, 2004). In contrast to phosphates which bind to soil particles, nitrogen is soluble and readily leaches into and contaminates groundwater (Ranalli and Macalady, 2010).

2.1.2 Ammonium

Ammonium and ammonia exist interchangeably within the water column, although the ammonium form predominates, with ammonia forming with an increase in pH and temperature (DWA Water Quality Guidelines Vol 7, 1996). Ammonia is more toxic than ammonium, with effects including toxicity to fish and invertebrates, and whereas ammonium is not toxic, it does contribute to eutrophication (DWA, 1996). Ammonium found naturally in freshwater bodies results from excretion by biota, reduction of nitrogen gas by micro-organisms, the decomposition of inorganic and organic nitrogenous compounds as well as atmospheric gas exchange (Dallas and Day, 2004). Elevated levels of ammonium are indicative of animal contamination from farmlands or anthropogenic waste water. Ammonium is preferentially assimilated by flora as it does not have to be reduced before uptake (Dallas and Day, 2004; Triska and Higler, 2010). Instream processes increasing the concentration of ammonium including re-suspension of sediments resulting in desorption of ammonium (Simon, 1989), and ammonification of organic material during decomposition (Chapra, 1997). Processes that decrease the instream concentration of ammonium include biological assimilation, sorption to sediments and nitrification of ammonium to form nitrate (Chapra, 1997). Nitrification is a two-step process and requires the involvement of different genera of bacteria. Equation (2.1) represents the process facilitated by bacteria of the genus *Nitrosomonas* (Triska and Higler, 2010), whereas Equation (2.2) represents the process facilitated by bacteria of the genus *Nitrobacter* (Triska and Higler, 2010). The energy created by nitrification is used in the reduction of inorganic carbon to form biomass. The first step of nitrification is:

$$4NH_4^+ + 6H_2O \rightarrow 4NO_2^- + 8H^+ + 4H_2O \tag{2.1}$$

The second step in nitrification is:

$$4NO_2^- + 2O_2 \rightarrow 4NO_3 \tag{2.2}$$

2.1.3 Phosphorus

Within surface waters, phosphorus is essential for the growth of flora and is generally the limiting nutrient; thus, phosphorus controls primary productivity in many systems (McDowell *et al.*, 2003). Phosphorus is found in three different forms, firstly Total Phosphorus (TP), secondly Total Dissolved Phosphorus (TDP) and thirdly, Soluble Reactive Phosphorus (SRP). Total Phosphorus is the measure of all the forms of phosphorus. Total Dissolved Phosphorus is the TP in solution, ie, not including the particulate phosphorus. Soluble Reactive Phosphorus is the soluble, inorganic fraction of phosphorus otherwise known as ortho-phosphate. SRP is readily filterable by plants. The concentration of phosphorus found in streams is dependent on the hydrology, geology and land use of a catchment (Grobler *et al.*, 1984). The main contributors to natural phosphorus sources are the decomposition of organic matter and the breakdown of phosphorus rich rock occurring naturally within a catchment. Anthropogenic sources of phosphorus originate from agricultural runoff, industrial effluents and municipal wastewaters (Bowes *et al.,* 2005; McDowell et al., 2003). Detergents are a major source of phosphorus in municipal wastewaters (Bowes *et al.,* 2005). Land use has been linked to the phosphorus loading in rivers, and urban areas and certain agricultural activities have been shown to be the most likely diffuse sources of phosphorus in rivers (Dabrowski and de Klerk, 2013). Dairy farms, feed lots and intensive short period crops which require substantial fertiliser application are included as agriculture practices that have higher phosphorus contributions (Dabrowski and de Klerk, 2013; Ranalli and Macalady, 2010). Phosphorus is often bound to sediments, and is therefore often transported along with inorganic sediment (Ranalli and Macalady, 2010; Stutter and Lumsdon, 2008). The instream phosphorus concentration is controlled by two processes: 1) biotic physiological processes including uptake of phosphorus by plants and; 2) sediment geochemical processes including the adsorption and desorption of phosphorus from sediment (McDowell *et al.,* 2003).

2.2 Nutrient sources and important processes affecting water quality variables

2.2.1 The relationship between flow and water quality

Flow (water quantity) is a direct and primary driver of water quality variable concentrations. Natural flow acts to dilute the instream concentrations of rivers affected by anthropogenic sources of both conservative and non-conservative water quality variables; however, in an undisturbed system, natural flows introduce nutrients and salts from the catchment into the stream system. Flow additionally controls the residence time of water quality variables in a river, with higher flow events flushing water quality loads downstream. Natural flow can have a beneficial or detrimental effect on water quality, depending on the land use within a catchment. Higher natural flow can dilute point sources of water quality variable loads, but can also introduce diffuse sources (Bowes *et al*., 2008).

2.2.2 Point and diffuse sources

Point sources are easily identifiable and usually discharge municipal waste water or industrial effluent to a specific and confined point (Pegram and Gorgens, 2001). In contrast, diffuse sources usually originate from surface runoff and sub-surface flow from a catchment and occur over an extended spatial and temporal range (Pegram and Gorgens, 2001).

Diffuse source inputs are directly linked to the geology and land use within a catchment as well as the management practices affecting the land use (Jewitt, 2002; Ranalli and Macalady, 2010).

Diffuse sources of water quality variables can originate from both anthropogenic and natural sources. Within South Africa, the natural background water quality of undisturbed catchments can be characterised by the predominant geology of the catchment (Pegram and Gorgens, 2001). Natural sources of nutrient input affecting water quality include erosion of soil and rock, animal waste, the breakdown of decaying vegetation, atmospheric deposition and gaseous exchange.

Anthropogenic diffuse sources of water pollution include agricultural runoff, urban runoff, landfill seepage and mining activities (Simpson and Stone, 1988). Depending on the specific agricultural practice, agricultural runoff can contain animal waste, excess fertiliser, herbicides and insecticides. Low flows in a river can be affected by irrigation return flow carrying soluble nutrients to the river. Erosion resulting from surface runoff carries faecal matter, soil and nutrients that have accumulated on the catchment surface to the stream.

Urban areas have been shown to be the greatest contributor of diffuse pollutants to surface water resources (Hongbing *et al.*, 2009; Wang *et al.*, 2011; Wei *et al.*, 2010). Urban areas are characterised by large areas of impermeable surfaces such as concrete, asphalt and roofing. The impermeable surfaces increase surface runoff significantly as infiltration is impaired. Urban areas that have been researched for pollutant runoff include rooftops, grass lawns, parking lots and roads. Parking lots and roads were shown to have the greatest pollutant loading (Wei *et al.*, 2010). Grass lawns have the highest infiltration rate of the urban areas studied and thus have the lowest runoff. Nutrients are sorbed to colloids within soils, further decreasing the load of nutrients originating from grassed areas (Wei *et al.*, 2010). Municipal areas with poorly maintained infrastructure affect low flows by contributing untreated sewage to the river from leaking sewerage infrastructure (Bowes *et al.*, 2005). The 'pit-latrine' toilet systems used in under-developed urban areas with no formal wastewater removal contribute raw sewage during large rainfall events as these toilets overflow. The 'bucket system' is also prevalent in these areas, where sewage that is not collected by municipal services is dumped in shallow pits or thrown on open land, leading to polluted runoff. Dairy farms and feedlots tend to concentrate animals and feacal matter, leading to increases in downstream nutrient concentrations. Irrigated areas tend to increase instream nutrient concentrations as a result of return flows that flush nutrients out of the soil. However, the type of irrigation application directly affects the contribution to the total nutrient load, with the less efficient irrigation techniques, such as overhead irrigation and 'big gun' irrigation generally resulting in greater instream nutrient concentrations than the more efficient irrigation techniques such as drip line irrigation.

The concept of antecedent rainfall conditions and 'first flush' events are important when considering diffuse sources. Antecedent literally means 'preceding', and in relation to catchment hydrology, refers to the rainfall and runoff that has occurred in the recent past. Antecedent rainfall has an influence on the diffuse load of water quality variables transported due to a particular event, as extended dry periods allow a build-up of water quality variable loads on the catchment surface (Britton *et al.,* 1993). A rainfall-runoff event following an extended dry period is likely to be associated with a larger diffuse load than a runoff event within an extended wet spell (Hongbing *et al.,* 2009). The 'first-flush' phenomenon is similar, except it is intra-event specific, and refers to an initial spike in diffuse load associated with a rainfall-runoff event, followed by a receding trend as the storage of water quality variable load on the catchment surface becomes depleted (Hongbing *et al.,* 2009; McDiffett *et al.,* 1989). A weak but positive relationship between total antecedent dry days and total runoff nutrient load has been identified by Wang *et al.* (2011). Hongbing *et al.* (2009) indicated that there was a weak trend in peak pollutant concentration preceding the peak runoff, with most nutrient concentrations decreasing rapidly after the peak (with the exception of nitrates). Nitrates have been shown to seep into groundwater (Ranalli and Macalady, 2010), and this could explain why nitrates do not follow a 'first flush' pattern, as ground water input to a river represents a slower drainage process and can be prolonged beyond immediate rainfall events. The contribution of nutrients from diffuse sources from land uses such as urban areas is highly variable (Hongbing *et al.,* 2009), depending on antecedent catchment conditions, rainfall intensity and total runoff volume (Bowes *et al*., 2005). The high temporal variability of measured instream nutrient concentrations at a particular point downstream of an urban area during runoff events is illustrated in Figure 2.2. In addition to antecedent conditions, the spatial variability of the origin of nutrients within the catchment may explain the temporal variability in measured nutrient concentrations, as nutrient deposits originating at a point further away from the monitoring point will experience longer transport time to the monitoring point than closer deposits.

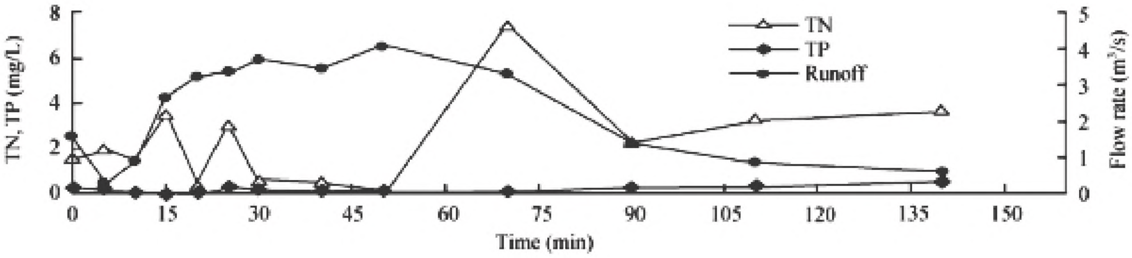

Figure 2.2: Graphs showing the variability of nutrient concentrations throughout a storm event (Taken from Hongbing *et al.* (2009)).

Point sources of nutrients to a surface water resource are usually associated with industrial or municipal waste water effluent (Bowes *et al.*, 2008; Marsili-Libelli and Giusti, 2008). Industrial effluent contains different pollutants depending on the type of industry. Nutrients are more commonly associated with treated municipal waste water released from WWTWs (Goel, 2009). WWTW effluent is a source of phosphorus and nitrogen, where the concentration of the nutrients is dependent on the level of sewage treatment. It has been suggested that the temporal variability of WWTW effluent flow rate and nutrient concentration is typically highly variable in South Africa (Slaughter and Hughes, 2013), which may perhaps be due to inconsistent management or overloading of WWTW capacity. This means that the effect of WWTWs on instream nutrient concentrations becomes difficult to model, and WWTWs begin to show characteristics of diffuse rather than point sources (Bowes *et al.*, 2005).

2.2.3 Eutrophication and instream processes

Water quality in rivers is affected by chemical, biological, physical and hydrological processes. The processes occur simultaneously and determine the fate and transport of the nutrients that enter the water system. Figure 2.3 provides an illustration of some of the processes affecting nutrients in water bodies as well as the interconnectivity of the processes. Eutrophication is the response to excess nutrients in the water body, which results in a rapid growth of plants. The decaying of plants results in anoxic conditions as oxygen is used up in the breakdown of organic matter. The resulting anaerobic conditions kills aquatic animals.

2.2.4 Hydraulic instream processes

The main hydraulic process affecting nutrients in a stream is longitudinal dispersion, otherwise known as downstream transport. During modelling of small streams, lateral dispersion of nutrients is usually ignored, and complete mixing is assumed (Chapra, 1997). The rate of downstream transport is dependent on the velocity of flow as well as the slope and roughness of the channel (Cole and Wells, 2008). Hydraulics control the suspension and settling of particles, affecting deposition and transport (Chung *et al.*, 2008). The roughness of the river has an effect on the physical processes occurring (see next section), for example, rivers containing rapids and waterfalls will have a greater ability to replenish dissolved oxygen than a slower moving river (Chapra, 1997). The greater the stream velocity the shorter the residence time of nutrients and the less chance there is for assimilation of nutrients by primary consumers (Dallas and Day, 2004). Hydraulic characteristics influence the transport and deposition of nutrients, this is highlighted by phosphorus, which is stored in sediment during low flow periods and is realesed into the system in high flow periods through sorption/desorption and precipitation/dissolution (Withers and Jarvie, 2008).

2.2.5 Physical instream processes

Physical processes control the gas exchange over the water-atmosphere interface (see Figure 2.4). Oxygen enters the water through this interface, with the process rate being enhanced by breakages of the surface of the water as occurs in rapids and waterfalls (Chapra, 1997; Chung *et al.*, 2008). Nitrate and nitrite volatilise to become nitrogen gas which is released from the water into the atmosphere across the water-atmosphere interface. Adsorption is the process by which gas or liquid molecules attach themselves to solid particles (Dallas and Day, 2004). The reverse of this process is known as desorption and both influence concentrations of phosphate in water. During periods of high phosphate concentrations, sediments act as sinks for phosphate, whereas the reverse occurs during periods of low phosphate concentration (Dallas and Day, 2004).

2.2.6 Chemical instream processes

Chemical processes affecting water quality include photodegradation, acid-base reactions, redox reactions, dissolution and precipitation (Dallas and Day, 2004). Photodegradation is the breakdown of material due to solar radiation and is involved in the oxidation of organic materials such as organic nitrogen and organic phosphate (Hu and Li, 2009). Acid-base reactions are defined as the protonation of bases as a result of deprotonation of acids. The acid donates a proton such as hydrogen to the base. Redox reactions are defined as the transfer of electrons which alter the oxidation state of the atom. The redox potential of water changes within the strata of a water body; the upper water layer is aerobic, whereas bottom sediments are anaerobic (Hu and Li, 2009). Dissolution refers to the chemical process where a liquid, solid or gas forms a solution. Precipitation is the opposite of dissolution, whereby a solid precipitates from a solution (Dallas and day, 2004).

Nutrients in surface waters are assimilated by primary producers during photosynthesis (Chapra, 1997). Photosynthesis is a complex process using the energy of the sun to convert nutrients into organic molecules (Chapra, 1997; Tao *et al.*, 2009) and is dependent on light, temperature and availability of nutrients (Chapra, 1997). In South Africa, problematic algal fauna include *Mycrocystis* (Robarts and Zohary, 1978) and a problematic invasive macrophyte is hyacinth (*Eichhornia crassipes*) (Deksissa *et al.*, 2004).

Another common biological process occurring within aquatic habitats is that of decomposition (Hu and Li, 2009). Organic matter found in surface waters originates from external sources such as point or diffuse sources, or from instream sources such as death of aquatic fauna and flora. Decomposition releases nutrients back into the water column, and the rate of decomposition is controlled by water temperature (Chapra, 1997; Hilton *et al.*, 2006).

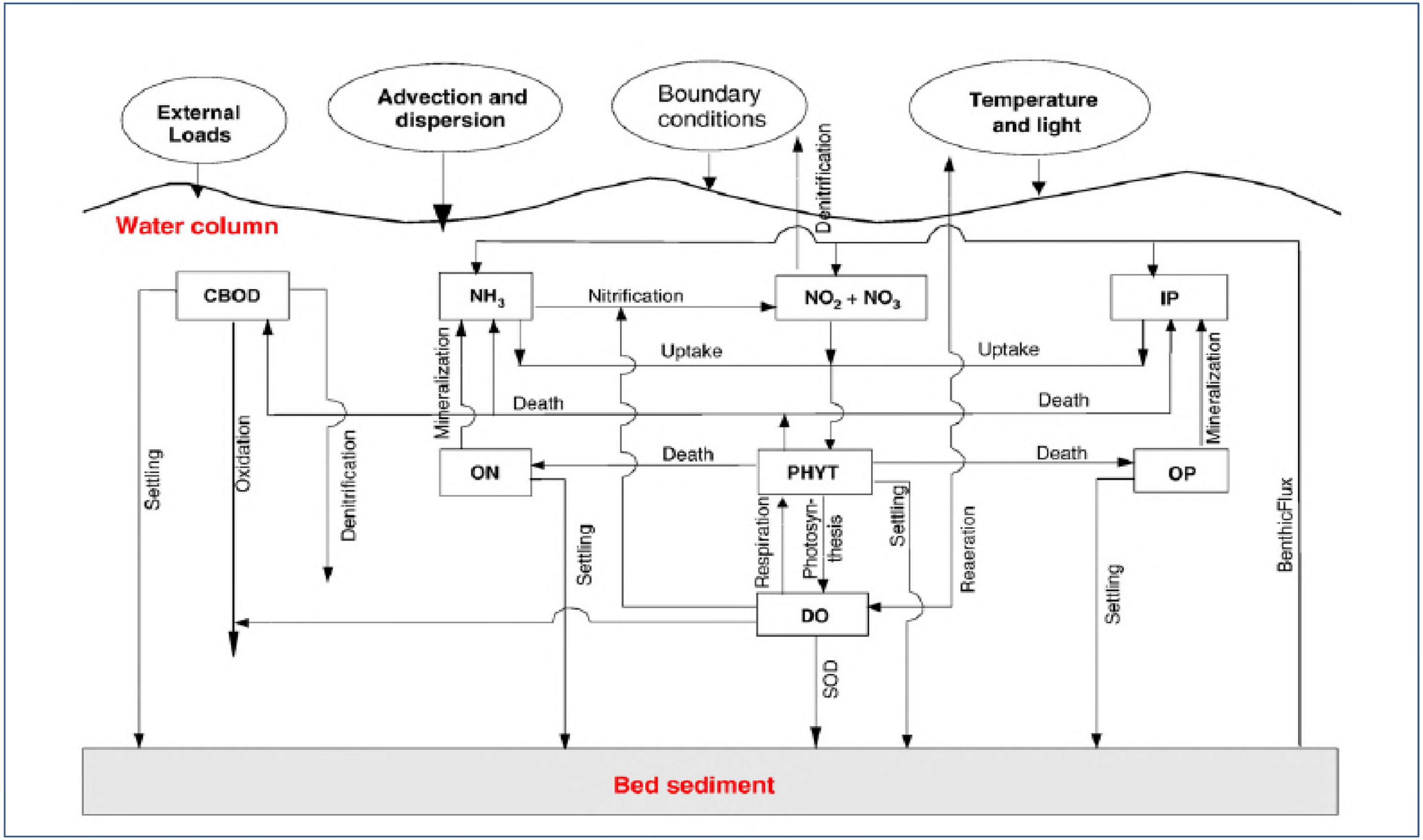

Figure 2.3: The processes occurring in a water body that affect nutrients (Hu and Li, 2009).

2.2.7 Eutrophication

Art (1993) describes eutrophication as:

'*The process by which a body of water acquires a high concentration of nutrients, especially nitrates and phosphates. High nutrient concentrations promote high growth rate in algae, resulting in algal blooms. As the algae die and decompose, high levels of organic matter and decomposing organisms deplete the water of available oxygen, causing death of other organisms, such as fish.*'

Phosphorus has been identified as the limiting nutrient to plant growth in most freshwater systems, and therefore, the main cause of high eutrophication levels (Heisler *et al.*, 2008; Wang and Wang, 2009); therefore, eutrophication can be mitigated by reducing phosphorus. Additionally, hydraulic flushing and streamflow regulation can be used to control eutrophication (Hilton *et al.*, 2006). Pollutants within rivers with high stream flow velocities have a short retention time as compared to rivers of lower velocity. In a fast flowing river where nutrients have a short retention time, benthic and filamentous algal species will dominate (Hilton *et al.*, 2006). In a river with more sluggish flow, suspended phytoplankton and macrophytes will dominate (Hilton *et al.*, 2006). For example, water hyacinth (*Eichhornia crassipes*) have been found to proliferate in the slower moving reaches of the Crocodile River in Mpumalanga (Deksissa *et al.*, 2004). Residence time affects the growth of algae, the longer the residence time the greater the assimilation of nutrients will be.

Eutrophication is controlled not only by availability of nutrients, but additionally by other factors such as the availability of light and the stream velocity in rivers (Hilton *et al.*, 2006). Macrophytes as well as benthic, epilithic, planktonic and epiphytic algae access nutrients from different sources. Macrophytes and benthic algae can access nutrients from sediments and the water column, except for hyacinth which are mostly free floating and obtain nutrients solely from the water column. Epilithic (attached) and epiphytic (found growing on other aquatic plants) algae and planktonic algae can only access nutrients directly from the water column. Figure 2.4 conceptually illustrates the controlling factors of epiphyton (algal) growth.

A relationship between eutrophication and harmful algal blooms has been identified (Heisler *et al.*, 2008). Harmful algal blooms are defined as algal blooms consisting of toxic algal species as well as high biomass producers that cause anoxic and hypoxic conditions, thereby resulting in damage to aquatic life (Heisler *et al.*, 2008). For example, the toxic blue-green algae

Microcystis has been found in various dams within South Africa, including Bridle Drift Dam (Walmsley and Butty, 1980) and the Hartebeespoort Dam (Robarts and Zohary 2010; van der Westhuizen and Eloff, 1985).

2.3 Water quality modelling

2.3.1 Modelling introduction

Rouch *et al.* (1998) defines a water quality model as a tool to estimate how water quality constituents of interest will change over temporal and spatial scales in the absence of observed data. Water quality modelling finds practical use in water resource management under Integrated Water Resource Management (IWRM), as it allows the links between water quality and water quantity to be considered under different management scenarios. Water quality models can therefore assist the process of making management decisions to avoid detrimental water quality conditions. Other applications of water quality modelling include hypothesis testing, extension of existing data as well as calculation of Total Maximum Daily Loads (TMDLs) and water quality trading programmes (Greenlagh and Sauer, 2002). All models are a simplification of reality, and even the most complex models do not come close to the complexity of the natural environment (Oreskes *et al.*, 1994). As such, anyone using the results from a model must do so with the knowledge of the limitations of the specific model, and the assumptions and limitations of the model must be made transparent (Refsgaard *et al.*, 2007).

There are a range of water quality models available, each associated with strengths and weaknesses. The selection of a model is dependent on a number of criteria. These include, but are not limited to the expertise of the modeller, output requirements of the simulation, the data available, and the temporal and spatial resolution of the model.

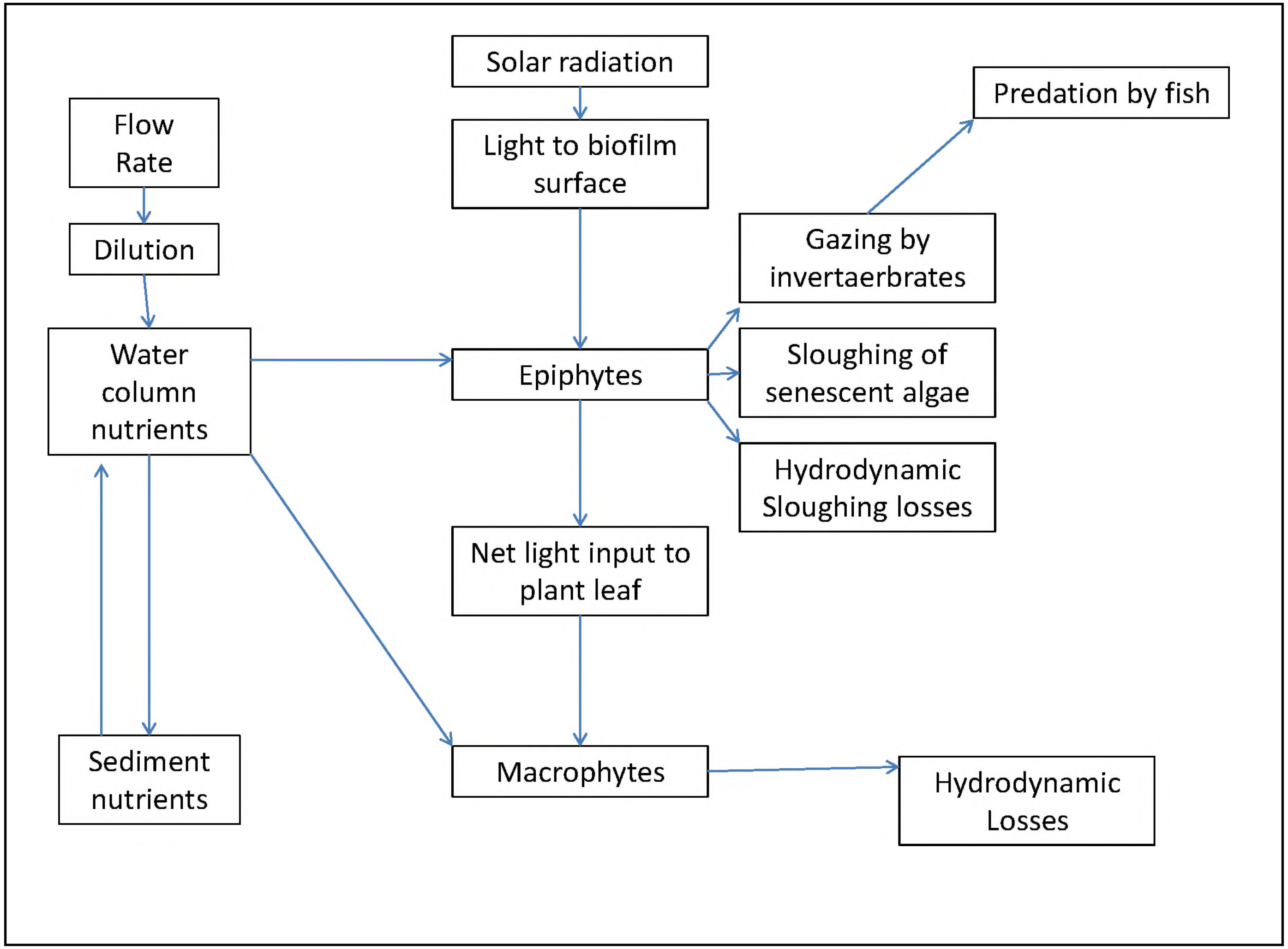

Figure 2.4*:* A conceptual representation of the eutrophication cycle (Hilton *et al*., 2006).

2.3.2 Simple models versus complex models

Model complexity plays an important role in the selection of a model. The complexity of a model takes six factors into account (Evans *et al.*, 2013), namely:

1. The level of process representation.
2. The type of water body modelled.
3. The level of spatial detail.
4. The level of temporal detail.
5. The water quality variables the model simulates.
6. The way processes are represented mathematically.

The level or degree of process representation refers to the detail in which each process is simulated. The type of water body typically simulated ranges from lakes to streams to estuaries. Each type of water body has different physical characteristics that require different modelling approaches, with lakes and reservoirs being more complex to model. A number of different approaches are available to model each type of water body. Rivers can be modelled considering one dimension of transport, assuming lateral dispersion to be negligible. This assumption is generally valid for small, low order streams (Chapra, 1997) where mixing is complete. Water quality models that only consider the longitudinal dimension assume that variations in water quality occur in the direction of transport (Bowie *et al.*, 1985), where streamflow is assumed to be the major transport mechanism. This is a simple way of modelling rivers; more complex methods may take lateral dispersion and mixing into account, which may be necessary to accurately model large, slow moving rivers. For water quality modelling of lakes and estuaries, a multi-dimensional model is necessary to take circulatory patterns, stratification and mixing into account (Bowie *et al.*, 1985).

The most conceptually complex model possible would include all processes in a natural system, at a minute spatial and temporal scale, taking all heterogeneity in account (Evans *et al.*, 2013). Arguably, it might be assumed that the more complex the model, the more accurate the model will be. It is argued by Lidenshmidt (2006) that more complex models are characterised by less structural uncertainty as compared to simpler models, as biological, chemical and physical processes are better represented. Lindenschmidt (2006) conceptualised the effects of complexity on error sensitivity and utility of the model as seen in Figure 2.5. Although simulating more processes does decrease the potential for errors in results, the assumption of increasing model accuracy with increasing model complexity is not necessarily true (Bergstrom, 1991; Lindenschmidt *et al.*, 2007).

Complex models are usually characterised by a large number of model parameters which control the rate of processes represented by the model. These kinds of models typically suffer from equifinality.

Complex models typically require a large amount of data for calibration as well as time and expertise to set up, which come at a large financial burden, and are thus impractical for use within most water management institutions (Andersson *et al.*, 2005). Very often, default values are assigned to the many parameters within a complex model, because of the unavailability of observed data and the difficulty of measuring some of the process rates represented by the parameters (Andersson *et al.*, 2005). The assignment of default parameter values within a complex model negates the model's overall utility and accuracy (Hughes, *pers. Comm.* 2013).

Bergstrom (1991) found that a point of diminishing returns is reached with increasing model complexity. This principle is demonstrated by a study by Lindenschmidt (2006) which looked into water quality modelling and started off with a simple model and continually added more complexity into the model. Lindenschmidt (2006) showed that the most accurate results were obtained when the model was at its most complex state. However, the accuracy of the model was not affected greatly by the removal of some minor processes. A cost-effective strategy for choosing the most suitable model is to choose the simplest model that will still provide 'accurate/acceptable' answers. What is an acceptable output from a model is context dependent. While a scientific study of a river may require high temporal or spatial resolution time series simulations of water quality, under most circumstances, water resource managers are more interested in the water quality risk associated with management decisions (Evans *et al.*, 2013). An estimation of risk could be more easily and clearly provided by water quality frequency distribution curves rather than complete and accurate time series (Hughes, *pers. Comm.* 2013).

Simpler models are characterised by relatively abbreviated mathematical equations with relatively fewer processes and fewer variables represented (Evans *et al.*, 2013). Typically, simpler models will focus on a few water quality variables that are of relevance to management. Simpler models also aim to identify the most important processes affecting the identified variables, and these processes are mechanistically or statistically represented within the model. Simple models should also aim to use the available historical monitoring data.

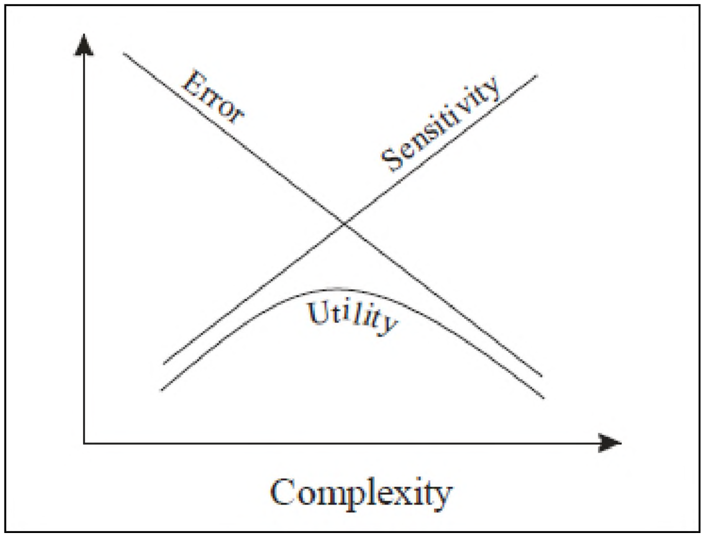

Figure 2.5: A visualisation of the effect complexity has on sensitivity and error of a model (Lindenschmidt, 2006).

2.3.3. The modelling process

The modelling process is conceptually represented in Figure 2.6 (Chapra, 2003), and begins with the selection of an appropriate model. The nature of the problem will determine the main criteria for selection of a model. The availability of resources will influence the complexity and usability of the model selection (Chapra, 2003). Data availability limits the models that can be used. Projects lacking data will require greater funds to allow collection of data, which is typically time consuming and costly. There are many water quality models available, however, if none of the available models satisfy the demands of the problem, the modeller may decide to create a new model. New models can be created using techniques and algorithms already being used in other models, or existing models may simply be combined to satisfy the demands at hand. 'Off-the-shelf' models are normally less flexible than tailored models (Fawthrop, 1994). Model selection can be influenced by personal choice, with the modeller using a model they are familiar with, or that is accepted within the local community or requested by the end-user of the model results (i.e. the client). The information requirements of the client will influence the selection of the model.

Water resource managers may be more interested in an estimation of risk associated with management decisions, which can be provided by a simpler model than for example a model that provides detailed time series simulations of water quality that may be more suitable for the purposes of a scientific study (Evans *et al.*, 2013).

The next step in modelling is data capture. This can either be conducted through field sampling and laboratory work or through the collection of existing historical monitoring data. Usually, gaps in the existing data are identified before a sampling regime is decided. Existing historical monitoring data collected by governmental departments in developing countries tend to be sparse at both temporal and spatial scales, or even non-existent in many countries. An example is that of existing data collected by the South African Department of Water and Sanitation (DWS), which tends to have poor spatial and temporal resolution (Slaughter, 2011), but are abundant compared to those available in most other African counties. Geographical data are additionally required to segment stream lengths for modelling purposes and to delineate sub-catchment areas. These are easily obtained using Geographical Information Systems (GIS) software and digital orthographic photographs. Streamflow data are generally available for many of the larger rivers in South Africa. However, there are many rivers for which there are no observed flow data; therefore, simulations of streamflow to force a water quality model will additionally be required. Data sampling requires planning to benefit the project. Data are highly beneficial to the end result of the project; however, the financial and temporal burdens of field sampling and laboratory analyses limit the amount of sampling that can be achieved. Where only limited sampling is possible, field collection should be performed over periods that represent as many different seasonal or hydrological conditions within the catchment as possible (Bowes *et al.*, 2008). The spatial resolution adopted is required to be sufficiently fine to represent spatial variations of the water quality as well as to distinguish between major point and diffuse sources (Bowes *et al.*, 2008). Ideally, the spatial scale chosen should be as fine as possible considering financial and logistical constraints (Dekissa *et al.*, 2004).

Model setup is then attempted, with calibration data entered into the model and simulations performed. During this step, the ranges of values for parameters controlling model processes can be obtained from the literature, and Shanahan *et al.* (1998) has compiled a review of parameter values used in previous studies. These parameter values serve as a guideline for the range of possible realistic values for various parameters. Previous studies have been predominantly performed in Europe and the United States of America, and considerable differences may be expected for some parameter values applied to models in South Africa or other countries where conditions differ from those countries with a long history of water quality modelling. Once the model is set up, it should then be calibrated against any historical observed data that exists. Calibration is defined as fitting a simulated dataset to an observed dataset, and is achieved by adjusting parameters to achieve an acceptable representation of observed data with the simulated results (Chapra, 2003). Acceptability is determined using a visual fit, or preferably, an appropriate statistical test such as a 'goodness of fit' statistic (Chapra, 2003).

Once calibration is adequately achieved, the generally accepted approach is to validate the model. During validation, the model setup with calibrated parameters is used to simulate historical conditions that are compared to an observed dataset that is independent of the dataset used during calibration. Ideally, validation should be against multiple independent observed historical datasets, collected under varying hydrological and seasonal conditions (Chapra, 2003; Shanahan *et al.*, 1998). While this is the standard approach, it has received some criticism. Thomann (1998) and Oreskes *et al.* (1994) question the logic of dividing data into 'calibration' and 'validation' sets, as more information is uncovered with increasing observed data, and a model is never completely validated. Slaughter (2011) found that when using QUAL2K applied to a low order stream, multiple datasets had to be used together to achieve calibration, as each dataset provided new information. For example, sources of diffuse nutrients became apparent within the dataset collected during a rainy period that were not apparent during a dataset collected during a low flow period.

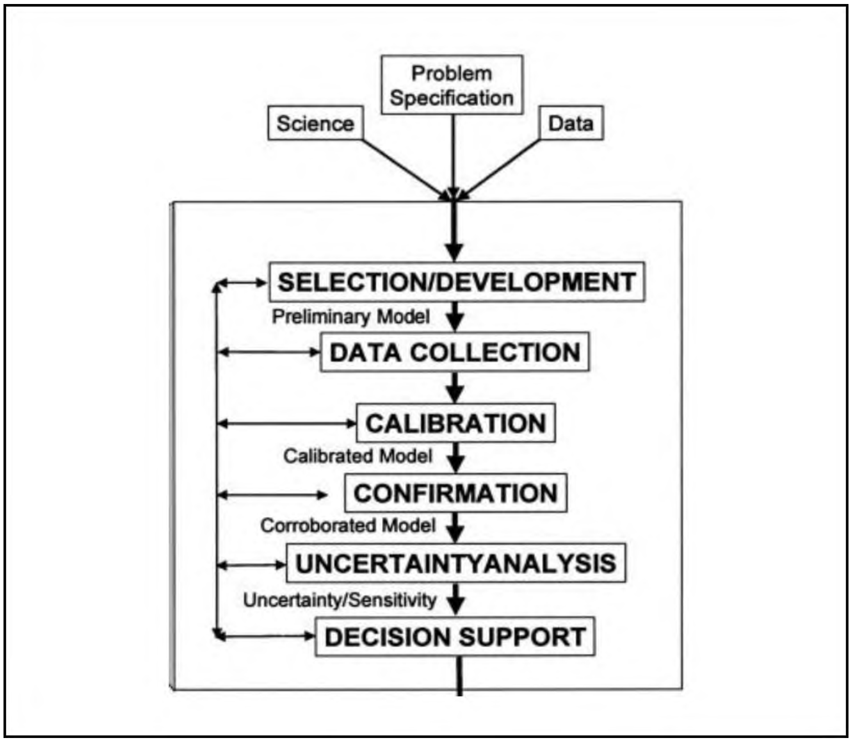

Figure 2.6: A conceptualisation of the modelling procedure (Chapra, 2003).

2.4 Different Approaches to Water Quality Modelling

2.4.1 Temporal Scale

Water quality variables show considerable variations within short time increments. Some water quality models such as QUAL2K (Pelletier *et al.*, 2006) operate over time steps of less than a day and take diurnal variations into account. These models ideally require data showing sub-daily water quality variations which greatly increases data demands and model complexity. Temporal averaging occurs within models operating over coarser time steps, which decreases data demands and model complexity. These models are especially applicable for larger catchments. Generally, models that operate at time scales coarser than daily are not appropriate for water quality modelling, as transient events, such as rainfall-runoff events, can have dramatic short-term effects on water quality (Dekissa *et al.*, 2004).

2.4.2 Steady state models versus dynamic models

Steady state models, such as QUAL2K (Pelletier *et al.*, 2006) or any other model where flow velocity is estimated using the Manning equation (Chapra, 1997), are designed to simulate water quality assuming a gradually variable representation of flow (Rouch *et al.*, 1998). Very few models have attempted to model variable flow because of the difficulty in modelling flow dynamics. Gorgens and de Clercq (2006) and Chung *et al.* (2008) are two examples from the literature where a dynamic model was applied.

2.4.3 Spatial scale

Spatial scale in water quality modelling ranges from the watershed scale, requiring the simulation of the entire catchment, to the local scale, where a small reach of river is modelled. Watershed models generally use land use and water use to simulate diffuse and point source inputs, whereas local scale models require point and diffuse inputs to be quantified externally and directly inputted. QUAL2K (Pelletier *et al.*, 2006) is an example of a local scale model which has found use in the simulation of Total Maximum Daily Loads (TMDLs) (Salvai and Bezdan, 2008). The TMDL approach is aimed at regulating point sources released by industries, and is an approach that has been adopted by the United States Environmental Protection Agency (USEPA) for many years. The Better Assessment Science Integrating Point and Non-point Sources (BASINS) model operates on a larger spatial scale and is used to manage watersheds (Wimberley and Coleman, 2005).

2.4.4 Empirical versus mechanistic models

Environmental modelling is referred to as empirical modelling when the mathematical equations used are based on statistical relationships determined from observed data, or when equations are constructed based on knowledge built from observing patterns within observed data (Reckhow and Chapra, 1999). Mechanistic models utilise equations that are based on scientific theory and understanding (Reckhow and Chapra, 1999) and aim to mathematically represent processes that affect water quality. Most models cannot be defined as either strictly empirical or mechanistic as they generally contain both mechanistic and empirical components within them. However, they are classified according to which approach is more dominant within the model structure. Empirical models tend to be site specific due to their reliance on local data. Mechanistic models are more robust in the field of application, but still have limitations. A general characteristic of empirical/statistical models is that they are appropriate for interpolation, but not for extrapolation, as statistical models do not explain how relationships work (Beck, 1987), and the rates driving processes represented within the observed data may change.

2.4.5 The principle of mass-balance

Mass-balance is used in modelling based on the principle of the conservation of mass. Mass cannot be created or lost, but can change form. So within all models, all input, transport, conversion of compounds and losses from the system are accounted for by balancing the mass of each variable modelled. Occasionally, removal of a load of a particular variable from the modelled system can be justified. Transfer of water from one catchment to another may mean that within a modelled catchment, a system loss or addition occurs that was not part of the original mass-balance. Natural sinks can additionally occur within aquatic environments. The most important natural sinks are riparian zones and wetlands which act as a sink for nutrients (Ranalli and Macalady, 2010) and lakes and reservoirs which act as sinks for various water quality variables including TDS (Dabrowski and de Klerk, 2013), toxic metals (Dabrowski and de Klerk, 2013), nutrients (Withers and Jarvie, 2008) and sediment (Gill, 1979).

2.4.6 Parameter calibration models

Mechanistic water quality models are based on a scientific understanding of the processes affecting water quality (Reckhow and Chapra, 1999). These models are usually characterised by the use of parameters that require calibration. These parameters typically control the rate of processes affecting water quality such as algal growth, decomposition, nitrification and oxygenation (Chapra, 1997). A good example of this type of model is QUAL2K (Pelletier *et al.*, 2006). These kinds of models require the modeller to have a basic understanding of the processes to be calibrated and how the parameters relate to the processes represented within the model, so that realistic values for parameters can be set. Realistic ranges of values for parameters can be guided by parameter values used in past studies, such as found in the review written by Shanahan *et al.* (1998). Complex models are typically characterised by many parameters, and it is often difficult to assign realistic values to parameters, as data to guide the process is usually lacking. Parameter models are additionally affected by equifinality (Bevan, 2006). A sensitivity analysis of a parameter calibration model is useful to determine which parameters are the most influential on model outcomes, and these parameters can be given the majority of attention in terms of assigning realistic values. Parameter values can also be regionalised (Chapra, 1997), i.e., relationships can be determined between parameter values and catchment characteristics. In this way, models for ungauged catchments can be assigned appropriate parameter values according to catchment characteristics.

2.5 Water quality models available

Water quality models are intended for use in environmental impact assessments and scientific research. Wang *et al.* (2013) suggests that there should be a standardised list of water quality models used for high importance reports to maintain a standard in the quality of the results. The Water Quality and Analysis Simulation Program (WASP) model (Ambrose *et al.*, 1993) was developed to simulate water quality for lakes, rivers, wetlands and estuaries (Wang *et al.*, 2013). WASP can be used to simulate one, two and three dimensions, and is used to assess the fate and transport of toxic and conventional pollutants (Hydrosphere, 2005). The Soil and Water Assessment Tool (SWAT) model (Arnold *et al.*, 1998) was developed by the United States Department of Agriculture and is a basin scale water quality and hydrological model (Arnold *et al.*, 1998). SWAT utilises input files from GIS coverage. QUAL2E (Brown and Barnwell, 1987) and QUAL2K, the updated version of QUAL2E, are complex models which simulate diel variation and water quality kinetics for one dimensional systems (Pelletier *et al.*, 2006). The QUAL models are most suited to point sources (Wang *et al.*, 2013). CE-QUAL-W2 (Cole and Buchak, 1995), the Branched Langrarian Transport Model (BLTM) (Jobson, 2001) and MikeII (DHI, 1992) are suitable for modelling water quality in rivers, wetlands and estuaries.

Some of the watershed scale water quality models that do not simulate point sources are described below. The Agricultural Non-Point Source pollution model (Young *et al.*, 1987) is a hydrological event model that simulates the transport of nitrogen, phosphorus, sediment and chemical oxygen demand for a single event. The Areal Nonpoint Source Watershed Environment Response Simulation (ANSWERS) model (Beasley *et al.*, 1980) uses the concept of distributed parameters to model runoff, infiltration and erosion of single events. The Dynamic Watershed Simulation Model (DWSM) (Borah *et al.*, 2002b) simulates runoff, riverbed erosion, sediment transport and nutrient transport for rural watersheds for a single events. The Hydrological Simulation Programs-Fortran (HSPF) model (Donigian, *et al.*, 1995) creates a historical time series for any point in a watershed for water quantity and quality. The HSPF model is incorporated into the Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) model which, is used to develop total maximum daily loads (TMDLs) (Borah and Bera, 2003). TOPCAT-NP, a version of

TOPMODEL (Quinn *et al.*,2007), can simulate nitrogen and phosphorus transport at both research and catchment management purposes using minimum input requirements.

2.6 Uncertainty

Uncertainty is an important part of modelling, taking into account the uncertainty due to the data collected and the equations and parameters of the model. The sources of uncertainty are conceptually represented in Figure 2.7. Uncertainty occurs due to errors in simulation that can be derived from: 1) input data used for running the model; 2) data used for validation of the model; 3) the model structure, where inaccuracies in the algorithms representing processes lead to errors and; 4) inaccuracies in the parameter values assigned to the model, that can be due to inaccurate calibration or equifinality (Lindenshmidt and Feishbein, 2008). Scarcity of data used for inputs to models on both spatial and temporal scales introduces interpolation uncertainty, as missing data are often filled in or 'patched' using interpolation techniques (Kennedy and O`Hagan, 2001). Errors in input data are also often due to sampling errors or errors in laboratory analysis. Structural uncertainty is due to imperfect process representation by algorithms and equations which make up the model. Uncertainty derived from parameter values used in the model is due to the use of parameters for which there are no observed data or are impossible to measure, and therefore, default or estimated values are used, or values used in previous studies are adopted (Kennedy and O`Hagan, 2001). Equifinality (Bevan, 2006) is an additional source of uncertainty in regards to values assigned to model parameters. Another form of uncertainty in modelling is termed epistemic uncertainty, which is due to the lack of understanding of science or ignorance of processes or catchment by the modeller. Epistemic uncertainty can be avoided or minimised by research of the modelled system, data collection and analysis of data (Refsgaard *et al.*, 2007).

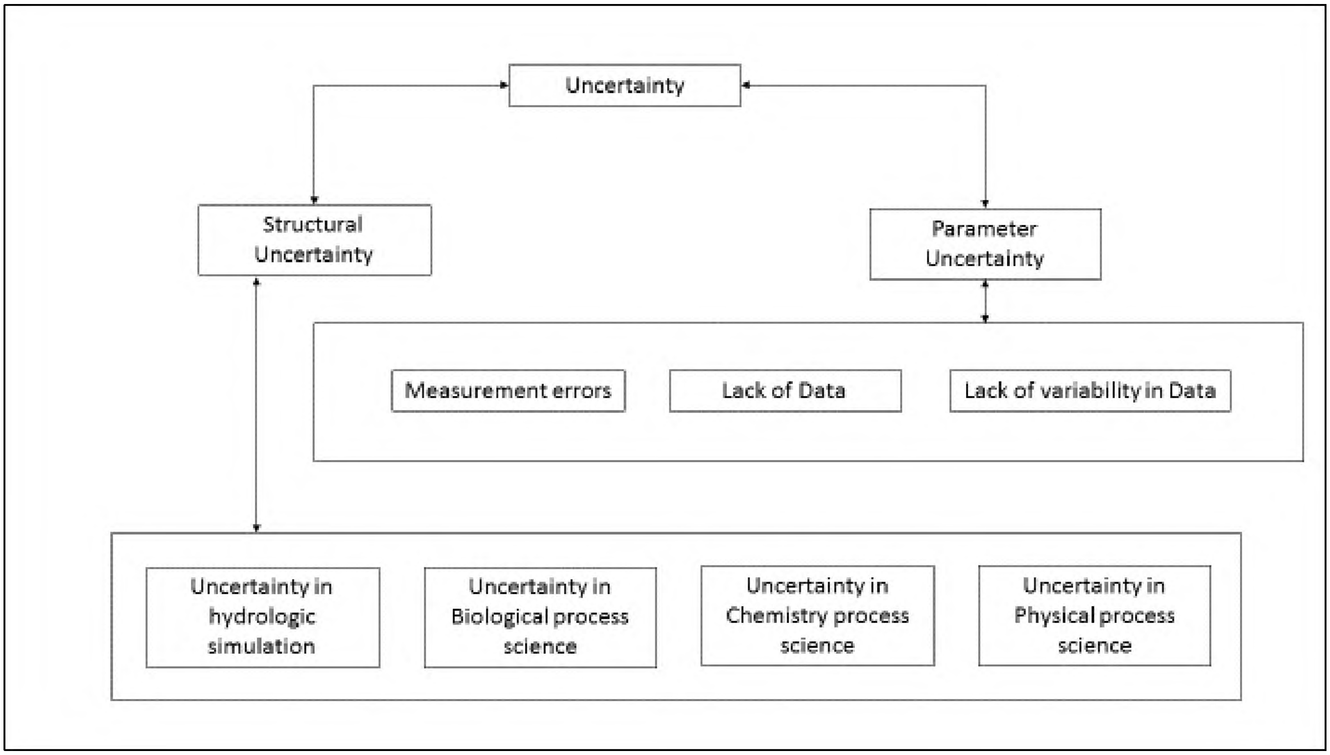

Figure 2.7: The conceptualisation of uncertainty in mathematical modelling.

3. STUDY AREA

The study was conducted on the Bloukrans River, a tributary of the Kowie River in the Eastern Cape Province of South Africa. The headwater tributaries of the Bloukrans River originate within the vicinity of the town of Grahamstown; therefore, the uppermost catchment is dominated by urban land use. The lower catchment has some agriculture (Dairy farms and cash-crops) but is mainly natural vegetation (valley thicket as classed by Acock`s vegetationFigure 3.2). The region receives year-round rainfall as it falls between the winter rainfall areas to the west and the summer rainfall areas to the east. Rainfall is dominated by thunderstorms during the summer months characterised by short-duration high-intensity events, whereas frontal rainfall dominates during the winter months, characterised by long-duration, low-intensity events. The annual evaporation is substantially higher than rainfall within the region, with an annual rainfall range of 600 mm–800 mm and annual potential evaporation range of 1 600 mm–1 800 mm. Although the western parts of Grahamstown are supplied by the reservoirs to the west, water supply to the central and eastern parts of Grahamstown is derived from a transfer scheme which transfers water from the Orange River via the Fish River. This means that more water is available for human use within Grahamstown than would be available using only local water resources and infrastructure; consequently, the effluent released from the Belmont Valley WWTW during low flows accounts for the majority of the total flow in the Bloukrans River. The release of a steady stream of effluent to the Bloukrans River has also modified the flow regime of the river from historically ephemeral to currently perennial flow.

Grahamstown is a relatively small city, but falls within the Makana local municipal area with a population estimated around 80 000 (Statistics South Africa, 2011), which ranks Makana 143 out of a total of 234 local municipalities in South Africa in terms of population size. There is very little industry within the watershed, and land use is predominantly residential. Some parts of the residential area are comprised of government subsidised housing and informal townships, both generalised as low-income areas. According to Statistics South Africa, although the majority of the population in Makana has access to flush toilets (74.5%), a small proportion of the population use pit latrines (16.1%), and a very small fraction of the population still utilises the ‘bucket system’ (3.6%). Pit latrines are deep holes dug into the earth and used until full. These pit latrines are then covered over with earth and a new pit is dug elsewhere. The ‘bucket system’ referred to earlier is the use of buckets for latrines. Waste buckets should be collected by the municipality and the waste treated at one of the treatment plants; however, this service is not always provided timeously, and residents are sometimes forced to discard the waste onto open land. Informal settlements are generally characterised by large areas of exposed soil which is highly compacted and contribute to a high percentage of runoff from these areas, comparable to runoff from tar or cement surfaces.

The Bloukrans River receives treated and sometimes untreated waste water from the Belmont Valley WWTW. According to Statistics South Africa, the proportion of the population in Makana with access to flush toilets has increased from 33.6% in 2001 to 71.9% in 2011. In addition, over the last decade, some major infrastructure projects have occurred within Grahamstown, such as the building of new residences at Rhodes University, and the development of several new flat complexes in the town. However, much of the wastewater infrastructure in Grahamstown has not been upgraded within the democratic era, and is in dire need of maintenance. The situation is complicated further by a lack of funding and technical expertise within the Makana Municipality. Consequently, Grahamstown sewerage infrastructure is often compromised, resulting in untreated wastewater being released from broken pipes and transported in surface runoff, ultimately ending up in the Bloukrans River.

Figure 3.1 shows a map of the sites investigated on the Bloukrans River within this study, whereas Table 3.1 provides further description of the sites. The water quality of the river at Site-1 is influenced by municipal runoff from Grahamstown, which includes leaking sewerage pipes, storm water drains and surface runoff, and carries nutrients from lawns, roads and construction sites to the Bloukrans River. Grahamstown has many sewerage and potable water leaks. The water from these leaks flow into tributaries of the Bloukrans River, directly influencing flows and water quality. Site-2 represents the Belmont Valley WWTW final effluent outlet. Samples from Site-2 were taken before the effluent reaches the Bloukrans River; therefore, these samples provide a direct measure of the final effluent quality from the treatment works. Sites-3–Site-5 (refer to Figure 3.1) are all situated within the Belmont Valley, where the water quality in the Bloukrans is affected by the surrounding agriculture. A dairy farm is situated between Site-3 and Site-4 which contributes nutrients through the runoff of animal waste from the milking parlour and surrounding area where animals are concentrated and there is a build-up of faecal matter. Runoff from this area reaches the Bloukrans River downstream of Site-3. A channel was observed during a recent heavy rainfall event, carrying nutrients directly from the milking parlour to the Bloukrans River, directly before Site-3. The dairy pastures between Site-3 and Site-4 are irrigated using an overhead application method, which contributes to return flow carrying some nutrients to the Bloukrans River. The remaining area in the Belmont valley is either left as natural vegetation (valley thicket) or vegetable farming under drip irrigation. As compared to other irrigation practices used in the valley, drip irrigation is a much more efficient application of irrigation water and thus, results in very little return flow and a lower impact on the quality of surface water. A large valley is situated between Site-5 and Site-6 that is within the watershed of the Bloukrans River and is partly under commercial agriculture, and elevations of certain nutrients were observed between these two sites. The elevations in nutrient concentrations were presumably due to the inputs from this agricultural area, as the rest of the land within the catchment consists of natural vegetation with very little to no human habitation in subcatchment 5 (see Figure 4.1).

Table 3-1: Bloukrans River water quality sampling sites.

Site	Description	Location
1	Outflow of Grahamstown Catchment	33°18’52.20”S 26°33’10.20”E
2	Belmont Valley WWTW effluent outlet	33°18’56.73”S 26°33’31.33”E
3	Bloukrans River Downstream of WWTW	33°19’05.01”S 26°34’06.30”E
4	Bloukrans River 6 km downstream of site 1	33°19’25.50”S 26°35’59.20”E
5	Bloukrans River 12 km downstream of site 1	33°19’40.10”S 26°38’35.00”E
6	Bloukrans River at the Bloukrans bridge, 42 km downstream of site 1	33°23’26.10”S 26°31’44.93”E

3.1 Findings from the catchment

Previous water quality data were analysed for trends within the Bloukrans River catchment. Sampling performed from 1992 to 1995 (Unpublished data, pers. comm. Prof Denis Hughes) contained some data for runoff events within the catchment. These data showed that nutrient load increased with increasing flow over an event, but concentration showed varying trends. Although these data are from the same catchment, human impacts on the catchment have changed since the data were captured. These data were used for the calibration of the hydrological equations for subcatchment 1 (see figure 4.1). However the nutrient concentrations observed during 2012 and

2013 appear to have increased as compared to the past. Flow at the gauging weir is also higher for the 2012 to 2013 time period. This could be explained by the additional flow entering the Bloukrans River from a number of leaking potable water and sewerage pipes within Grahamstown.

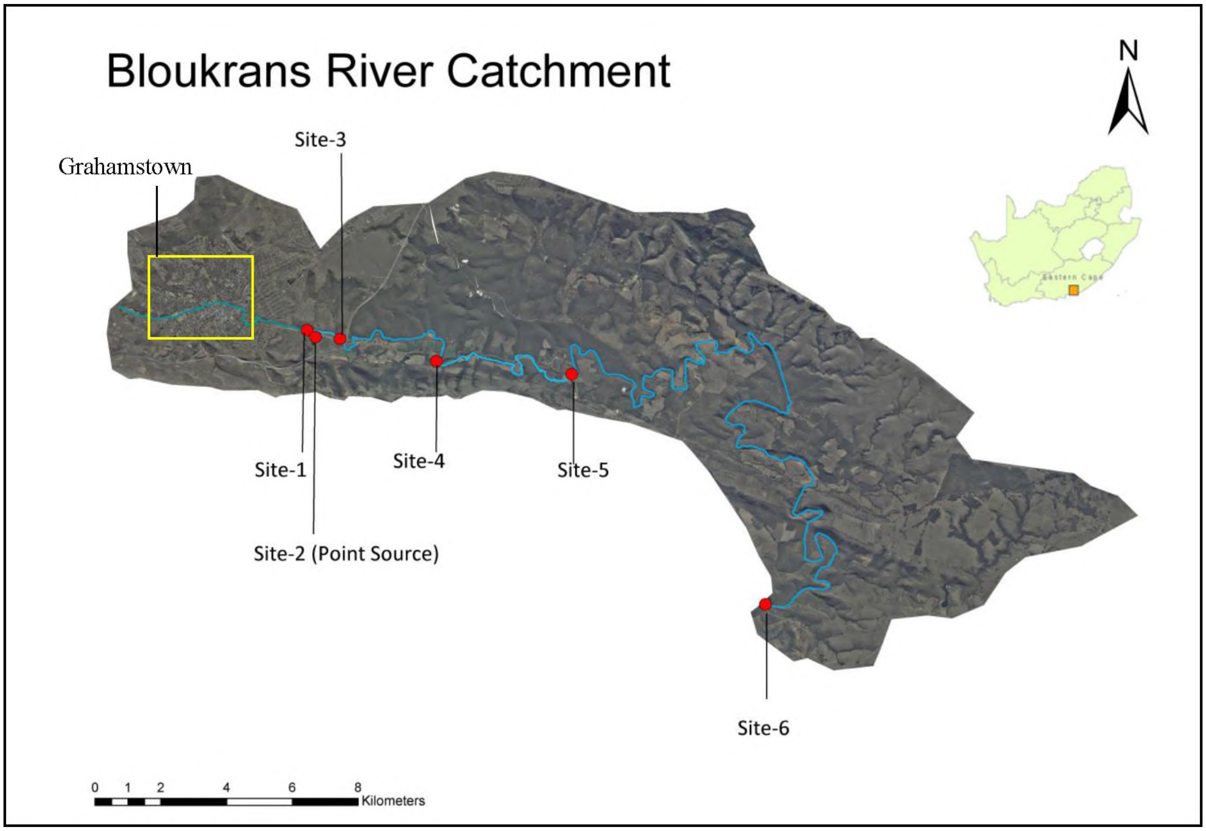

Figure 3.1: Bloukrans River and surrounding area showing sampling points.

The two graphs in Figure 3.2 show the same data; the load plot (Figure 3.2a) shows a trend of increasing load with increasing flow whereas Figure 3.2b shows a declining trend of concentration with increasing flow. This indicates that even during a rainfall-runoff event when the river is receiving diffuse sources of nutrients (Jarvie *et al*., 2005; Malan and Day, 2002), the increased water volume acts to dilute the concentration levels. However, Mcdiffett *et al.* (1989) indicated an increase of nitrogen concentration on the rising limb of an event hydrograph and dilution of nitrogen concentration later in the runoff event. The decline in concentration with increasing flow indicates a point source pattern (Bowes *et al*., 2008); however, the data are showing a pattern over a three year period which is not wholly representative of current conditions in the catchment.

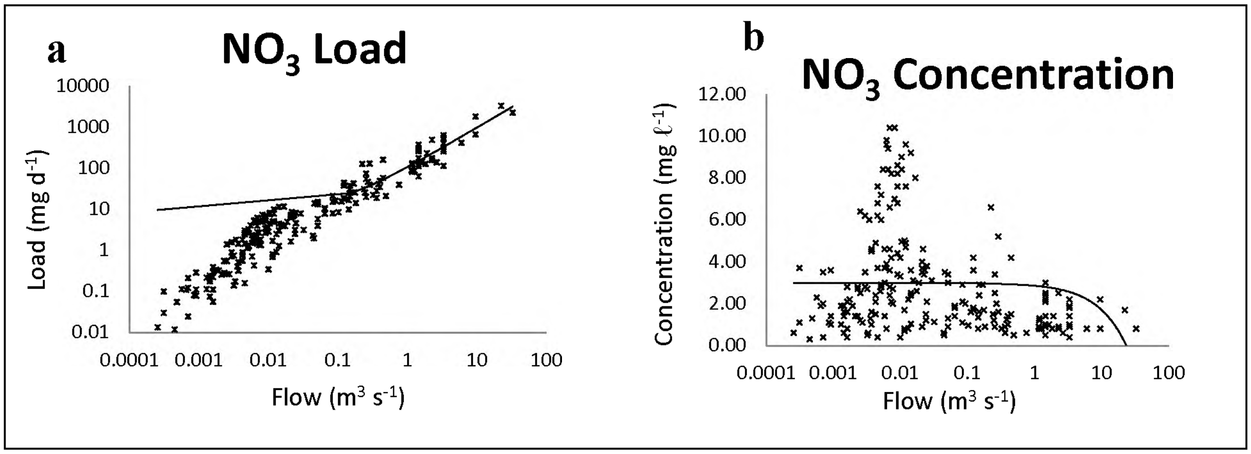

Figure 3.2: The different trends shown between nitrate load (a) (Please note log scale on y-axis) and concentration (b) within the Bloukrans River. Solid lines represent trendlines of the data. This data is representative of Site 1.

Britton *et al.* (1993) indicated a seasonal variation in the relationship between nitrate concentration and flow. The grouping of high nitrate concentrations around the 0.01m^3 s^{-1} flow may occur during the falling limb of the hydrograph, when there is still a high load of nitrates within the river but less dilution is occurring; however, it is more likely due to sewage contamination at low flows (pers. comm. Dr. Andrew Slaughter). However, 0.01m^3 s^{-1} is a low flow for the Bloukrans River. A number of the very high nitrate concentrations occur at low flows a few days after an event, and this may indicate that nitrates are not moving in a 'plug flow' as discussed by Park and Lee (1996) and are actually remaining in the system after the high flows have decreased. This assertion is supported by data collected during 2012 and 2013 where the highest nitrate concentration was measured three days after an extreme runoff event. The explanation for elevated nitrate levels after the hydrograph has reduced to low flows is difficult to determine as the source of the nitrates is difficult to identify and measure. Elevated nitrate levels could be due to nitrification of organic matter carried to the stream during runoff events. However, it is more likely that nitrate contaminated groundwater is entering the stream (Pionke *et al.*, 1999) The elevated nitrate concentrations may be due to a compromised sewerage system, affected by the rainfall event on previous days, as the current municipal infrastructure is failing, and in a constant state of leaks and blockages. However, the data shown were taken over 20 years before this study and thus, such a state of disrepair of the sewerage system may not have been prevalent. The elevated nitrate and phosphate levels shown in Figure 3.2 and 3.3, respectively, cannot be attributed to any particular hypothesis as there is little to no literature to support the theories. In regards to the 2012 event, it can be argued that the sewer network in Grahamstown was still overflowing; however, the volume of water in the catchment and river was far lower than the peak event and thus, the dilution was lower than during the peak of the event. Ignoring the cluster of high concentrations at low flows, the nitrate concentrations tend to range between 0–4 mg ℓ$^{-1}$ with no visible relationship to flow. The lack of dilution at higher flows indicates that a high load of nitrates is transported to the river during rainfall events. Variations in the nutrient concentrations at high flows can be explained by differing antecedent catchment conditions. High concentrations at high flows indicate 'first flush' events, where the catchment has been dry for a period of time, allowing nutrients to build up on the surface (Simpson and Stone, 1988). 'First flush' events are dependent on the duration and intensity of the rainfall event as well as the time available for nutrients to build up.

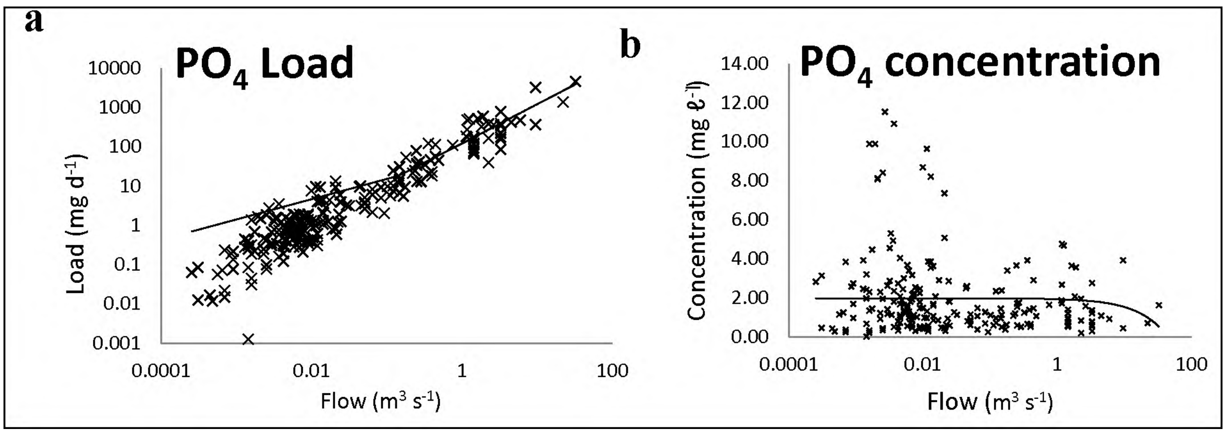

Figure 3.3: Phosphate load (a) and concentration (b) relationship to flow in sub-catchment 1. (Concentration is mg PO_4).]

Instream ortho-phosphate at Site-1 showed similar trends to nitrate (Figure 3.2) although ortho-phosphate load is lower than nitrate load. The relationship of phosphate concentration with flow shows a high degree of scatter at lower flows around 0.01 m^3 s^{-1} (see Figure 3.3b), most of the points are at relatively lower concentrations. The elevated ortho-phosphate concentrations at low flows generally occur a few days after high flows and could be explained by breakdown of organic matter that was transported into the stream during a rainfall event or as a result of compromised sewerage systems. However, there are only ten cases of phosphate concentrations above 6 mg ℓ$^{-1}$ out of the 219 ortho-phosphate samples taken, and the elevated concentrations did not occur around the same time but were spread out over the sampling period. There was no seasonality observed for both elevated ortho-phosphates and nitrates. The relationship between flow and phosphate concentrations has shown a seasonal trend (Britton *et al.*, 2003). Ortho-Phosphate concentrations, within South Africa, show a trend of increasing concentration with increasing flow; this is due to a high proportion of phosphorus binding to sediments (Jordan *et al.*, 1997; Malan and Day, 2002). Runoff from urban areas is characterised by high phosphate loads (Hughes and van Ginkel, 1994). The sampling method used measured only dissolved phosphate and not the phosphate bound to sediments. Typically only dissolved phosphorus is measured.

4. DATA FOR MODELLING

Observed data are required for modelling and are used for calibration, parameterisation and verification. The accuracy of the data used for calibration affects the accuracy of the results obtained from the model. Data availability is often limited, particularly in developing countries and in smaller catchments with few stakeholders (Masili-Libelli and Giusti, 2007).

4.1 Subcatchment delineation

The Soil Conservation Service (SCS) (Mishra and Singh, 2003) equation used in the Mass Balance Nutrient (MBN) Model requires the subcatchment area of the modelled catchment to calculate runoff. The surface area contributing to runoff to each sampling point on the Bloukrans River was calculated (Figure 4.1). First, the catchment area contributing runoff up to Site-6 was delineated on a topographical map in ArcMAP 10.1 (ESRI, Inc) using 1:50 000 river and relief coverages, so as to delineate the entire catchment area of the study. The sampling points were marked on the Bloukrans River. Working from each sampling point away from the river on each river bank, the highest points along ridges were followed until the catchment boundary was reached. These lines represent the watersheds between each subcatchment within the study area catchment. Data gathered from the exercise in ArcMAP is shown in Table 4-1.

Table 4-1: Subcatchment area and length of the river within each subcatchment

Subcatchment	Area (km^2)	River length (Km)
1	32	6.84
2	6	1.11
3	10	5.16
4	17	6.40
5	129	33.00

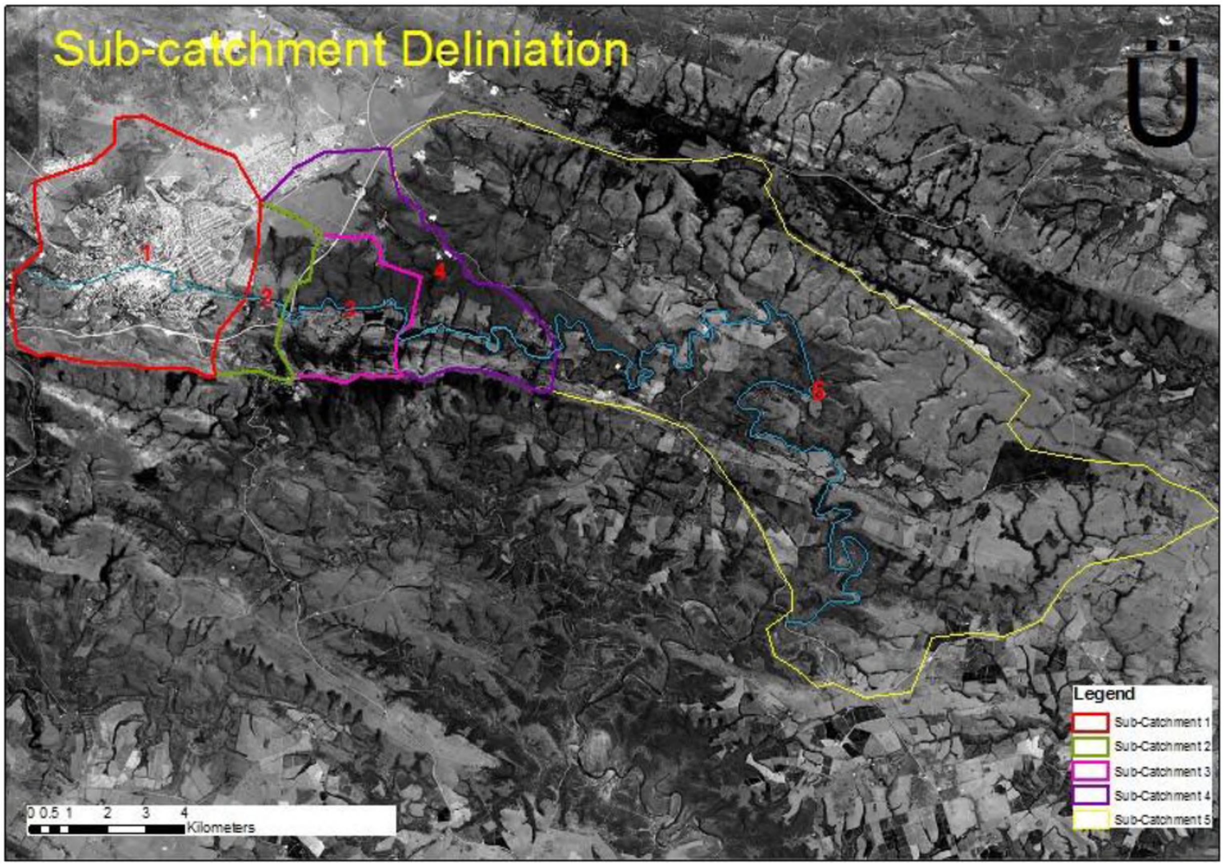

Figure 4.1: Delineation of subcatchments within the Blounkrans River catchment using topographical boundaries and sampling sites as the exit node for each subcatchment.

4.2 Streamflow

To simulate the streamflow at each sampling point, a simple hydraulic model was created. A survey of the cross-section channel profile was conducted at each sampling point. The survey was performed by positioning a ranging rod at a number of points across the channel, with the distance from the dumpy level (optical surveying device) and the ranging rod measured. By measuring the change in elevation between the ranging rod and the optical surveying levelling instrument, river profiles could be created (see Figure 4.2). A number of downstream measurements were taken at each site to determine the channel slope. The data collected were then used to create stream cross sectional profiles using Microsoft Office 2013 Excel. A cross sectional profile was not performed for Site-2 (the wastewater treatment works effluent outlet) as the channel is very small and overgrown, and any channel profile determination would be inaccurate. In addition, Site-1 and

Site-3 are close enough to be able to exclude groundwater additions and, therefore discharge for Site-2 was calculated by determining the difference in flow between Site-3 and Site-1.

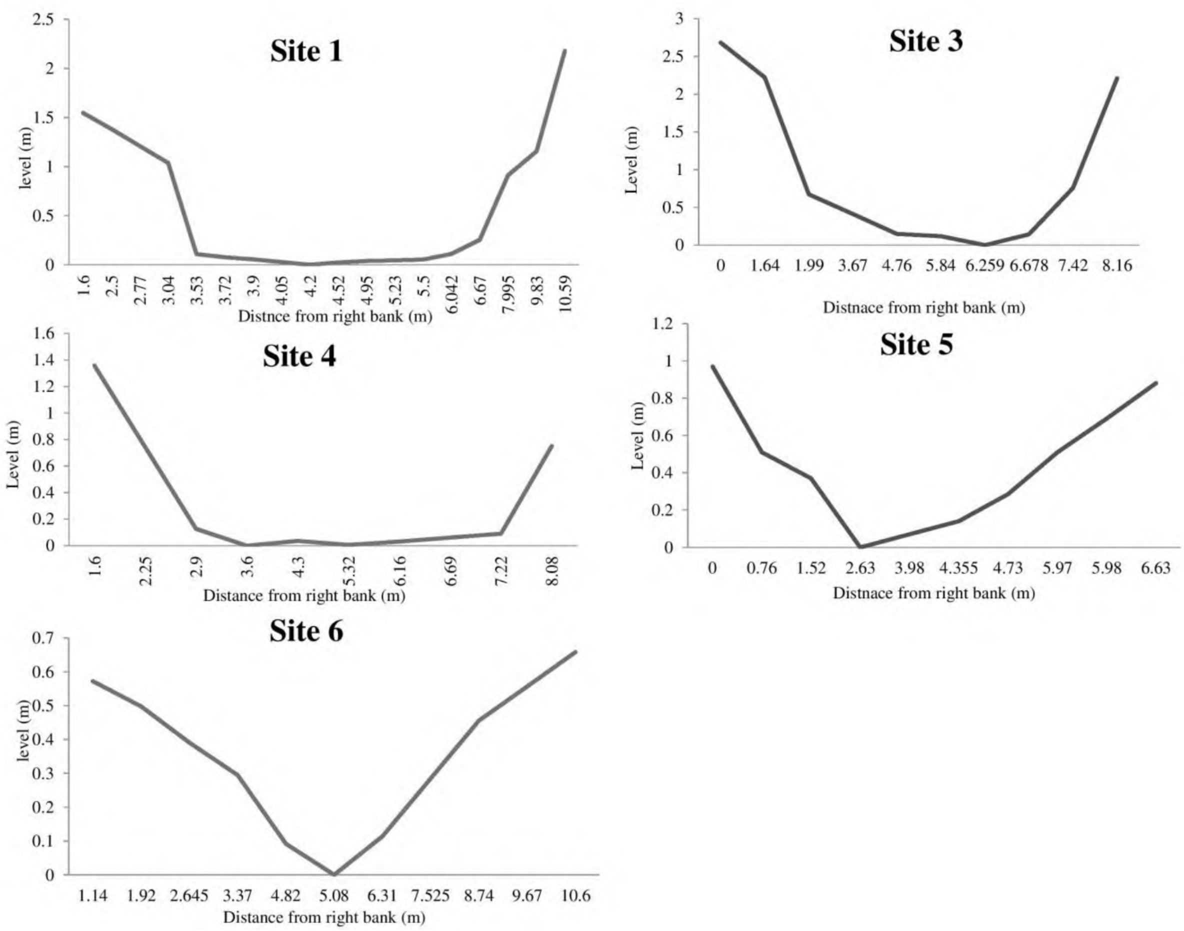

Figure 4.2: River cross sectional profile for each of the study sites on the Bloukrans River.

Streamflow velocity was measured using a flow meter at different points across the cross sectional profile of each site. The flow velocity was measured at a depth approximately at 75% of the total depth. The Manning's n formula was then used to determine channel roughness. Channel roughness, is influenced by a number of factors causing friction in a river channel including channel bed composition, size and type of channel vegetation.

$$V = \frac{k}{n} R_h^{\frac{2}{3}} . S^{\frac{1}{2}} \tag{4.1}$$

V is the cross sectional average velocity (m s^{-1}), k is a conversion factor, n is the Gauckler-Manning roughness coefficient, R_h is the hydraulic radius of the channel (m) and S is the slope of the hydraulic head loss line ($\ell\ \ell^{-1}$) and is the slope of the channel bed when the water depth is constant. An excel spreadsheet was setup to determine the hydraulic radius for a given water depth.

4.3 Observed water quality data

Data for water quality variables were required for the simulation of nutrients. Water quality models that attempt to simulate most of the processes affecting water quality require the input of water quality variable data that influence the processes. Sampling was dispersed over a wide range of catchment conditions as possible with the limited number of sampling trips. Two low flow, one medium flow and two high flow samples were taken for the purpose of this study. The water quality variables and the instruments used in the field to measure them for this study are shown in Table 4-2.

Table 4-2: Water quality variables measured and the instruments used in the project

Variable	Instrument	Unit of measure
Dissolved oxygen (DO)	Cyberscan DO 300 meter	mg ℓ^{-1}
Temperature	Mercury in glass	^{o}C
Turbidity	Orbeco-Hellige 966 meter	Nephelometric Turbidity Unit (NTU)
Electrical conductivity (EC)	Cyberscan 200 meter	mS m^{-1}

4.4 Nutrients

Grab samples were collected for each site and analysed in the laboratory for nitrate N (NO_3-N), nitrite N (NO_2-N), ammonium N (NH_4-N), ortho-phosphate P (PO_4-P), total nitrogen (TN) and total phosphorus (TP) using the methods prescribed by APHA (1992). Each grab sample was collected in a sample bottle which was acid washed prior to use. The sample was collected with the bottle opening facing upstream so as to ensure minimal or no contamination of the sample. In addition, it was ensured that each sample contained no air by completely filling and sealing the bottle under the surface of the water. Samples were stored at 4 °C and were analysed within 24 h of being taken.

Non-conservative water quality variables, including nutrients, are highly variable on both temporal and spatial scales. This variability is due to the influence of various processes on the variables. A grab sample is therefore only a snap shot of the state of the non-conservative variables in the system. Within this study however, time and financial constraints did not allow for more comprehensive sampling. It must therefore be assumed that the grab samples collected are representative of the overall condition of the system. QUAL2K uses a single diel variation sampling period, usually performed over 24 hours, to determine temporal variation in the river.

4.4.1 Nitrate

Nitrate (NO_3^-) is analysed in the laboratory using spectrophotometry (APHA, 1992). A 50 mℓ sample is treated with pre-calibrated reagents. Reagents have to be prepared prior to analyses and are only suitable for use for four weeks after being prepared. For nitrate analyses, hydrochloric acid, sulfanalic acid, zinc chloride, NO_3^- buffer colour reagent and sodium acetate are required. Hydrochloric acid solution of a 1:4 ratio is prepared by mixing 75 mℓ milliQ water with 25 mℓ concentrated (32%) hydrochloric acid. Sulfanalic acid is prepared by dissolving 0.6 g of sulfanalic acid in 70 mℓ hot milliQ water, cooling and finally adding milliQ water until the volume of the solution reaches 100 mℓ. Zinc chloride reagent is composed of 1 g of zinc added to 200 g of sodium chloride and mixed. The buffer-colour reagent is prepared by adding 1 mℓ of concentrated hydrochloric acid to 10 mℓ milliQ water, then adding 0.6 g N-1-naptheylenediamine dihydrochloride dye and topping up the solution to 100 mℓ with milliQ water and mixing. Sodium acetate is prepared by dissolving 16.406 g sodium acetate ($NaC_2H_3O_2$) and filling to a volume of 100 mℓ with milliQ water. Reagent bottles are wrapped in aluminium foil to prevent photodegradation and stored in a refrigerator at 4 °C.

A calibration curve is constructed by preparing known concentrations of nitrate using KNO_3, and then measuring the absorbance using the protocol described below. The absorbance from the spectrophotometer readings are then plotted against the concentration of the respective samples. A linear regression is fitted to the trend line, and the equation describing the line can then be used to calculate nitrate concentration for a given absorbance. Outliers on the graph are removed to achieve a better fit.

Within the protocol, 50 mℓ of sample is treated with 1 mℓ hydrochloric acid and 1 mℓ of sulfanalic acid solution and then mixed. A total of 1.5 g of zinc chloride powder is added and then the sample is stirred for 7 min. Subsequently, 1 mℓ of NO_3^- buffer-colour reagent is added and mixed, after which 1 mℓ of sodium acetate is added then mixed. After mixing for 5 min, 250 µℓ of treated sample is placed in triplicate into a microplate reader. The samples in the microplate reader are then read at 540 nm in the spectrophotometer. The lower detection limit of this method is 1 mgℓ$^{-1}$ NO_3^-. In addition, the highest concentration on the calibration curve using this method is 15 mgℓ$^{-1}$ NO_3^-, and samples containing nitrate concentrations above this threshold require dilution.

4.4.2 Nitrite

Nitrite N was analysed using the method by APHA (1992), in which the measurement of nitrite only requires one reagent. The NO_2 buffer-colour reagent is prepared by adding 125 mℓ milliQ water to 52.5 mℓ concentrated hydrochloric acid, followed by 2.5 g sulfanilamide and 0.25 g N-1-napthylethyleneamine dihydrochloride and 40.99 g anhydrous sodium acetate. The volume of the reagent is then filled to 250 mℓ with milliQ water. The bottle is wrapped in aluminium foil to prevent photodegradation. Measurements of absorbance for known concentrations of nitrite are then conducted. The trend line obtained from plotting concentration against absorbance is used to calculate nitrite concentrations of river samples. Within the protocol, 2 mℓ of NO_2 buffer-colour reagent is added to 50 mℓ of sample. After 15 min, 250 µℓ of sample is placed in triplicate into a microplate. The absorbances of the samples are then read at 540 nm using a spectrophotometer.

4.4.3 Ammonium

For the analyses of ammonium, the Spectroquant 1.14752.0001 test kit was used. The test kit measures NH_4-N in a range from 2 mgℓ$^{-1}$ to 75 mgℓ$^{-1}$. The test kit is calibrated by processing known concentrations of ammonium using NH_4Cl as per the protocol below, and measuring absorbance of triplicates of each sample at 660 nm in the spectrophotometer. The concentration is plotted against the absorbance for each sample, with the fitted regression equation of the trend line from the graph is the used to calculate the NH_4^+ concentrations of river samples. Processing the samples involved adding 5 mℓ of river water sample to a test tube, proceeded by 0.6 mℓ of reagent NH_4-1, followed by one level blue microspoon of NH_4-2 reagent. After waiting 5 min, four drops of NH_4-3 reagent is added to each sample, which is then left to stand for 5 min. Using an autopippette, 250 µℓ of each sample is placed into a microplate, which is then read at 660 nm in the spectrophotometer.

4.4.4 Phosphate

Phosphate is analysed using the Spectroquant 1.14848.0001 test kit. The absorbance of known concentrations of PO_4^{2-} processed using the protocol given below are measured in a spectrophotometer at 660 nm. The concentrations are plotted against absorbance with the equation of the trend line from the graph used to calculate the phosphate concentrations of treated river water samples. Within the protocol, 5 mℓ triplicates of each sample are placed in individual test tubes. Each test tube is then treated with five drops of PO_4-1 reagent and mixed, followed by one level microspoon of PO_4-2 reagent. The treated sample is then left to stand for 5 min. Finally, 250 µℓ of each treated sample is placed into a microplate and the absorbance of samples are read at 660 nm in the spectrophotometer.

4.4.5 Total nitrogen (TN)

TN is a measure of all nitrogen in a sample, consisting of ammonium, nitrite, nitrate and organic nitrogen. Total nitrogen was anaylsed using the spectroquant 1.14763.0001 test kit. Measurement of TN allows the determination of organic nitrogen content, provided that the inorganic forms of nitrogen are also measured separately. Since TN includes the measure of organic nitrogen, digestion of the sample is required. Digestion is achieved by placing 10 mℓ of sample into an empty reaction cell along with one level microspoon of reagent N-1K and six drops of reagent N-2K. The reaction cell is then placed in a thermoreactor at 120 °C. After 1 h, the reaction cells are removed and left to cool to room temperature. A reaction cell with a premixed solution has one level microspoon of reagent N-3K added to it, along with 1.5 mℓ of the digested sample, which is fed carefully into the reaction cell as the reaction generates heat. The cell is left to stand for 10 min, after which it is read using a Spectroquant. This test can measure N in a range from 0.5 mgℓ$^{-1}$ to 15 mgℓ$^{-1}$. Concentrations of > 15 mgℓ$^{-1}$ require dilution of the primary sample before any reagents are added.

4.4.6 Total phosphorus (TP)

As with TN, TP is a measure of total phosphorus in a sample and includes total dissolved phosphorus and particulate phosphorus. Total Phosphorus was analysed using the Spectroquant 1.00673.007 test kit. As such, the protocol for measuring TP requires digestion of the sample. The protocol involves placing 5 mℓ of sample in a reaction cell along with one cap-full of reagent P-1K. The reaction cell is then placed in a thermoreactor at 120 °C for 30 min. After digestion, the reaction cell is left to cool to room temperature. Subsequently, five drops of reagent P-2K is placed in each reaction cell and mixed. One cap of reagent P-3K is then added, and the reaction cell is then tightly closed and mixed until the reagent is completely dissolved. After standing for 5 min, the cell can then be placed in the spectroquant for analyses. The test can measure PO_4-P in a range from 0.05 mgℓ$^{-1}$ to 5 mgℓ$^{-1}$. Concentrations of above > 5 mgℓ$^{-1}$ require dilution of the primary sample, before any reagents are added.

4.5 Chlorophyll

To determine the algal content both in the water (phytoplankton) and on the river bed (periphyton), chlorophyll concentration was measured according to the protocol suggested by Holm-Hansen and Riemann (1978). For phytoplankton, a 200 mℓ sample of water taken at each site was filtered through a Whatman GF/F filter paper and stored for later analysis in a test tube containing 8 mℓ of 90% acetone. This was replicated three times for each site. To measure periphyton, a rock was selected randomly from the river bed at each site. Using a plastic ring, algal biomass of an area of 6.16 cm^2 was scraped off using a scalpel. The scrapings were then rinsed using distilled water and filtered using a Whatman GF/F filter. The filter was then stored for later analysis in a test tube containing 8 mℓ of 90% acetone. Samples for periphyton were also replicated three times at each site. The analysis of chlorophyll-a concentration was performed according to the method by Arar and Collins (1997).

4.6 Field results

Table 4-3 summarises the results of observed nutrient concentrations in the Bloukrans River during the study.

Table 4-3: Field results for the Bloukrans River.

Site 1					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3 s^{-1})**
12-06-2012	2.85	90.79	4.85	0	0.145
03-09-2012	16.22	61.99	3.72	0	0.21
25-10-2012	2.97	220.61	23.62	0	0.5
26-02-2013	15.68	175.81	2.74	2.67	0.046
26-10-2013	6.66	95.06	1.02	0.59	0.53

Site 2					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3 s^{-1})**
12-06-2012	2.98	329.92	8.37	0.59	0.15
03-09-2012	20.38	152.89	9.33	0.72	0.11
25-10-2012	0.816	1156.54	0	0	0.41
26-02-2013	2.94	138.27	1.73	7.37	0.164
26-10-2013	6.68	194.00	2.79	4.83	0.13

Site 3					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3 s^{-1})**
12-06-2012	3.29	315.66	7.18	0.175	0.25
03-09-2012	0	99.33	5.45	0	0.322
25-10-2012	2.38	349.5	0	0	0.91
26-02-2013	6.39	223.19	2.46	4.77	0.21
26-10-2013	6.22	159.15	1.08	1.86	0.66

Table 4-3 continued.

Site 4					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3.s^{-1})**
12-06-2012	3.65	315.47	2.75	0	0.33
03-09-2012	0	95.58	0.82	0.13	0.37
25-10-2012	1.09	184.5	3.53	0	1.88
26-02-2013	0.21	103.13	0.41	3.51	0.225
26-10-2013	2.93	38.00	1.07	1.85	0.69

Site 5					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3.s^{-1})**
12-06-2012	0	164.13	1.34	0.03	0.37
03-09-2012	0	47.25	0.21	0	0.4
25-10-2012	1.36	40.013	1.59	0	2.24
26-02-2013	0	41.99	0.085	2.3	0.299
26-10-2013	8.21	76.26	2.08	2.48	0.71

Site 6					
Date	**NH_4 (mg ℓ$^{-1}$)**	**NO_3 (mg ℓ$^{-1}$)**	**NO_2 (mg ℓ$^{-1}$)**	**PO_4 (mg ℓ$^{-1}$)**	**Flow (m^3.s^{-1})**
12-06-2012	0	132.18	0.184	0	0.47
03-09-2012	19.33	26.17	0.03	0	0.52
25-10-2012	0.33	21.91	0.84	0	3.63
26-02-2013	0	6.49	0.017	0.52	0.32
26-10-2013	4.34	43.96	0.54	1.46	0.89

To expand our knowledge of the nutrient dynamics within the Bloukrans River, field data were analysed for trends and points of interest. In this section, the observed trends and anomalies in the nutrient data collected are shown visually and discussed. An understanding of dynamics and processes affecting water quality in the catchment is necessary for scientific judgement during both model construction and the calibration and confirmation of both models used.

Figure 4.3 shows the results of instream nitrate determination for each site collected during low flow conditions on the 26th February 2013. Here, it is evident that the highest nitrate concentration is observed at Site-3, which is expected as this site occurs just downstream of a WWTW point source. From Site-3 downstream, instream nitrates show a continual decline, indicating that no further significant sources of nitrate are operating within the study area during low flows, and that instream fate processes rapidly remove nitrate from the system. Some minor diffuse sources of nitrate may occur within the study area, even during lower flows. For example, the dairy farm and irrigation that occurs within subcatchment 2 could introduce nitrates to the river. A groundwater sample taken within this subcatchment contained nitrates and therefore, groundwater flow into the river could also be a source of nitrates.

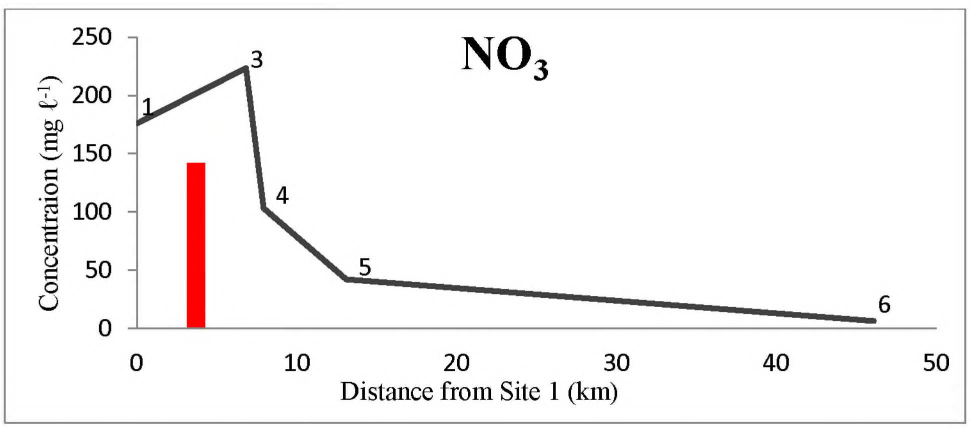

Figure 4.3: A visualisation of the changes in instream nitrate concentration from upstream to downstream according to sampling performed during low flow conditions on the 26/02/2013. Numbers 1 to 6 refer to the sampling sites (see Figure 3.1) Site-2 is shown as the red bar as it is not an instream point.

Diffuse inputs of nutrients were observed during runoff events and high flow conditions within the catchment. Figure 4.4 shows a diffuse input of nitrates above Site-5, where an increase in instream nitrates is observed. Diffuse inputs could be caused by applying excessive fertilisers to crops or pastures, thereby resulting in a build-up of nutrients near the surface of the soil, which are susceptible to transport during high rainfall and runoff events.

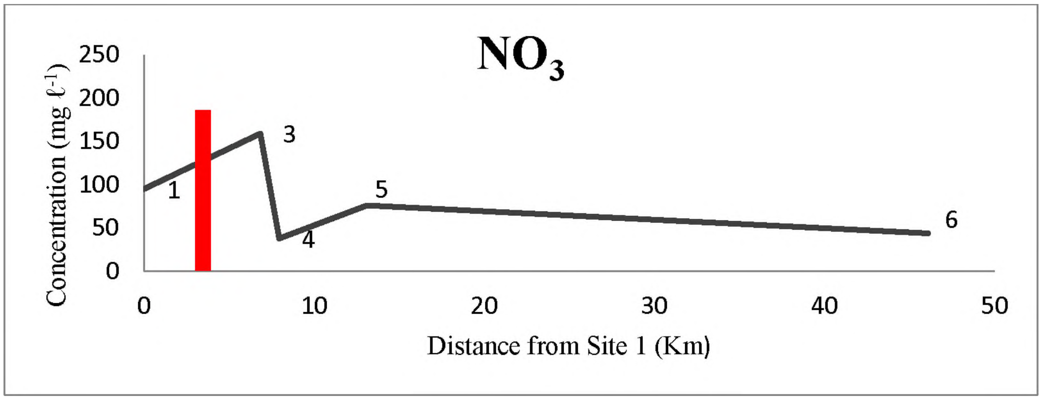

Figure 4.4: A visualisation of the changes in instream nitrate concentration from upstream to downstream according to sampling performed during high flow conditions on the 26/10/2013.

Ammonium is the favoured nitrogen compound for assimilation, is converted to nitrite through nitrification and is the first nitrogen compound to be removed from solution. However, in aerobic conditions such as the Bloukrans River, Ammonium will be converted to nitrate. Figure 4.5 shows the rapid removal of ammonium from instream solution during low flows. Site-2 is shown as the red bar as it is not an instream point.

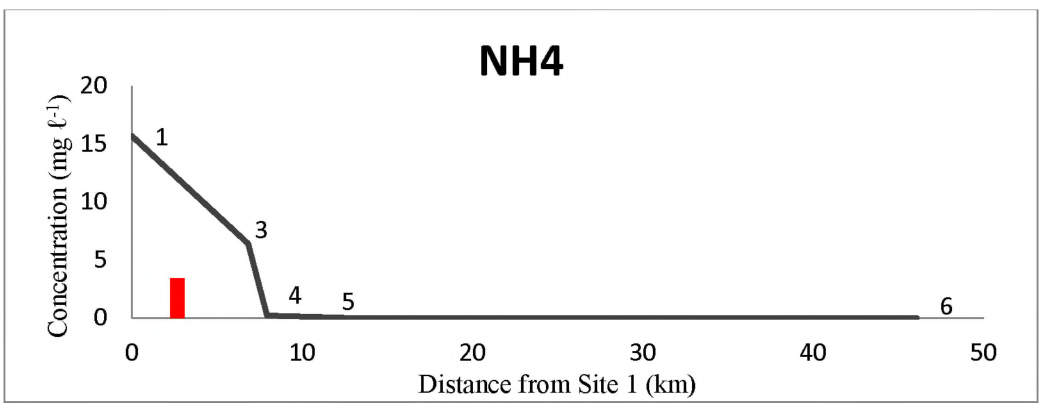

Figure 4.5: Ammonium data from the 26/02/2013 sampling trip showing ammonium dynamics in the Bloukrans River during low flows. Site-2 is shown as the red bar as it is not an instream point.

Site-5 in Figure 4.6 indicates an increase in ammonium concentration within subcatchment-4. The increase in ammonium could be attributed to the decomposition of organic matter; however, this increase of ammonium in subcatchment 4 was not observed during any other sampling trips. It must however be considered that this sampling trip was conducted after extensive flooding within the area, and as such the increase in ammonium in subcatchment 4 could be attributed to diffuse source input. However, an extreme event had occurred four days prior to the sampling, which according to theory, should have washed off almost all the nutrients from the catchment. Therefore, the ammonium increase could be attributed to the breakdown of organic matter deposited during the flooding event within subcatchment 4.

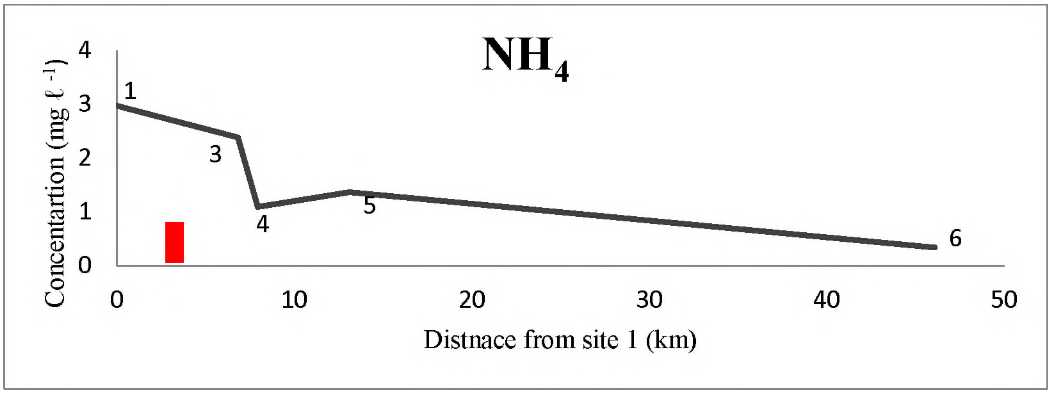

Figure 4.6: Ammonium data from the 25/10/2012 sampling trip showing diffuse inputs of ammonium between Site-4 and 5 illustrated by the rise in concentration. Site-2 is shown as the red bar as it is not an instream point.

Figure 4.7 shows an increase in phosphate concentration upstream of Site-4. The sampling occurred during medium flow. The increase in phosphate concentrations is a good example of a diffuse source upstream of Site-4.

Data collection was very limited; however, the purpose of this study was to investigate water quality modelling on an unmonitored catchment and attempt to model water quality using limited data. With the limited data collection programme, an attempt was made to try and spread the limited collection over as broad a range of hydraulic conditions as possible. Although limited data increases uncertainty of processes occurring in the catchment, a broad range of monitored conditions does decrease the uncertainty within the small dataset. Increasing the number of sampling trips would help support or refute certain hypotheses developed from the limited dataset.

Determining water quality processes occurring in the catchment becomes more difficult with limited data. However, it is necessary for practical assessment in unmonitored catchments where financial and temporal limitations dictate the depth of the monitoring and modelling to be performed.

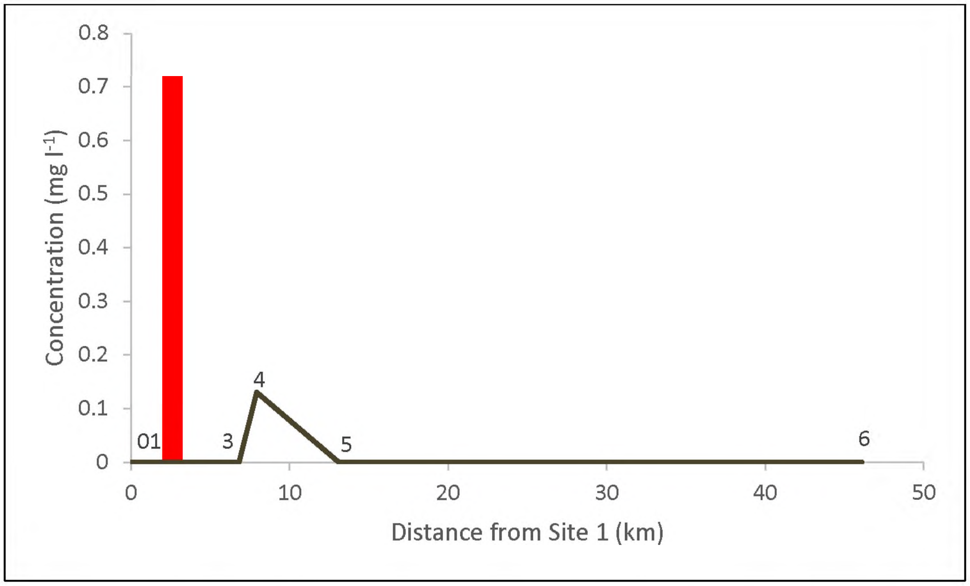

Figure 4.7: Phosphate data from the sampling on the 03/09/2012 showing diffuse inputs upstream of Site-4. Site-2 is shown as the red bar as it is not an instream point.

5. COMPLEX WATER QUALITY MODEL: QUAL2K

5.1 Introduction

QUAL2K is the updated version of the river water quality model QUAL2E, originally developed by the USEPA (United States Environmental Protection Agency). QUAL2E has been used in Europe and the USA for load allocations and environmental impact assessment, and was initially intended for use in total maximum daily load (TMDL) allocations (Brown and Barnwell, 1984). QUAL2E is best suited to well-mixed streams, assuming that advection and dispersion in vertical and horizontal directions to be negligible, and to only significantly occur in the direction of flow (Brown and Barnwell, 1984). One improvement of QUAL2K over QUAL2E is that QUAL2K simulates bottom algae; therefore, QUAL2K is more applicable for low volume, high velocity streams. To determine the water quality impact of waste loads, the model is run as a steady state, whereas the model has to be run as a dynamic system to determine the effect of meteorological diurnal variation on water quality.

QUAL2K simulates streamflow as ‘plug flow’, whereby the river reach is divided into segments, and water and nutrients loads move as a ‘plug’ from one segment to the next (Park and Lee, 1996).

QUAL2K provides a very simple estimate of uncertainty by simulating maximum and minimum values for each nutrient. This estimation is driven by the user specified variability of the point and diffuse source nutrient concentrations.

A study performed on the Nakdong River in Korea by Kanne *et al.* (2005) demonstrated QUAL2K to be more accurate than QUAL2E by comparing simulated results to field measurements. Slaughter (2011) had moderate success modelling water quality in the Bloukrans River with QUAL2K during 2009, which motivated the choice of QUAL2K for the current study, as the model had shown promise and an experienced user of QULA2K was available.

QUAL2K uses Microsoft Excel as a platform, with different spreadsheet pages used to encapsulate specific parts of the model, such as pages to specify parameters for specific processes as well as pages that show model output.

5.2 Model Setup

QUAL2K set up for modelling requires values to be assigned to numerous parameters which cannot be easily measured in the field and cannot be practically measured in the laboratory due to the complexity of the processes they represent. The strategy adopted in the current study was to use starting parameters in the model adopted from a previous study on the same system, and to adapt the parameters as required during calibration. These starting parameter values were thus assumed to be the same as the values used by Slaughter (2011) when modelling the same river, and later refined during calibration. Time of sunrise, solar noon and sunset are the first parameters to be assigned values and are important for the phytoplankton growth model. The time zone of the area modelled is then selected as Bravo, or two hours off Greenwich meridian time. The 'Headwater' page is then prepared. This page contains the data collected from Site-1, and initially data were only input for the time slot at the specific time sampling occurred. However, this resulted in unresolvable problems with the model resulting in the model not operating properly, and to eliminate this issue, data were input for each time slot, assuming that values of water quality variables remained constant throughout the day. Subsequently, data from Site-6 were entered into the 'Downstream' page. The data for reaches were then entered into the model, specifying the length of each individual reach, as well as the upstream start and downstream end of each reach. QUAL2K improves on QUAL2E in that QUAL2K can simulate reaches of varying length and size, whereas QUAL2E requires segments of equal length and size. Channel slope and Manning`s n co-efficient are also determined from the measured sites and entered into the model. Next, an initial and sensible value for each rate parameter for the processes being modelled is entered into the model, with initial values chosen from Slaughter (2011), but later changed iteratively during the calibration process to obtain model simulated data within the limits of the observed data. Certain processes are highly sensitive to changes in rates. A strong correlation between ammonium nitrification rate and dissolved oxygen re-aeration rate was observed during this process. The following pages in the model require weather data for the specific day. Data that could be obtained from a weather station was then entered into the model, including air temperature and wind speed. Estimates of cloud cover and shading had to be made based on past weather data and knowledge of the sites. Water column rates entered were the same values as used by Slaughter (2011), as were the surface heat transfer model and light parameters. A point was set up to simulate the Belmont Valley WWTW. Water quality data inputs for each site were then entered into the water quality data sheet. Minimum and maximum data from all available data were entered into the respective water quality sheets. Diel data obtained from Slaughter (2011) was used to run the diel page in QUAL2K.

5.3 Calibration

The calibration of QUAL2K was performed by adjusting model parameters so that the simulated results match the observed data. Calibration was focused on nitrates, ammonium and phosphates. Increases in streamflow between subcatchments were modeled as diffuse flow with no nutrients found in the diffuse flow. Diffuse flow for subcatchment 2 (see Figure 4.1) was given a nitrate signature as a water table sample taken within the subcatchment near the river had nitrates. The nitrate concentration in the diffuse source was adjusted to obtain a suitable fit of simulated data to observed data. The nitrates found in the water table sample were assumed to be from the sludge dams as well as the fecal matter from the dairy animals. Calibration was achieved on data from the field trip on the 3 September 2012 by adjusting the rates for; re-aeration, organic N hydrolysis, ammonium nitrification, nitrate denitrification, sediment denitrification, organic P hydrolysis, organic P settling velocity and phytoplankton maximum growth rate. Adjustment of rates was done in the 'Reach Rates' page in the QUAL2K framework. Adjustment off reach rates was done by eye using the figures output by the model. Rates were adjusted accordingly until a satisfactory fit of the simulated data to the observed data was achieved for each nutrient simulated. The results of the calibration are visible in Figures 5.1 through 5.3. Field data collected on the 12/06/2012 was used as the calibration dataset. This data set was used for calibration as it was determined to be the median value for flow.

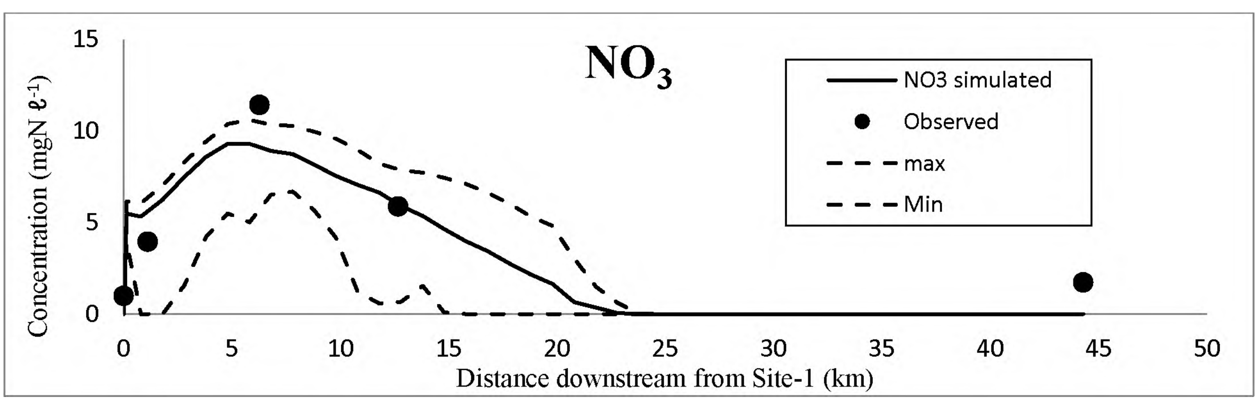

Figure 5.1: The QUAL2K calibration of nitrate for the Bloukrans River.

The calibration of nitrates proved successful with a satisfactory fit of simulated nitrates to observed nitrates as shown in Figure 5.1. Although some outliers are visible on the calibration graph, the fit is still acceptable and the general trend of the fate of nitrates is represented by the simulated data.

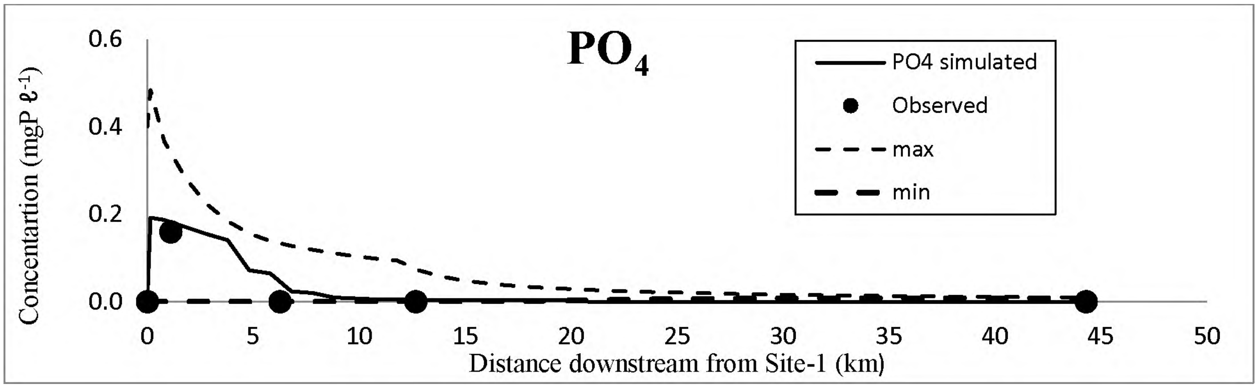

Figure 5.2: Phosphate calibration in QUAL2K for the Bloukrans River.

Phosphate calibration produced a good fit of simulated data to observed values. However the uncertainty in the upstream reaches is rather high. However the uncertainty can be expected as QUAL2K is most suited to be operated as primarily a point source model, and thus should be used for low flows. The lack of observed diffuse phosphate sources accounts for the low uncertainty in the lower reaches of the catchment.

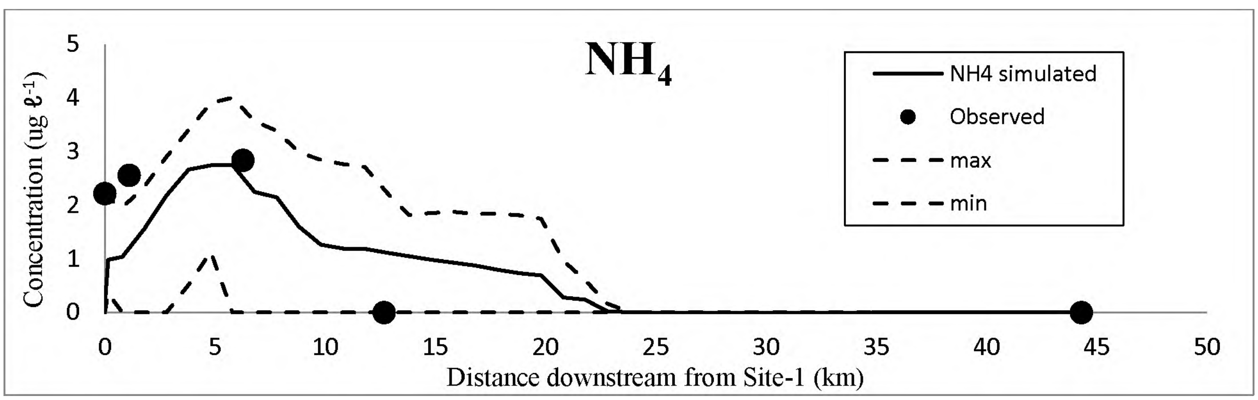

Figure 5.3: Ammonium calibration in QUAL2K for the Bloukrans River.

Ammonium is sensitive to changes in parameters such as dissolved oxygen re-aeration and nitrification of ammonium, and was thus the most difficult nutrient to calibrate. The difficulty of calibration resulted in the ammonium calibration having the poorest fit out of the three nutrients calibrated in QUAL2K. The calibration is relatively poor; however the simulation produced the general trend of ammonium concentrations observed in the Bloukrans River. Calibration values used in QUAL2K for the Bloukrans River are shown below in Table 5-1.

Table 5-1: Parameter values for QUAL2K.

Parameter	Unit	Maximum	Minimum	Calibration value
Re-aeration	d^{-1}	100	0.05	0.05
Organic N Hydrolysis	d^{-1}	3	0.05	0.5
Ammonium Nitrification	d^{-1}	15.8	0.025	1.00
Nitrate denitrification	d^{-1}	2	0.05	1.00
Organic P Hydrolysis	d^{-1}	0.3	0.05	0.3
Organic P settling velocity	d^{-1}	0.25	0.05	0.25
Inorganic P settling velocity	d^{-1}	2	0	1.00
Phytoplankton max growth	d^{-1}	3	0.58	9999
Phytoplankton respiration	d^{-1}	0.8	0.02	0.5
Phytoplankton death	d^{-1}	0.17	0.003	0.01
Phytoplankton settling	d^{-1}	4.0	0	0.01
Bottom algae max growth	d^{-1}	1.5	0.2	9999
Bottom algae respiration	d^{-1}	0.8	0.02	0.5
Bottom algae death	d^{-1}	0.8	0	0.01

A sensitivity analysis was performed on QUAL2K to assist with calibration. The results of the simple sensitivity analysis are shown in Figure 5.4 to 5.9. The nutrient most affected by the parameter was used to determine the sensitivity of the parameter, changing the parameter value within the range of values suggested for the parameter in Bowie *et al.* (1985). The sensitivity analysis was performed to better understand the relationships of variables within the system.

Re-aeration was most sensitive at Site-4 and Site-5 (refer to Figure 5.4). Sensitivity is illustrated by the spread of symbols for the change in parameter values, a small spread or no spread indicates an insensitive parameter. Figure 5.4 indicates a lack of sensitivity of re-aeration at Site-3 and Site-6. The lack of sensitivity at Site-3 could be due to the inflow of waste water effluent above the site, or the effects of re-aeration are not noticed over the short river reach. The lack of sensitivity at Site-6 could be due to the narrow range of observed ammonium concentrations for this site, and as such, the model will not be significantly affected by adjusting parameters at this site.

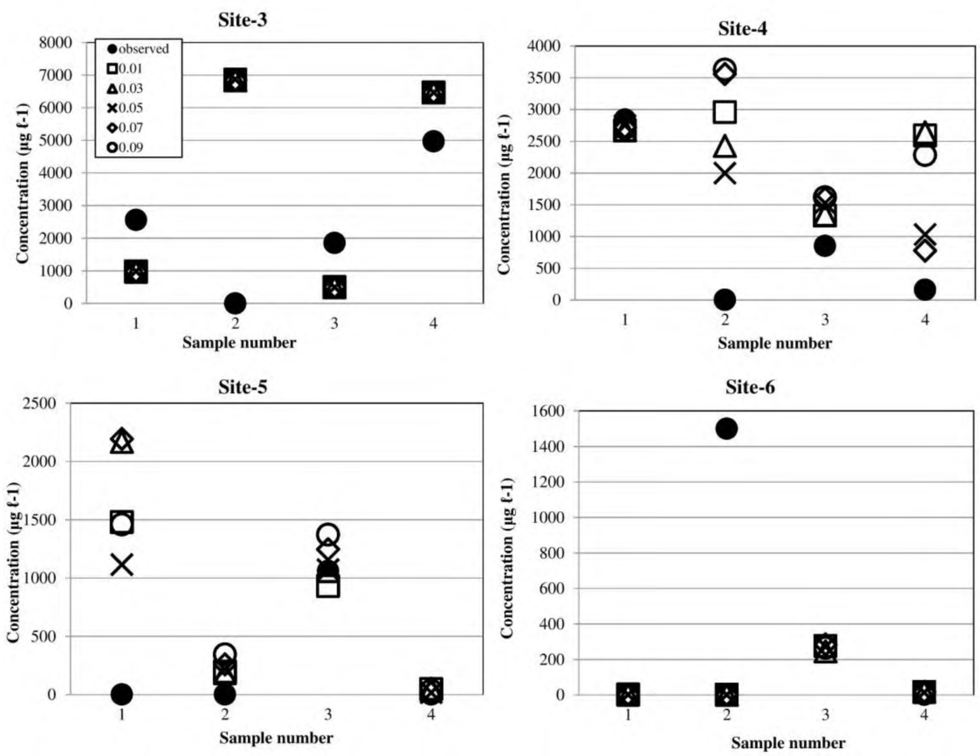

Figure 5.4: Sensitivity results for re-aeration, using the ammonium concentration.

Nitrification sensitivity analysis indicated that ammonium concentration was sensitive to nitrification for Site-4 and Site-5 only (refer to Figure 5.5). Site-3 and Site-6 showed no sensitivity for nitrification.

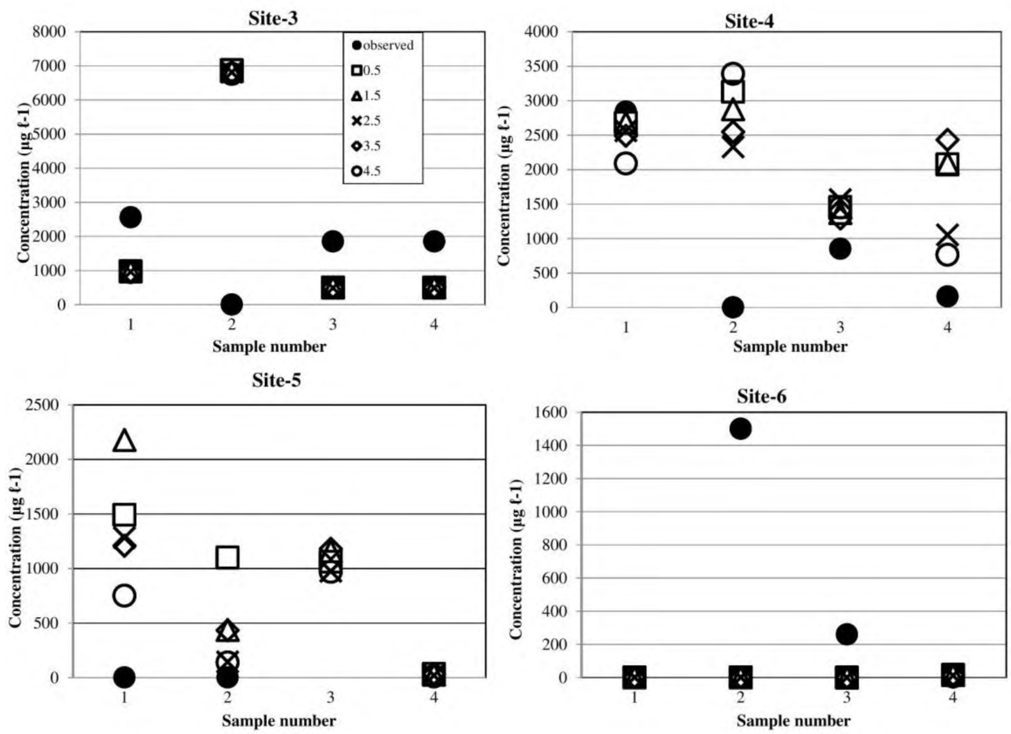

Figure 5.5: The sensitivity analysis for nitrification, using ammonium as an output.

The denitrification sensitivity analysis indicated some sensitivity for Site-5 (refer to Figure 5.6). The remaining three sites showed no sensitivity for adjusting the nitrification. The lack of sensitivity could be due to the high nitrate concentrations observed in the Bloukrans River.

Inorganic settling sensitivity analysis showed inorganic phosphorus settling to be an insensitive parameter. Site-4 and Site-5 showed inorganic settling to be slightly sensitive.

Bottom algae growth rate was tested for sensitivity by analysing the effect of changing parameter values on the phosphate output of the model. Phosphate output was chosen to test the sensitivity of the bottom algae parameter as the sensitivity would be better represented by the lower concentrations when compared to nitrates. Site-4 and Site-5 showed a moderately sensitive parameter as shown in Figure 5.8.

Phytoplankton sensitivity analysis indicated sensitivity at all the sampling sites analysed. The higher parameter values used in the analyses indicated lower sensitivity than the lower values.

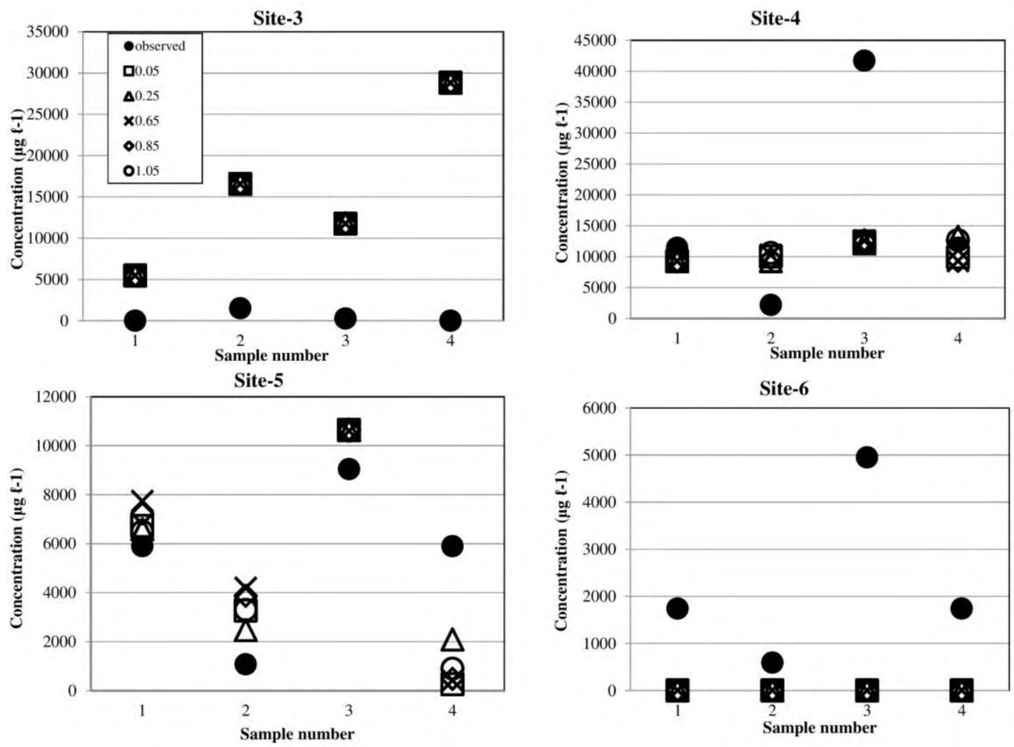

Figure 5.6: The sensitivity analysis on denitrification using nitrates.

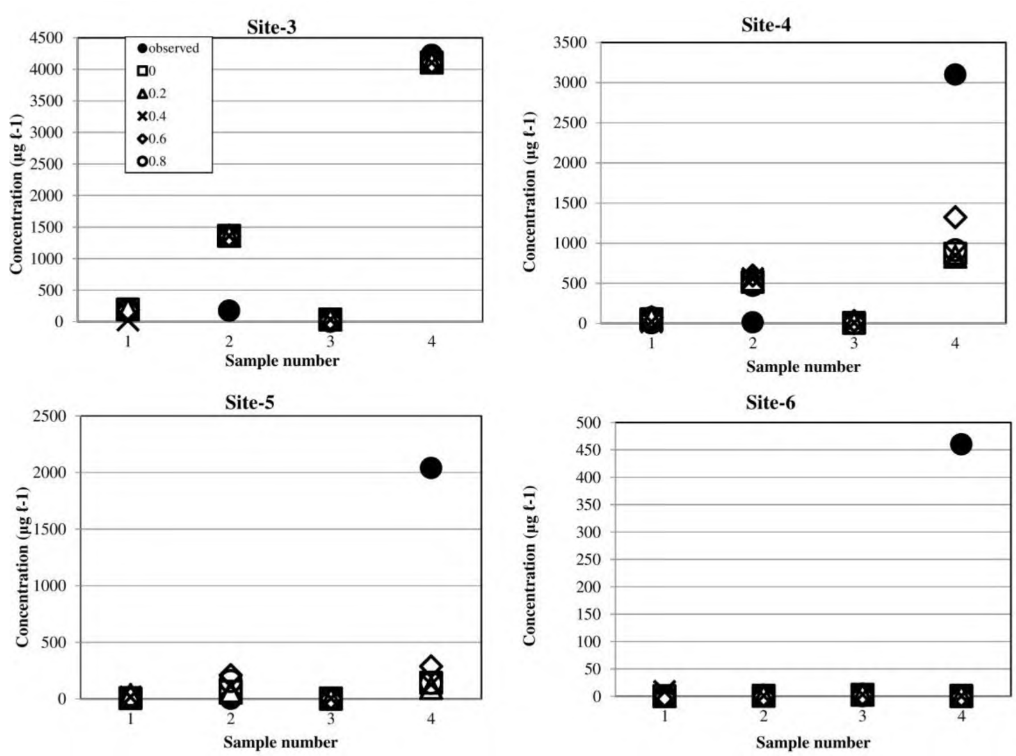

Figure 5.7: The sensitivity analysis on inorganic phosphorus settling using phosphate.

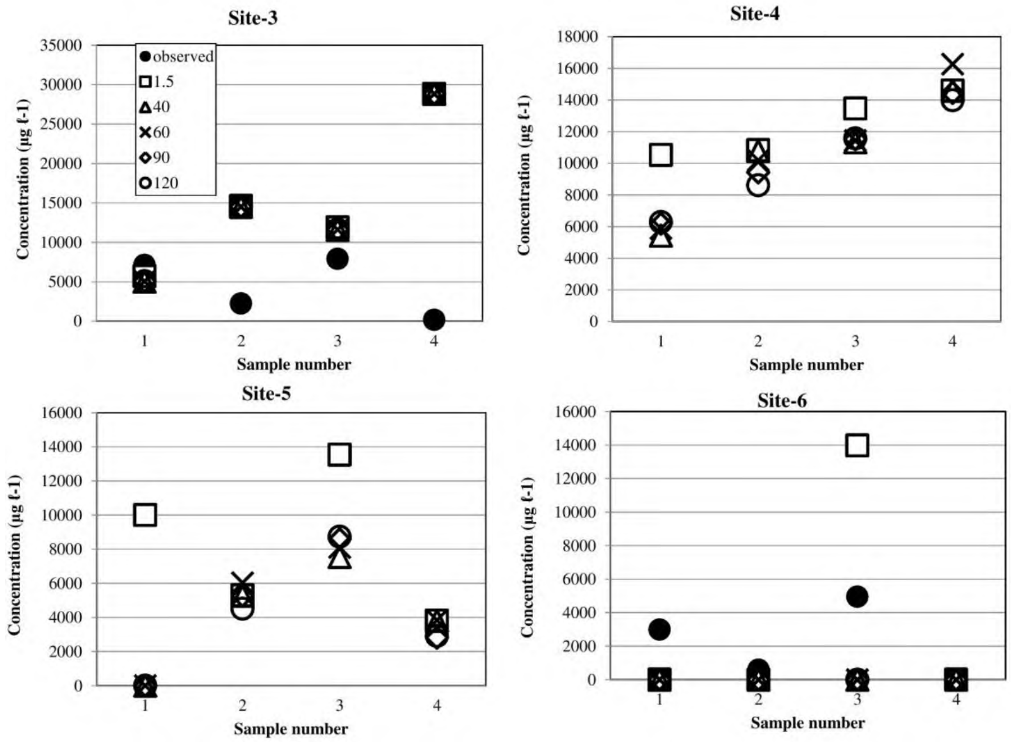

Figure 5.8: The sensitivity analysis on bottom algae growth rate using phosphate concentrations.

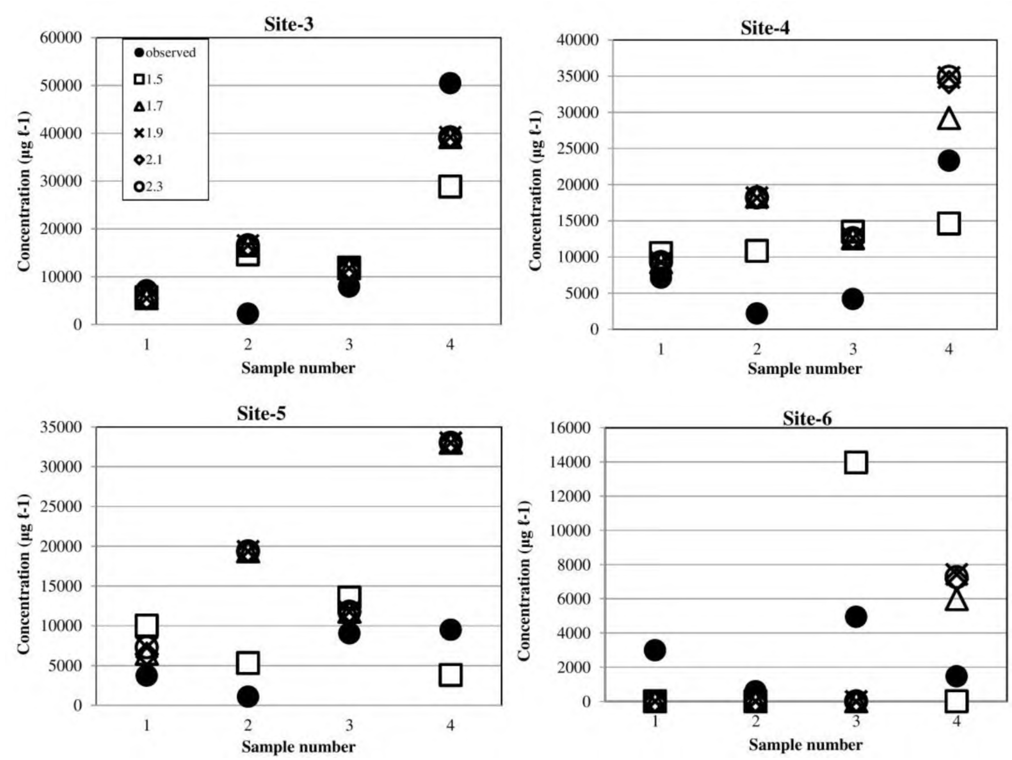

Figure 5.9: Phytoplankton growth rate sensitivity analysis using phosphate concentrations.

The sensitivity analyses for QUAL2K indicated re-aeration, nitrification and bottom algae to be the most sensitive parameters; however, the complex relationship that exists between the parameters causes difficulty when calibrating the model.

5.4 Results

QUAL2K performed acceptably for the calibration of nutrients as described in the previous section. However, the calibrated model required validation, as outlined in Chapter 2. Recently, it has been argued that the correct term to use is 'confirmation' (see Chapter 2), although the current study will continue to refer to 'validation'. The validation of a model is achieved by comparing a separate dataset from that used for calibration to the simulated data obtained from the calibrated model. Validation provides an indication of how well the model simulates conditions outside the temporal boundaries of the calibrated data, and is a test of how well the water quality processes in model represent reality. Validation was done against the 4 remaining datasets from the sampling undertaken for this study.

The results of nitrates validation within QUAL2K were unsatisfactory (Figure 5.10).

The observed data were collected over a range of flow conditions. Although the trend of the observed data was matched by the simulated data, there appeared to be problems with the point source input within the model. Validation 1 showed the contribution of nutrients by the point source to be underestimated, whereas the opposite occurred for validation 2 and 3. The problems experienced in simulating the point source contribution could be due to issues within the data analyses. As the actual output of the Belmont valley WWTW could not be measured and was unknown, it was assumed that there was no diffuse flow input from subcatchment-2. The flow measured at Site-1 was subtracted from the flow measured at Site-3 to determine the input from the WWTW. The undersimulation within the model could be due to dilution of the nitrate concentration by input of water in subcatchment 2, with the flow assigned to the point source in QUAL2K consequently being too high. The oversimulation of nitrates in validation 2 and 3 could have occurred due to the overestimation of the actual flow from the WWTW and thus, the dilution of nutrients was not representative of the actual dilution occurring in the river as a higher load was assumed to be entering the system. Subcatchment 2 contains a site of overhead irrigation and a dairy farm. Return flow from the irrigation area could be rich in nitrates due to the solubility of nitrates and the high feacal deposition on the subcatchment. The nitrate rich return flow could result in elevated observed nitrate concentrations at site 3. Data collected during the 12/06/2012 field trip indicated a diffuse input of nitrates in subcatchment 2; however, this was not observed in the data collected during subsequent trips. Although QUAL2k does allow the input of diffuse sources, it is up to the user to decide when to input a diffuse source and the quality and quantity of the input, which must be quantified through measured data or simulation within a separate model. QUAL2E was originally intended to simulate point sources only, whereas QUAL2K has the added ability of simulating both diffuse and point sources.

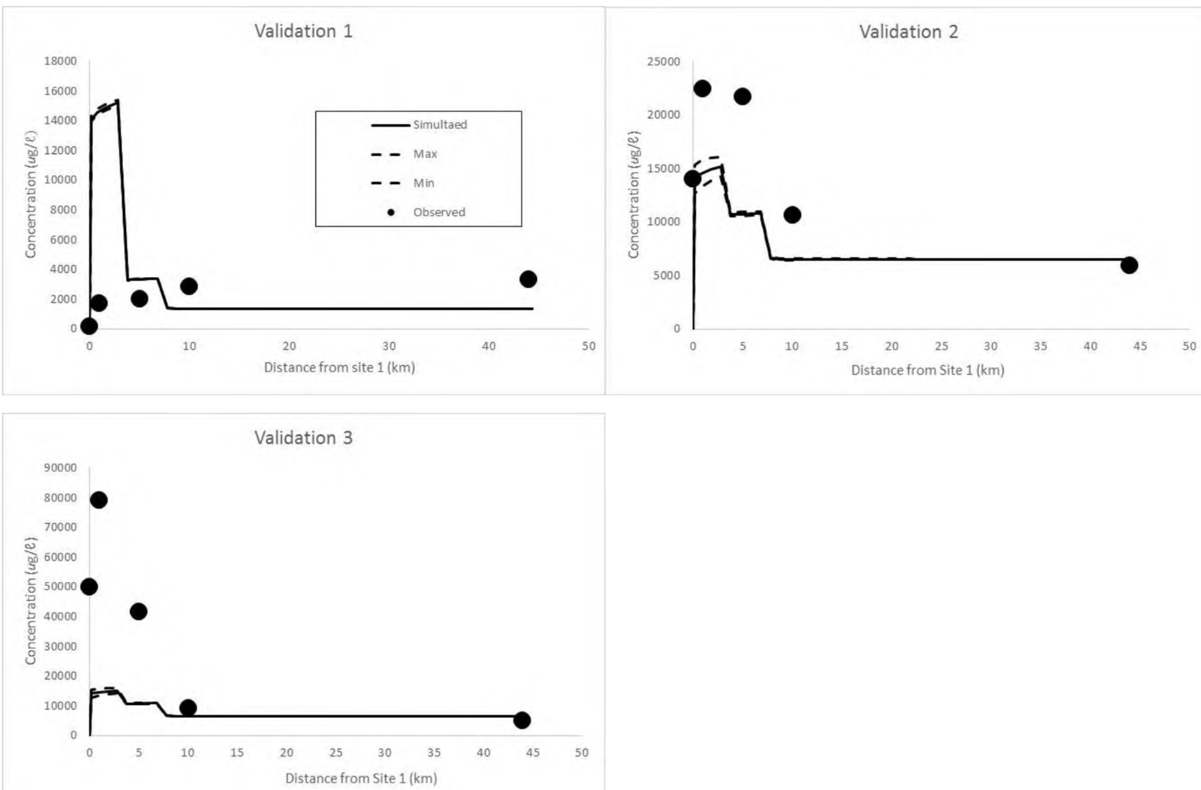

Figure 5.10: The validation results for nitrate using the calibrated QAUL2K model.

The validation of phosphate simulations were only satisfactory for validation 1 (see Figure 5.11). Validation 2 showed an under simulation of phosphates for subcatchment 2 (indicated as the 40 km upstream observed point). Validation 2 data were collected during high flows after an extreme rainfall event. Validation 3 showed an oversimulation of phosphates from the point source. However phosphate was consumed quickly within the Bloukrans River, and all validation results demonstrated that by 30 km upstream from the last monitoring point, the model was simulating the correct phosphate. The previously mentioned problem of the point source not being correctly represented by the model due to the inaccuracy of method of determining flow from the WWTW affected not only nitrates, but all water quality variables investigated in the current study. Overall, the phosphate validation results were unsatisfactory, as was observed by Slaughter (2011) who simulated water quality in the Bloukrans River using QUAL2K. The poor simulation of phosphate may be due to the misrepresentation of one or more processes affecting phosphate within the model structure.

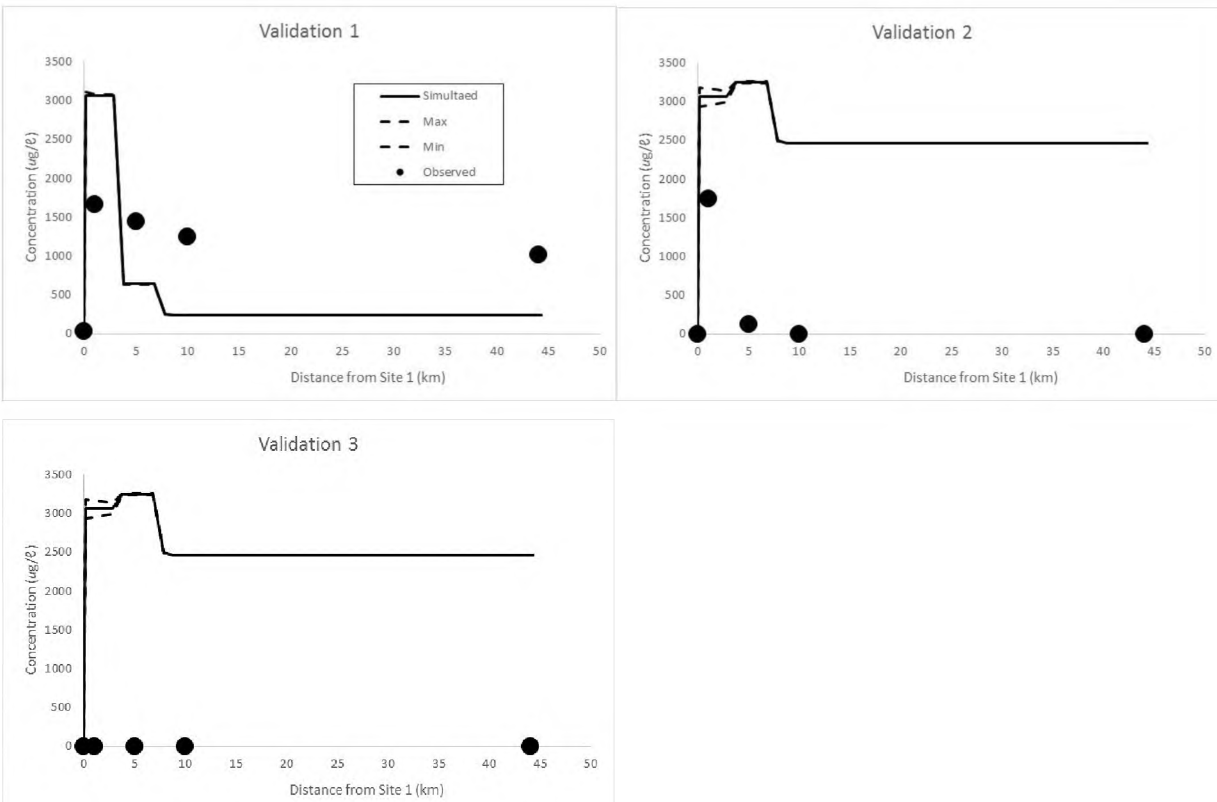

Figure 5.11: Phosphate validation results for QUAL2K.

Simulation results for ammonium showed oversimulation for validation 1 and 3 in the upper subcatchments, and satisfactory model results in the lower subcatchments (see Figure 5.12). Validation 2 indicated an undersimulation in the upper subcatchments and an oversimulation of ammonium in the lower subcatchments. Simulation of nutrients for Subcatchment 2 and the effect of the point source continued to be a challenge.

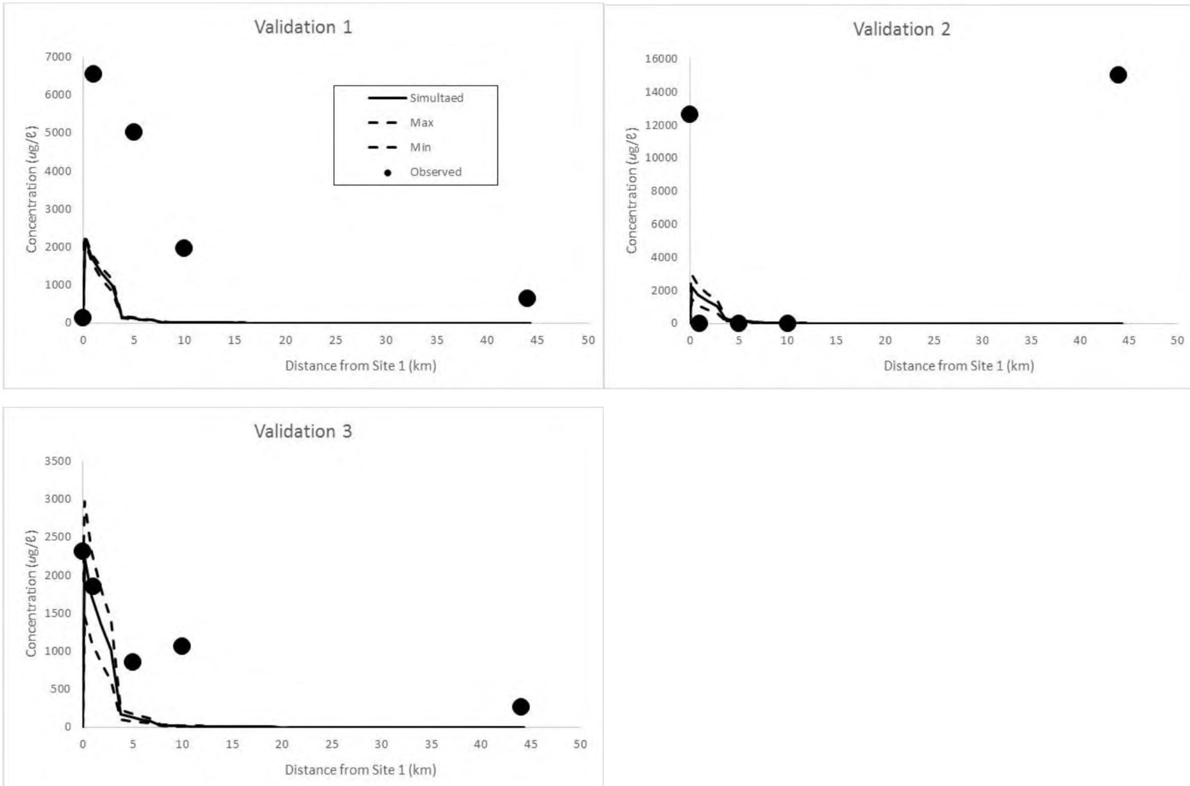

Figure 5.12: Ammonium validation results from QUAL2K.

5.5 Discussion

QUAL2K was used by Slaughter (2011) to model nutrients in the Bloukrans River with moderate success; however, all sampling and modelling for the study by Slaughter (2011) was conducted under low flow conditions. Slaughter (2011) similarly found the simulation of phosphates by QUAL2K to be a challenge. The current modelling project aimed to simulate water quality for a large range of conditions. Modelling within QUAL2K proved time consuming due to the lack of a manual providing estimated parameter values or default settings for unlimited algal growth. The need for most inputs to be measured or determined from data also proved time consuming. The use of QUAL2K to simulate nutrients over a wide range of conditions did not result in successful simulation of observed conditions. The shortcoming within the model predominantly accounting for the poor simulations was the representation of the point source in the model. The inaccurate representation of the point source may have been due to the method for determining the flow of the WWTW outflow for the sampling, resulting in the overestimation of nutrient loads entering the Bloukrans River. However not all simulations led to overestimations. The crude nature of determining streamflow and outflow of the WWTW may have led to inaccuracies in the data. However, this method was the most accurate measure available to the project and would be the method used in streamflow measurement of small streams. The simulations of nitrate did not accurately represent the consumption of nitrates from the system, which may have been due to dilution, assimilation by algae and macrophytes, denitrification or the release of nitrogen gas due to the high nitrate concentrations found. The model appeared to not be sensitive enough to achieve sufficient consumption of nitrates by the adjustment of parameters values. The high consumption rate of phosphates appeared to have been simulated relatively well; however, the high variation of phosphates found in the WWTW effluent may have contributed to the poor simulation of the phosphates in QUAL2K. The simulation of ammonium was similarly compromised by the poor representation of the WWTW point source in the model. However, the overall trend in ammonium concentration was relatively well represented in QUAL2K. Overall, QUAL2K did not perform to a satisfactorily level over a range of conditions; the method utilised by the model to simulate a point source may only be affective for an effluent with a very low variation in discharge quantity and quality. QUAL2K is data intensive compared to the MBN model. The data required to run the model is more time consuming and costly to measure. The requirement of diel data considerably adds to the amount of observed data required. The model was run on what was assumed to be the minimum data requirements to obtain a results by the model, which may have contributed to the relatively poor simulation of nutrients. QUAL2K has been applied successfully and is the model of choice for point source modelling in the USA and Europe. However, most previous studies using QUAL2K modelled much larger river systems where the influence of the point source on the overall water quality was not as severe as in the case of the Bloukrans River.

6. SIMPLE MASS BALANCE NUTRIENT MODEL

6.1 Introduction

The simple Mass Balance Nutrient (MBN) model is a Microsoft Excel based decision support system. The model was developed 'in-house' at the Institute for Water Research, specifically for the Bloukrans River system. Loucks *et al.* (2005) stated that a simple, but nevertheless useful approach to water quality modelling is to assume dilution to be the greatest factor affecting nutrient concentrations. Dilution modelling requires quantification of point and diffuse inputs to the river and assumes nutrient chemical species to be conservative. In actual fact, it is known that nutrient species are non-conservative (refer to Chapter 2). The modelling of the Bloukrans River using QUAL2K showed a strong influence of periphyton growth on nutrient concentrations and thus, it was decided to implement a simple algae model modified from CE-QUAL-W2 (Cole and Wells, 2008) within the MBN model framework. The simple algae model in addition takes into account nitrogen speciation (nitrification of ammonium to nitrate). A simple regression was taken from observed data to simulate the nutrient signatures originating from the Grahamstown urban area and surrounding upland catchment (see Figure 6.1). As this approach is simple, it does contribute to a high degree of uncertainty to the model.

The framework of the MBN model allows for separate nutrient signatures to be assigned to runoff events and low flows. Low flows are severely impacted by highly variable flow sources originating from the urban area. Certain nutrients showed stronger relationships to flow within the river; this was especially true for nitrates. Phosphates and ammonium showed high variability within this relationship, with very little correlation to flow; thus, they were difficult to model accurately.

The MBN model divides the modelled river into segments. Each segment is associated with a specific volume, and a mass balance of each water quality constituent is calculated for each time step. This is similar to the 'plug flow' technique used in QUAL2K described in Chapter 5.

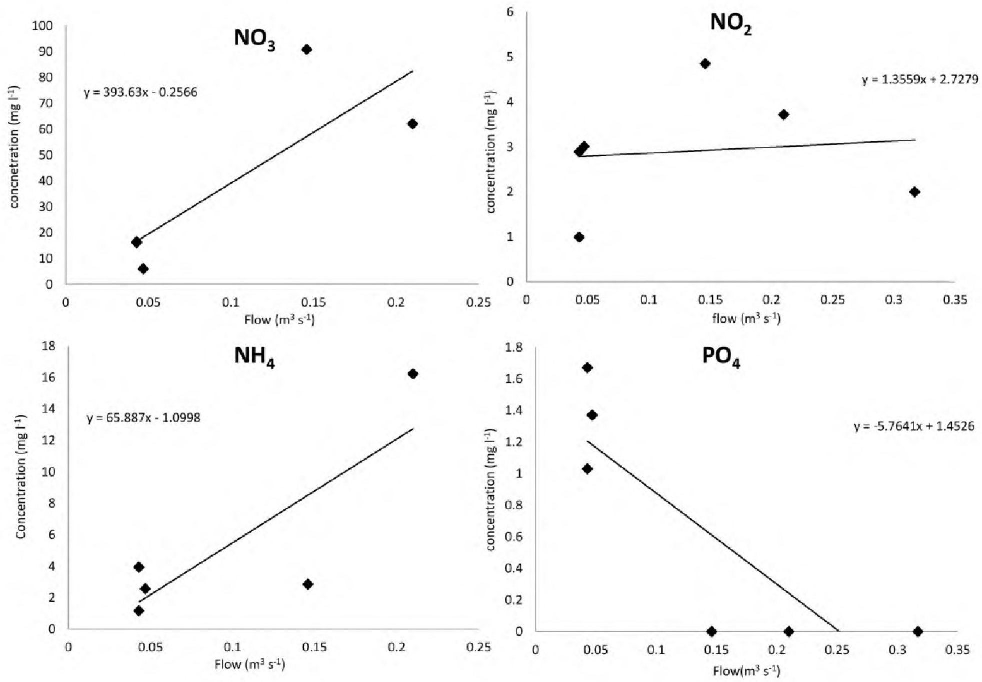

Figure 6.1: Simple regression curves derived from observed data for the Bloukrans River used in the Mass Balance Nutrient model.

The MBN model was run on a daily time step. The subcatchments were treated as model segments for the calculation of the hydrology, with daily volume being calculated by converting daily flow into a volume, which then enabled the conversion of nutrient concentrations to daily loads. Flow was assumed to be steady state throughout each day. A simple equation was used to converting loads to concentrations and vise verse:

$$C \text{ (mg } \ell^{-1}) = \text{load (mg)/volume } (\ell) \quad (6.1)$$

Although algae present in the system do assimilate nutrients from the water, the death and decay of algae release nutrients back into the water.

As input data, the model requires rainfall and evaporation data for the calculation of flow, as well as maximum and minimum nutrient concentrations from the WWTW to calculate nutrient concentrations. The Soil Conservation Service (SCS) (Mishra and Singh, 2003) rainfall-runoff equation was used to convert rainfall and evaporation data into flow values for the Bloukrans River. The runoff for each subcatchment (see Figure 4.1) was simulated separately. Using the data from Site-1 and comparing concentrations to flow, an algorithm was created to derive concentrations from surface runoff for a given flow value. A single ground water sample was collected to obtain an indication of interflow nutrient concentrations, and this value was applied as a constant to the interflow flow fraction, with only nitrate being found in the groundwater sample at a relatively small concentration.

6.2 Modelling procedure

The simple model was created using Microsoft Excel. The first step within the model is to simulate runoff in each subcatchment. Runoff simulation was accomplished using the SCS algorithms as shown in Equation 6.2 through 6.3:

$$Q = (P - I_a)^2/(P - I_a + S_{pm}) \tag{6.2}$$

Where Q (mm) is runoff, P (mm) is precipitation, S_{pm} (mm) is the potential maximum storage and I_a is the initial abstraction. Potential maximum storage is the difference between absolute maximum storage (S_{AM}) set at 240mm and the current storage (S) set at 150mm in the soil. (S_{AM}) is the amount of water the soil can hold when it is at the driest possible point, and is determined considering depth, porosity and water retention characteristics of the given soil. The initial abstraction (I_a) is calculated using Equation 6.3.

$$I_a = cS \tag{6.3}$$

The initial loss co-efficient is dependent on rainfall amount, intensity and duration as well as antecedent conditions and season, as found by Schulze *et al.* (1992). Rainfall duration and intensity has a correlation to seasonality and thus, the c parameter is adjusted for seasonality using the RDIST (rainfall distribution) parameter as shown in equation 6.5. To calculate storage, Equation 6.4 is used:

$$\Delta S = P - Q - E \tag{6.4}$$

Where E is actual evaporation (mm). The adjustment of the c parameter for seasonality is calculated using Equation 6.5:

$$c' = c * (RDIST/24)^{\frac{1}{2}} \tag{6.5}$$

RDIST is the rainfall distribution factor, and factors for changes in intensity and duration of rainfall events according to the season. *RDIST* values used January: 8 February: 10 , March: 12 ,April: 13 , May: 14 , June: 15, July: 15, August: 14, September: 12 , October:14 , November:14 , December: 8

Low flows are calculated separately to runoff, and account for sub-surface flow from the water table and groundwater into the channel. This was achieved using the Pitman low flow equation (Pitman, 1973) as shown in Equation 6.6.

$$Q_{GW}\,(mm) = FT \times (S/S_{AM})^{POW} \tag{6.6}$$

The *FT* (maximum soil moisture runoff (mm)), set at 2.6 for the impervious area and 4 for the pervious areas, and *POW* (power of relationships) set at 2 for the impervious areas and 3 for the pervious areas, parameters are adjusted during the calibration process to fit the observed data. The determination of low flows is important to facilitate the simulation of water quality, as low flows may dilute instream nutrients, or as in the case of catchments dominated by marine derived geology, low flows may contribute to higher instream salinity.

Evaporation (E) is calculated separately for the pervious and impervious areas, but both using Equation 6.7; however, the values of S, S_{AM} and R parameters will differ between the pervious and impervious area.

$$E = \; E_{REF} \times (1 - (1 - S/S_{AM})/((1 - R) \times (1 - PE/PE_{MAX}) \;\;) \tag{6.7}$$

Where E_{REF} is the reference evaporation, R is a model parameter, PE (mm) is potential evaporation set at 1500 mm/a, and PE_{MAX} (mm) is maximum potential evaporation. In Subcatchment-1 (refer to Figure 4.1), the urban area (Grahamstown) is simulated as an impervious area. The impervious area is characterised by low infiltration and storage due to the impermeable nature of roads and buildings, which contribute to a high runoff for a given precipitation. The surrounding grassland and farm lands were modelled as pervious areas. Pervious areas are characterised by comparably high infiltration and storage when compared to an impervious area. The infiltration and storage is determined by the depth, porosity, connectivity of pores, water holding capacity and antecedent conditions of the soil. Using the SCS algorithm, surface runoff and sub-surface interflow were simulated separately for a more realistic representation of the system.

Failing municipal infrastructure within the Makana Municipal area posed complex problems when modelling nutrients. Leaking sewerage and water pipes contributed a significant amount of flow to the Bloukrans River (see Figure 6.2). The problem of sewerage leaks within the Makana district is well documented by the Kowie Catchment Campaign (www.kowiecatchmentcampaign.org.za, last accessed 17 January 2014).

Figure 6.2: A sewerage leak flowing into the upper catchment of the Bloukrans River near Nathaniel Nyaluza School during 2013.

The sewerage leaks contribute nutrients and flow, whereas leaking tap water pipes act to dilute the nutrients emanating from the sewerage leaks. It was thus decided to model Subcatchment-1, which consists of vegetation and the urban spread of Grahamstown, as both a diffuse source of nutrients and a point source. The point source model accounts for the sewerage and water leaks within Grahamstown. Although the actual quantity and quality of water contributed by these leaks was never measured, a calibration process was used to effectively model the leaks. Point sources are responsible for elevated nutrient concentrations at low flows, whereas diffuse sources are responsible for elevated concentrations at high flows. The point source was modelled using a random number generator linked to maximum and minimum flow and a separate random number generator to estimate each nutrient concentration within a range of a maximum and minimum concentration, similar to the method used by Slaughter and Hughes (2013). Maximum and minimum concentrations used for each nutrient were calibrated; observed concentrations were used only as a guideline as natural flow at Site-1 diluted point source concentrations. Sub-catchment 1 was also modelled as a diffuse source, contributing nutrients during runoff events.

Diffuse nutrient sources were simulated for both surface runoff and sub-surface interflow. Surface runoff nutrients were modelled using the equations derived from graphs by plotting nutrient concentration against flow. For nitrate concentration [NO_3] in the stream at Site-1, Equation 6.8 was used to represent the relationship between concentration and flow. Equations 6.8–6.11 were only used to simulate runoff concentrations for subcatchment 1. Knowledge of the system showed no addition of nutrients at low flows for downstream subcatchments, which was confirmed by model calibration. However, during runoff events, the input of nutrients will occur in downstream subcatchments; thus, nutrient signatures were assigned to runoff values. Knowledge on runoff nutrient contributions is limited, and hydrologic modelling of exact flow paths is necessary to accurately simulate transport of nutrients from the catchment to the stream. Antecedent rainfall conditions within the catchment add more complexity to the simulation of nutrients carried from surrounding landscapes to the river. 'Antecedent' literally means 'before', and the recent rainfall record within a catchment as well as land use will determine nutrient storage available within the catchment. A dry period will allow a build-up of nutrients on the catchment surface. A large rainfall event following a dry spell with be associated with a short pulse of high nutrient concentration runoff, or a 'first-flush' event (Simpson and Stone, 1988). During prolonged wet spells, there is a limited load of nutrients stored within the catchment, and runoff will have a relatively low nutrient concentration. Due to the simple approach adopted within the MBN model, the wash-off of nutrients was simulated using a statistical approach as opposed to a mechanistic approach; however, limited data were available to determine flow-nutrient concentration relationships.

Nitrate concentration [NO_3] in streamflow was calculated using Equation 6.8.

$$[NO3] = (Q \times 393.63) - 0.26 \tag{6.8}$$

Nitrite concentration [NO_2] in streamflow was calculated using Equation 6.9.

$$[NO2] = (Q \times 63.51) - 2.02 \quad (6.9)$$

Ammonia concentration [NH_4] in streamflow was calculated using Equation 6.10.

$$[NH4] = (Q \times 17.542) + 2.59 \quad (6.10)$$

The concentration of phosphate [PO_4] was calculated using Equation 6.11.

$$[PO4] = (Q \times (-0.0072)) + 1.64 \quad (6.11)$$

No nutrient signature was assigned to interflow or runoff within subcatchments that showed no indication of diffuse nutrient input. Subcatchments characterised by diffuse nutrient inputs were assigned nutrient signatures that were adjusted to simulate the characteristics of the subcatchment. Subcatchment 1 was assigned a nutrient signature for high flows only, whereas a point source model was used to simulate the effect of leaking wastewater and potable water pipes on instream nutrient concentrations. A single groundwater sample collected during the study showed the presence of only nitrate; however, this sample was collected in Belmont Valley, and might not be representative of the nutrient concentrations of the interflow originating from the town of Grahamstown. Concentrations (mg ℓ^{-1}) of the separate nutrients were then converted to a load (mg) using Equation 6.12.

$$L = C * V \quad (6.12)$$

Where, L is load (mg), C is concentration (mg ℓ^{-1}) and V is the volume (ℓ).

Flow simulated using the SCS runoff equation and the Pitman low flow equation was converted from $m^3 s^{-1}$ to ℓd^{-1} to obtain the daily volume, and to convert nutrient concentrations to ℓd^{-1}.

The Point Source Model (PSM) (Slaughter and Hughes, 2013) was created to simulate nutrient and flow inputs from the Grahamstown WWTW. No relationship between flow and nutrient concentration was evident between the observed flow and nutrient data collected for the Belmont Valley WWTW; thus, a random number generator was used to create a range of random flows between the minimum and maximum flow measured. A separate random number generator was used to determine nutrient concentrations, as the concentrations of nutrients and the flow from the WWTW varied randomly and showed no correlation to one another. The parameter values used within the PSM are shown in Table 6-1. Although this method does not provide an accurate simulation for a given day, the PSM does achieve an accurate frequency distribution over an extended period of time for nutrient loads originating from the point source.

Table 6-1: Maximum and minimum flow and nutrient concentrations used to simulate effluent discharge from the Belmont Valley waste water treatment work using the Point Source Model (Slaughter and Hughes, 2013).

Variable	Maximum	Minimum
Flow (m^3 s^{-1})	0.112	0.028
Nitrate (mg ℓ^{-1})	329	65
Nitrite (mg ℓ^{-1})	10.39	8.37
Ammonium (mg ℓ^{-1})	20.38	1.65
Phosphate (mg ℓ^{-1})	0.9	0.59

The simulations from QUAL2K and chlorophyll data collected in the field indicated that benthic algae (periphyton) were dominant in the stream (see Figure 6.3), and the algal community was one of the main factors affecting nutrient concentrations within the modelled stretch of the Bloukrans River.

After preliminary calibrations, it was decided to implement a simple algae model within the MBN model. Equations adopted from the CE-QUAL-W2 model were modified to simulate benthic algal growth, respiration, decay and nutrient uptake in a simplified manner. CE-QUAL-W2 is utilised for simulating water quality in lakes and reservoirs, but has been shown to be best suited to long, narrow water bodies (Cole and Wells, 2008). Although the algorithms used within CE-QUAL-W2 have been modified for use within a river water quality model, the broad conceptual understanding of algal processes are the same for reservoirs and rivers. Since the MBN model is much simpler than CE-QUAL-W2 model, various processes included in algal modelling within CE-QUAL-W2 were excluded from the processes represented within the MBN model. Table 6-2 summarises these changes.

Figure 6.3: Strings of filamentous algae (*Batrachospermum*) attached to the stream bed of the Bloukrans River at Site 5.

Table 6-2: Comparison of the algal simulation between the Mass Balance Nutrient model and the CE-QUAL-W2 model.

Variable	MBN model	CE-QUAL-W2
Dissolved oxygen	No	Yes
Predation by Zooplankton	No	Yes
Algal grouping	Single group representing all algae	Multiple taxonomic groups can be simulated
Algal assimilation	Allows for the assimilation of NH_4 as well as NO_3	Only simulates the assimilation of NH_4

Estimations of reach length and hydraulic radius for each modelling segment were used to calculate benthic algae biomass within the modelled segment. Water temperature was calculated using a simple regression model driven by maximum and minimum air temperatures (See Equation 6.13) (Rivers-Moore *et al.,* 2008).

$$WT_{max} = C + (A \times AT_{avr}) + (B \times AT_{min}) \quad (6.13)$$

Where WT_{max} is the maximum water temperature for the day, A (1.089), B (-0.097) and C (1.655) are model parameters, AT_{avr} is the average air temperature for the day and AT_{min} is the minimum air temperature for the day. Water temperature affects the growth and respiration rate of algae. Algal growth and respiration were determined using an optimal growth model approach (Chapra, 1997).

The equations were modified to exclude variables that were not required in the modelling of nutrients and algae, considering these processes to be negligible in effect on nutrient concentrations to warrant their inclusion in the current study. Negated variables included dissolved oxygen, inorganic carbon, silica, macrophytes, sediments, zooplankton and carbonaceous biochemical oxygen demand.

The rate equation for epiphyton growth is shown in Equation 6.14:

$$[\text{periphyton}]_{i+1} = [\text{periphyton}]_i + ((K_{eg} - K_{er}) \times [\text{periphyton}]_i) \quad (6.14)$$

Although K_{eg} (periphyton growth rate) and K_{er} (periphyton respiration rate) are set parameter values for growth and respiration at 25 °C, both are adjusted for water temperature accordingly using the Optimal Temperature Model (Chapra, 1997). Upper limits of periphyton concentration were placed to constrain the growth of periphyton in the model based on the hypothesis that there is limited substrate for periphyton to grow on and crowding effects would probably limit periphyton growth to some extent.

$$K_{eg} = 0 \qquad (T \geq T_{max} \text{ or } T \leq T_{min}) \quad (6.15)$$

$$K_{eg} = K_{eg.opt} \times \left(\frac{T - T_{min}}{T_{opt} - T_{min}}\right) \qquad (T_{min} \leq T \leq T_{opt}) \quad (6.16)$$

$$K_{eg} = K_{eg.opt} \times \left(\frac{T_{max} - T}{T_{max} - T_{opt}}\right) \qquad (T > T_{opt}) \quad (6.17)$$

Where T is water temperature, K_{eg} is epiphyton growth rate, T_{max} is the maximum water temperature that will enable algal growth, T_{opt} is the optimum water temperature for algal growth and T_{min} is the minimum temperature required for algal growth.

K_{er} is updated for temperature using the same temperature parameters and equations as K_{eg}. Algal growth is of course limited by nutrient availability. An approach was adopted of updating the values of K_{eg} and K_{er} accordingly to reflect the limiting nutrient effect on algal growth. Firstly, an assumption that nutrients are unlimited is made, and then nutrient uptake is calculated for each nutrient separately using the unaltered K_{eg} and K_{er} values.

Unlimited nitrate and nitrite uptake is calculated as:

$$Unlimited\ N\ uptake = (K_{eg} - K_{er})(\delta_{NA})\left([periphyton] \times \frac{A}{V}\right)(1 - P_{NH4}) \quad (6.18)$$

Unlimited NH_4 uptake is calculated as:

$$Unlimited\ ammonium\ uptake = (K_{eg} - K_{er})\ (\delta_{NA})\left([periphyton] \times \frac{A}{V}\right)(P_{NH4}) \quad (6.19)$$

Unlimited PO_4 uptake is calculated as:

$$Unlimited\ Phosphate\ uptake = (K_{eg} - K_{er})\ (\delta_{PA})\left([periphyton] \times \frac{A}{V}\right) \quad (6.20)$$

Where δ_{NA} is the nitrogen composition of algae represented as a fraction of wet biomass (set at 0.03), δ_{PA} is the phosphorus composition of algae represented as a fraction of wet biomass (set at 0.01), A is the area of river bed occupied by periphyton, V is the volume of water in the river for that particular day and P_{NH4} is the ammonium preference of algae represented as a fraction, where $1 - P_{NH4}$ would be the nitrate + nitrite preference of algae. The equations calculate the concentration of periphyton as mg ℓ^{-1}; hence, the surface area of periphyton and volume of water in the reach is used within the calculation.

Using the unlimited nutrient uptake concentrations and the known concentration of each nutrient in the reach, the limiting nutrient ratio is then calculated. The limiting nutrient ratio is calculated by dividing the available nutrient concentration by the required nutrient concentration considering the set algal growth parameter. If the ratio is < 1 for any of the three nutrients, indicating that a nutrient is limiting, then K_{er} and K_{eg} are adjusted accordingly by multiplying the K_{eg} and K_{er} updated for temperature by the lowest limiting nutrient ratio for phosphate, ammonium and or nitrate + nitrite. The periphyton concentration is then calculated using the K_{eg} and K_{er} updated for nutrient availability. Thereafter, nutrient uptake is calculated for updated available nutrient concentrations for each of the nutrients. Nitrification is taken into account in both the ammonium rate change equation and the nitrate-nitrite rate change equation.

$$[N]_{i+1} = [N]_i - ((K_{eg} - K_{er}) \times [\text{periphyton}]_i \times (1 - P_{NH4}) \times \delta_{NA}) + ([A]_i \times K_N \times \theta_N^{(T-20)} \quad (6.21)$$

Where $[N]_i$ is the nitrate + nitrite concentration at time step i, [A] is the concentration of ammonia, K_N is the nitrification rate, T is the water temperature and θ_N (set at 1.047) is a parameter value used to adjust K_N (set at 0.1) according to water temperature.

Rate equation for ammonium:

$$[A]_{i+1} = [A]_i - ((K_{eg} - K_{er}) \times [\text{periphyton}]_i \times (P_{NH4}) \times \delta_{NA}) + ([POM]_i \times K_{POM} \times \theta_{POM}^{(T-20)} \times \delta_{NPOM}) + ([DOM]_i \times K_{DOM} \times \theta_{DOM}^{(T-20)} \times \delta_{NDOM}) + ([OS]_i \times K_{os} \times \theta_{OS}^{(T-20)} \times \delta_{NOS}) - ([A]_i \times K_N \times \theta_N^{(T-20)}) \quad (6.22)$$

Where $[A]_i$ is the ammonium concentration at time step i, [POM] is the concentration of particulate organic matter, K_{POM} (0.01) is the degradation rate of POM, θ_{POM} (1.047) is a parameter value used to adjust K_{POM} according to water temperature (Chapra, 1997), δ_{NPOM} (0.03) is the nitrate + nitrite N composition of POM represented as a fraction, [DOM] is the concentration of dissolved organic matter, K_{DOM} (0.001) is the degradation rate of DOM, θ_{DOM} (1.047) is a parameter value used to adjust K_{DOM} according to temperature, δ_{NDOM} (0.03) is the nitrate + nitrite N composition of DOM, [OS] is the organic sediment in the reach represented as a concentration, K_{OS} (0.001) is the degradation rate of OS, θ_{OS} (1.047) is a parameter value used to adjust K_{OS} according to temperature and δ_{NOS} (0.01) is the nitrate + nitrite N composition of OS represented as a fraction,.

Rate equation for phosphate:

$$[P]_{i+1} = [P]_i - ((K_{eg} - K_{er}) \times [\text{periphyton}]_i \times \delta_{PA}) + ([POM]_i \times K_{POM} \times \theta_{POM}^{(T-20)} \times \delta_{PPOM}) +$$

$$([DOM]_i \times K_{DOM} \times \theta_{DOM}^{(T-20)} \times \delta_{PDOM}) + ([OS]_i \times K_{os} \times \theta_{OS}^{(T-20)} \times \delta_{NPOM}) \quad (6.23)$$

Where $[P]_i$ is the phosphate-P concentration at time step i, δ_{NPOM} (0.01) is the phosphorus composition of POM represented as a fraction, δ_{PDOM} (0.01) is the phosphorus composition of DOM and δ_{POS} (0.01) is the phosphorus composition of OS represented as a fraction.

Denitrification was assumed to be negligible due to the aerobic nature of the system; besides, since the MBN model does not simulate DO, denitrification could not be considered.

The breakdown of dissolved organic matter and particulate organic matter, which are due to death and decay of periphyton, release phosphates and ammonium back into solution. Settling of organic matter produces organic sediment where nutrients are stored until flushed out of the system by a large streamflow event.

Within the algae model, periphyton concentration was limited to a certain upper limit, as it is impossible for unlimited growth of periphyton to occur. The upper limit set for each catchment reach was based on observed data. Flushing of periphyton at high flows was achieved by assigning a flow rate threshold that had to be exceeded for flushing to occur. The assumption was made that exceedance of a certain threshold of flow would cause scouring of the organic sediment, effectively resetting the organic sediment storage within the reach. The flushing of organic sediment is an example of a nutrient sink, where a load of nutrients can effectively be taken out of the mass-balance accounting for that catchment. After a flushing event, the concentration of periphyton was set to the lower limit of the observed data, as it can be expected that a certain proportion of periphyton would be lost as well. Suspended DOM and POM are flushed in a similar manner. DOM, POM, periphyton biomass and organic sediment represent the storage of nutrients within a subcatchment. The flow required to be exceeded to flush periphyton, DOM, POM and organic sediment is decided by the modeller according to field observations as well as the characteristics of the specific subcatchment.

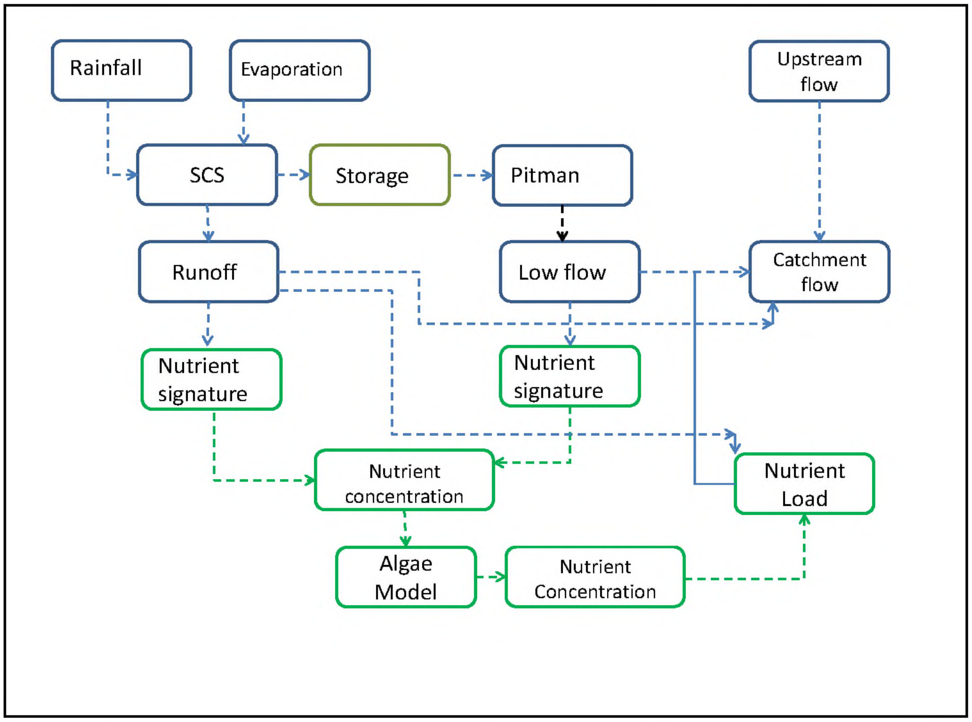

Figure 6.4: Conceptualisation of the Mass Balance Nutrient model structure.

6.3 Calibration

Calibration is the term given to determining the appropriateness of the parameter values used in the model setup, whereby the model parameter values are adjusted so as to obtain simulated results that are as closely representative of observed data as possible. Within the MBN model, the runoff and low flow modules were initially calibrated to simulate streamflow to match observed streamflow data as closely as possible. It is important that the water quantity processes in the model be simulated as accurately as possible, as errors within the quantity simulation are amplified within the water quality simulation. As the runoff from Subcatchment-1 (refer to Figure 4.1) is a driver of instream nutrients at sample Site-1 (refer to Figure 3.1) it is imperative to accurately simulate runoff and low flows. The parameters used in the SCS runoff equation required calibration for the Bloukrans River catchment. However, flow data for the Bloukrans River were limited to a series of flow depths for the 1992–1996 period, as well as seven observed points for each sample site over the 2009–2013 period. The evaporation data used for the period of the current study did not extend far enough to cover the temporal period of the flow depth data; therefore, the evaporation data had to be simulated using the Hargreaves and Samani (1982) daily evaporation equation as shown in Equation 6.24:

$$ET_0 = 0.408 \times 0.0023 \times (Tmean + 17.78)(Tmax - Tmin)^{0.5} R_a \qquad (6.24)$$

The co-efficient value of 0.408 is used to convert MJ m^{-2} d^{-1} into mm d^{-1}. The value of 0.0023 is the Hargreaves and Samani (HS) co-efficient used in the original equation. *Tmax* and *Tmin* were obtained from climatic data. Ra is the radiation index computed from latitude and Julian day. The HS evaporation values were adjusted to the reference evaporation by weighting the annual average evaporation of both values. The actual evaporation was then calculated using Equation 6.24. To assess whether the evaporation was being correctly simulated, the HS adjusted evaporation was plotted on the same graph as the actual evaporation for the 2012–2013 period. The graph should show a pattern of seasonality in the evaporation, with lower evaporation during winter months as compared to summer months. The graphs were additionally assessed for outliers, which would indicate errors in the data. Calibration of streamflow was then achieved by adjusting parameter values, either in the SCS runoff equation for simulating high flows or in the Pitman low flow equation when sub-surface flow required adjustment. Parameters values were adjusted iteratively until a satisfactory calibration was achieved. Although only flow depths were available for calibration, these data provide a good indication of drying and wetting patterns in the catchment, allowing for crude calibration of streamflow.

Although the calibration of streamflow appears crude (refer to Figure 6.5), the observed data are a mix of an average of multiple readings from a day or a single reading for a day, depending on data available. However, the simulated values show the average daily streamflow. Changes in catchment conditions within Subcatchment-1 may have resulted in the calibrated parameters used for the 1992–1995 period being inappropriate for the current observations in Subcatchment-1. Possible land-use changes within the subcatchment could include an increasing are of irrigated agricultural fields as well as a greater number of leaking water and sewerage pipes. The increasing population within the urban area has resulted in a larger volume of water in the system. The growing urban population would also result in a higher proportion of impervious area within the catchment as more land is developed.

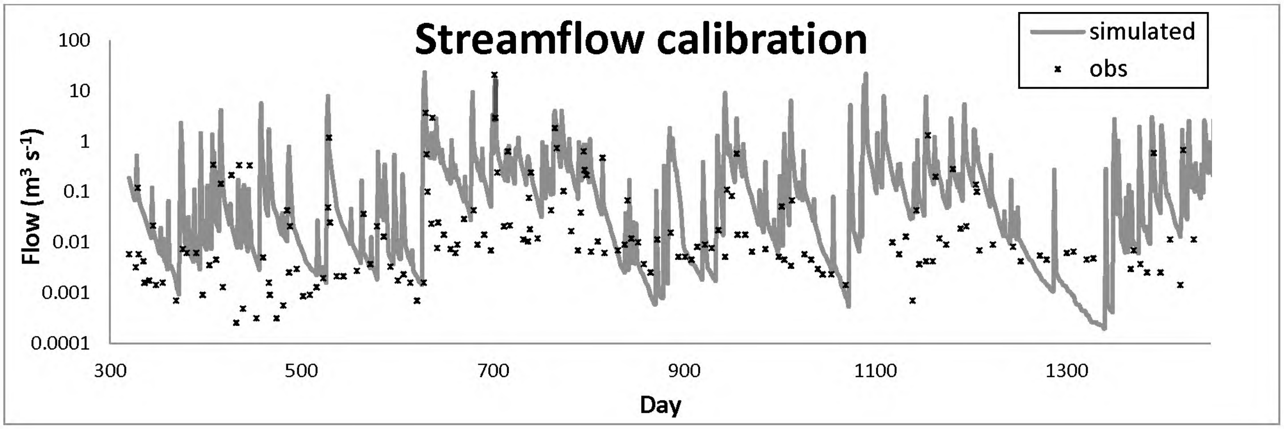

Figure 6.5: Soil Conservation Service streamflow calibration for Subcatchment-1. The simulation was run for the period from 1992 to 1995.

The streamflow parameters from the 1992 calibration were only useful for Subcatchment-1. The downstream subcatchments were calibrated by adjusting streamflow parameters in an attempt to match simulated data to observed data.

Calibration of the nutrients was accomplished by running the MBN model as a fate model and adjusting parameters in each sub-catchment to influence nutrient fates. When the model is run as a fate model, the upstream and point source inputs are input manually from observed data. By manually inserting observed values, the modeller avoids the uncertainties of the two point source models for the given day, as these are stochastic models. When calibrating the entire model as a fate model, it is not necessary to simulate flow and nutrient input for Subcatchment-1, as these values are inputted manually; however, when running the model as a dynamic model, it is necessary to simulate flow and nutrient input for Subcatchment-1. Subcatchment-1 consists of a point source to represent broken sewerage and water pipes, a pervious area to represent the area around Grahamstown that is not occupied by buildings or roads, and an impervious area to represent the built up parts of Grahamstown. Each area contributing streamflow and nutrients within Subcatchment-1 requires calibration. It is difficult and impractical to measure flow and nutrient concentrations for each part of Subcatchment-1; therefore, parameters are adjusted for each area until the overall output from the catchment matches the observed data. Scientific knowledge was in addition utilised to appoint nutrient contributions to each area. Nutrient signatures for each area were adjusted as well as flow parameters until satisfactory results were achieved.

The WWTW model did not require calibration due to the stochastic modelling approach used. Further data collection could show trends within the effluent flow and concentrations; however, the data collected during the present study showed no correlation. The waste water infrastructure of Grahamstown is used to transport some storm water; consequently, the system becomes flooded during large runoff events. During the 25th of September 2012 sampling trip, three outflows were identified at the Belmont Valley WWTW, with all three characterised by extremely high nitrate concentrations and very little of the other nutrient species. Two of the outflows originated from overflowing storage ponds and thus contained untreated sewerage. This observation is of relevance as it is the general opinion that point sources have the highest impact on the instream water quality during low flows, which is what would occur in an ideal situation. However, the inability of the WWTW to cope with high volumes of sewage often results in little or no treatment occurring when large volumes are encountered; consequently, large volumes of partially treated or raw sewage are released into the river.

All the subcatchments started with the same parameter values as Subcatchment-1 (refer to Figure 4.1); however, Subcatchment_1 was the only subcatchment with an impervious area. The land use within subcatchments below Subcatchment-1 included natural bush and agriculture, and were thus modelled by lumping the two land uses into a single land use. Streamflow calibration for Subcatchments-2 to Subcatchment-5 was achieved by adjusting the SCS and Pitman parameter values to obtain simulated data to closely match observed data. Calibration of streamflow within Subcatchment-2 was complicated due to irrigation during low flows. The irrigation was being applied to produce grazing for dairy cattle. Return flow containing nutrients was suspected to be entering the Bloukrans River within Subcatchments-2 and 3.

The initial calibration of nutrients was accomplished by treating the model as an instream nutrient fate model. Initially, the instream nutrients were simulated using the equations used to simulate nutrients for Subcatchment-1. However, most of these catchments showed no signs of nutrient input into the Bloukrans River. It was assumed that dilution was the main factor affecting changes in nutrient concentrations down the river reach. It became apparent that certain nutrients were being stored in the system, as dilution did not account for a sufficient decrease in concentration. Modelling runs that showed a good calibration of flow produced the most accurate nutrient concentration simulation.

The calibration results as shown in Figure 6.6 for the MBN model were achieved by operating the model as a fate model. Flow and nutrient concentrations were inputted manually for the Belmont Valley WWTW and Site-1. The calibration of nutrients was accomplished by adjusting the parameter values within algorithms that control nutrient concentrations within the subcatchment, until simulated values were a reasonable representation of observed data. The streamflow results show a satisfactory fit; however, it must be noted that the model was still being run as a dynamic model and as such, the input from the point source affected the results. As mentioned before, the PSM aims to represent the long-term frequency distribution of instream nutrient concentrations, and any one particular time series simulation may overestimate or underestimate quantity and quality for the specific day. Nitrate simulation was satisfactory, with the model representing the observed trends; however, the oversimulation of the nitrate in the wastewater effluent resulted in higher simulated values in lower subcatchments than observed values. Ammonium was highly variable within the catchment and did not show trends according to flow, and as such, calibration was difficult to achieve and resulted in poor, unsatisfactory calibration. The final observed point for the ammonium calibration indicates either a diffuse input of ammonium from irrigation return flow or a point source of ammonium is located in Subcatchment-5. The lack of a rise in nitrates within the same catchment indicates that this may not be as a result of a diffuse source and could be a laboratory error or an ammonium source close to the monitoring point. Phosphates were well represented in the upper catchment; however, the rapid loss of phosphorus could not be simulated, as dilution and algal uptake did not account for the rapid loss of phosphates in the system, this could be attributed to sediment uptake of phosphorus. Sediment uptake by phosphorus was not modelled as the upper catchment is an urban catchment and thus contained very little inorganic sediemnts. It must also be noted that although the simulated trend does not exactly represent the observed data, the variation between the two concentrations is minimal.

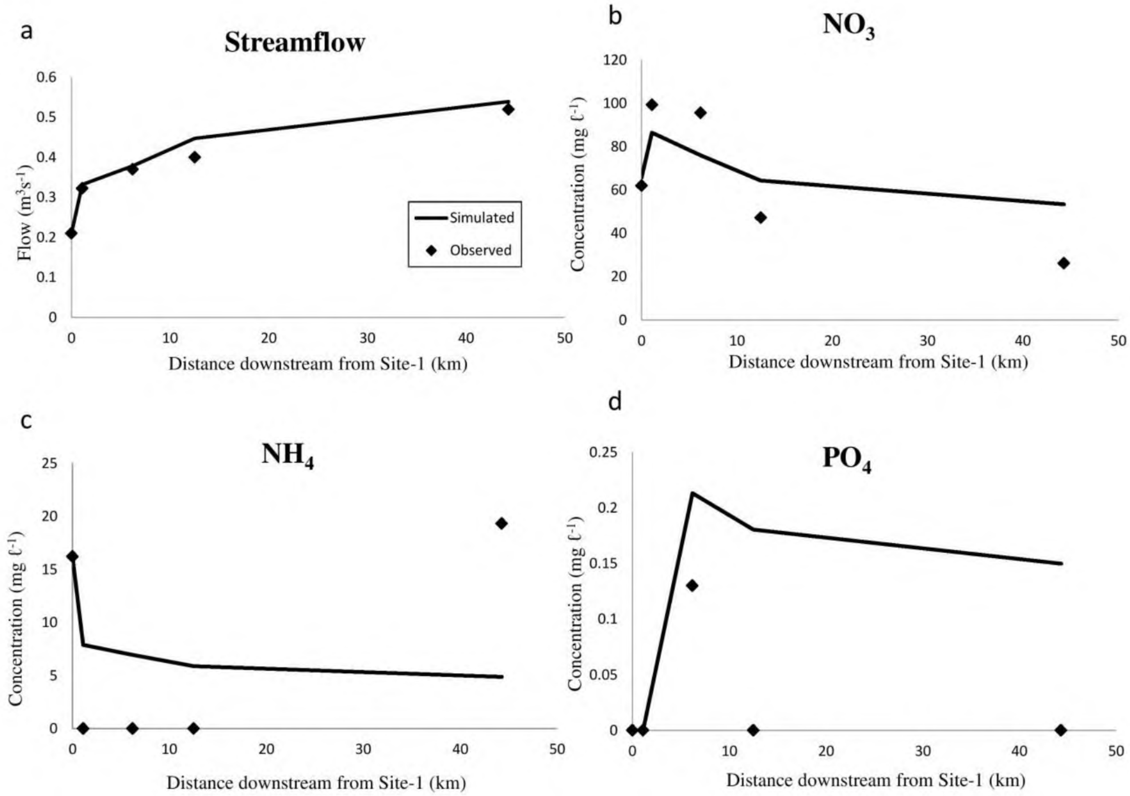

Figure 6.6: Calibration results for the Mass Balance Nutrient model using sample data collected on 03/09/2012.

The sensitivity analyses were performed on the streamflow generation module used in the MBN model (refer to Figure 6.7). For streamflow simulation, a modified SCS rainfall-runoff equation was used for runoff and the Pitman low-flow model was used to simulate low flows. Within Figure 6.7, c refers to initial abstraction, which is the loss of water due to interception and evaporation. Calibration values for c were 0.8 for the pervious catchments and 0.001 for the impervious catchment. Absolute maximum potential refers to the maximum water holding capacity of the soil horizon (mm), and the calibrated values were 170 mm for the pervious catchments and 2 0mm for the impervious catchment. *FT* and *POW* are the two parameter values from the Pitman low flow model, and the calibration values were set to 0.5 and 4 respectively for the pervious catchments and 2 and 4 respectively for the impervious catchment. The impervious catchment was most sensitive to changes in absolute maximum soil water holding capacity. The sensitivity analysis for the pervious catchment indicated that *FT* and *POW* were the most sensitive parameters. The analysis showing the effect that changes to streamflow parameters have on nutrient concentrations preformed using ammonium (NH_4), found that the Pitman FT parameter has the greatest influence on the ammonium concentration.

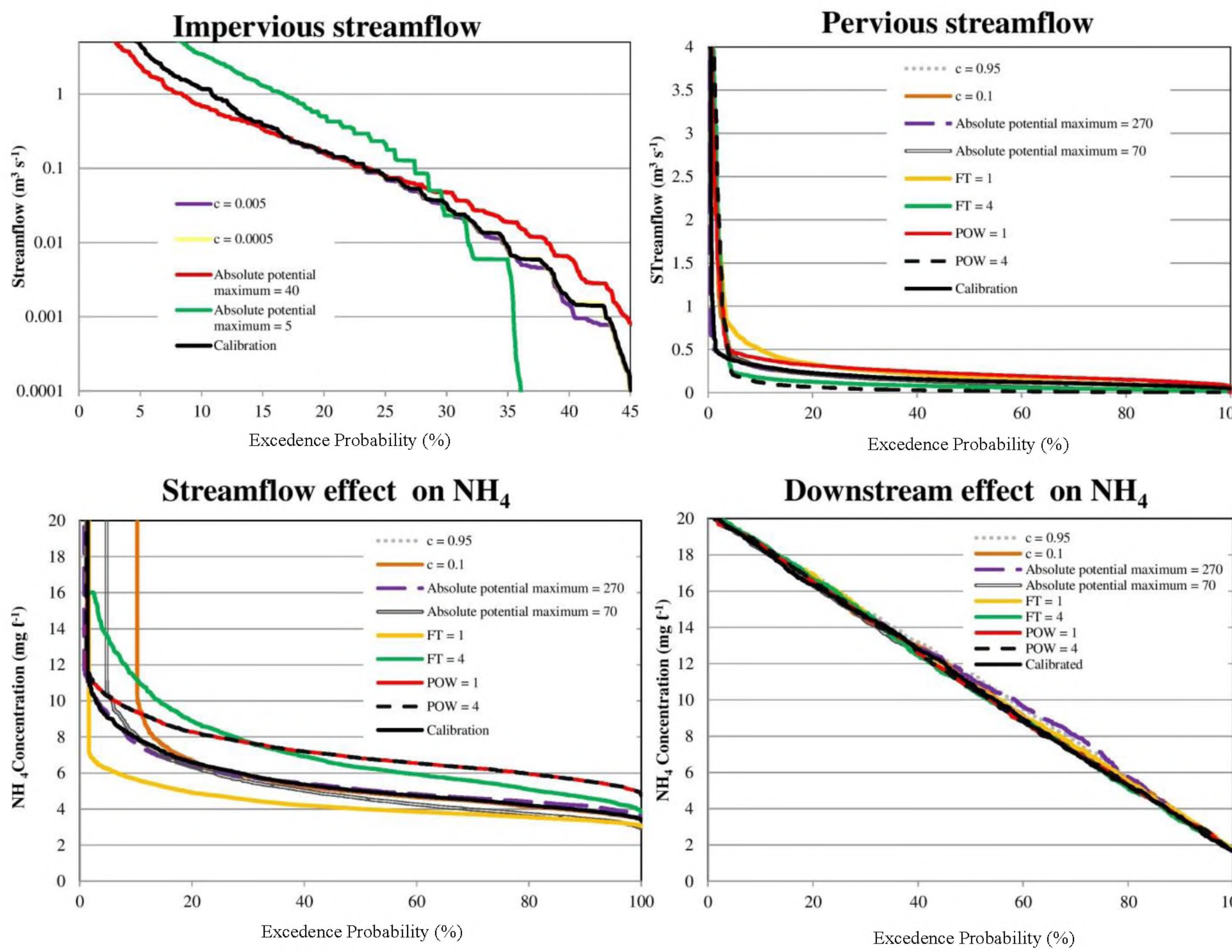

Figure 6.7: Results of the sensitivity analyses for the streamflow generation component of the mass balance nutrient model

Sensitivity analyses of the model for nutrient simulation was performed by individually adjusting each linear regression equation used to drive each nutrient. The m parameter is a constant that determines the gradient of the regression line, whereas c is a constant that determines the intercept on the y axis. Value of the m and c parameters were adjusted separately for the sensitivity analysis. Although the original regression equations were obtained from observed data, the equations were adjusted slightly during the calibration process. Figure 6.8 illustrates the sensitivity of each parameter for each nutrient.

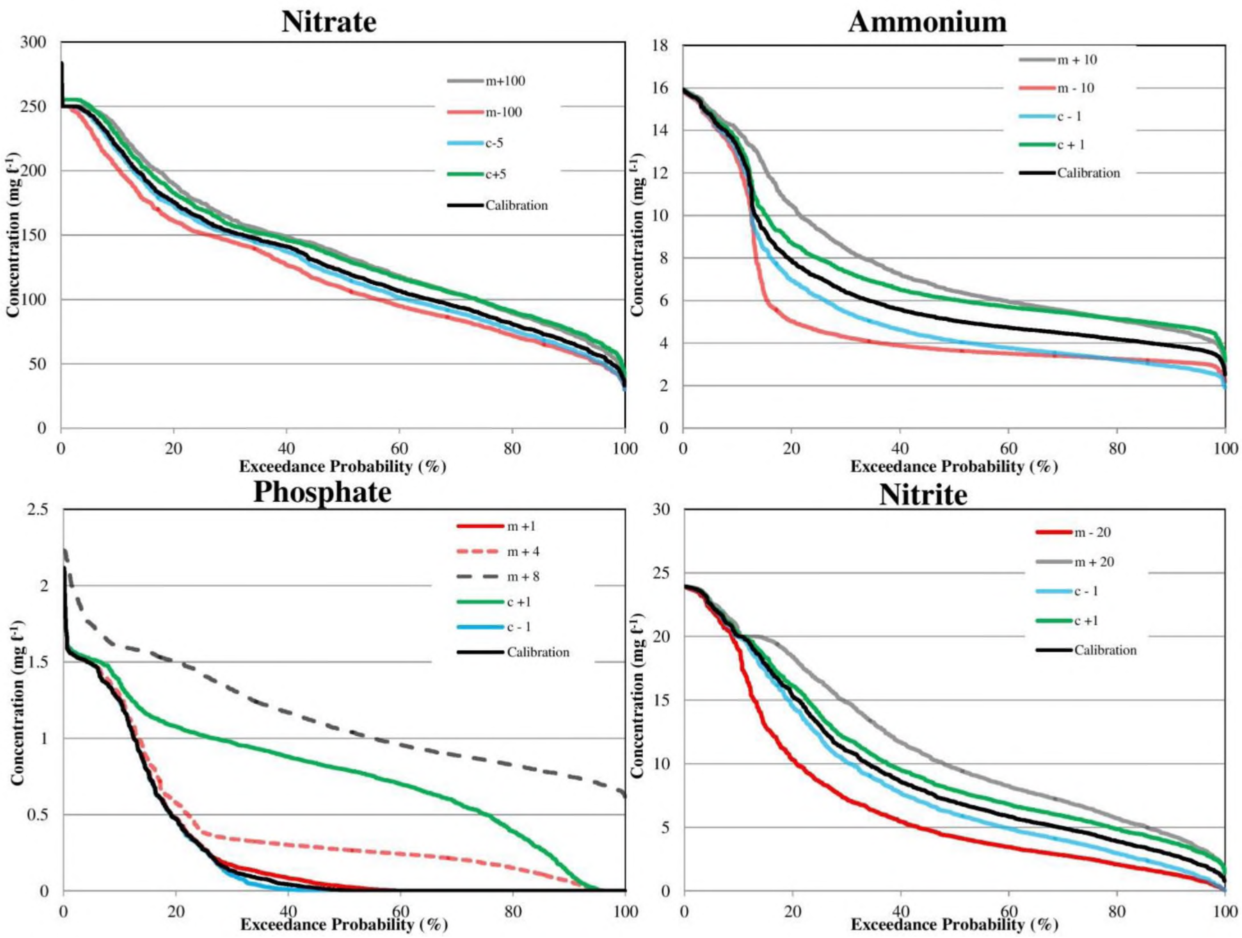

Figure 6.8: MBN model sensitivity analyses on nutrient parameters.

The sensitivity analyses performed on the algal model showed the ammonium nitrification parameter to be the most sensitive parameter; however, even the nitrification parameter was not highly sensitive and had a low impact on the overall ammonium concentration (see Figure 6.9). The ammonium concentrations in the river were generally high due to the large nutrient loads entering the system; therefore, it is possible that the nitrification parameter would have a larger impact on ammonium concentrations in a less eutrophic system.

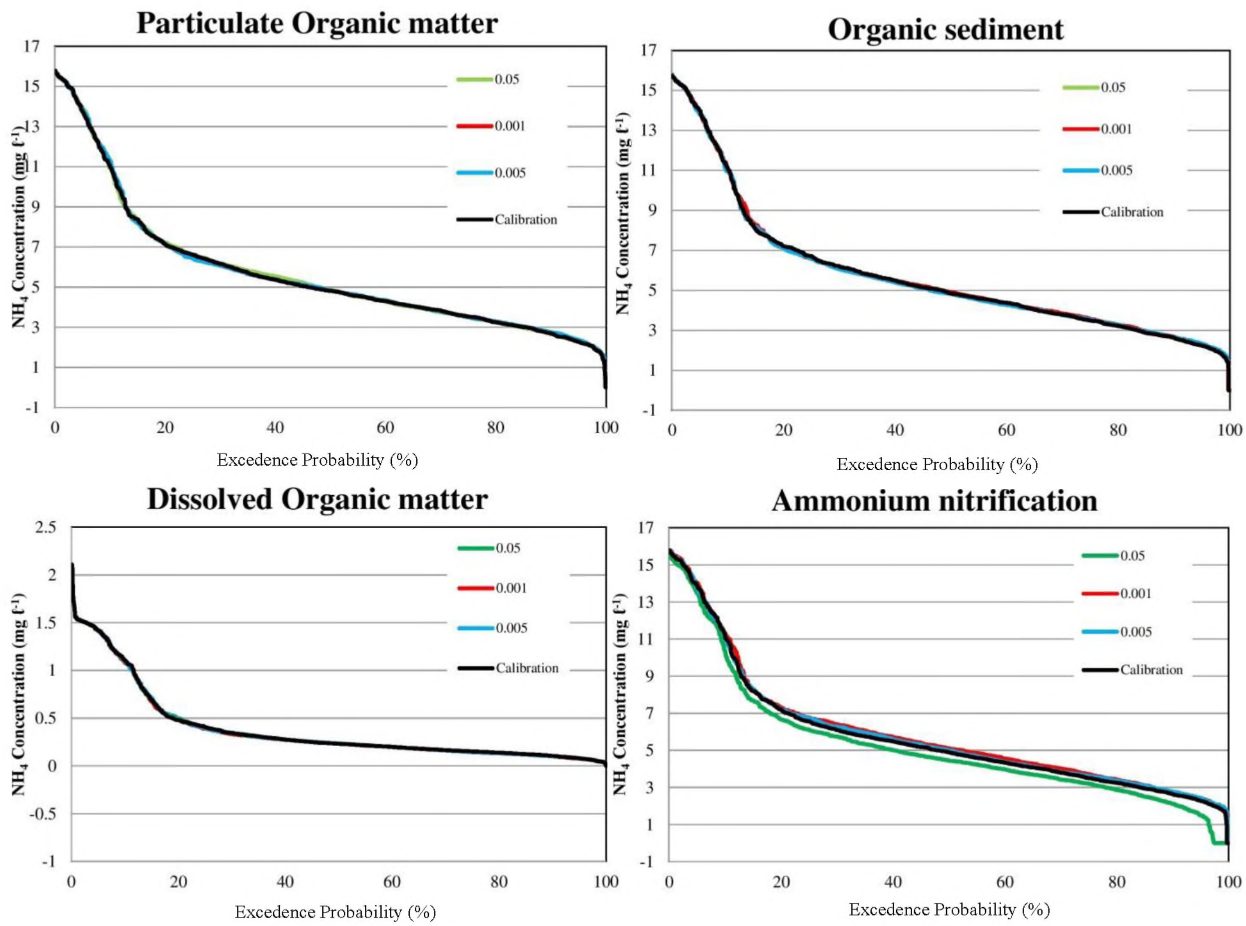

Figure 6.9: Results of the sensitivity analysis of the algae module in the mass balance nutrient model

6.4 Model results

The results from the MBN model are shown for use as both a fate and a dynamic model. Although this model can be run as a dynamic model, thereby accounting for inputs from the entire catchment, or a fate model, thereby accounting for only instream nutrient dynamics, each method has different uses for management. Both modelling approaches require the hydrological model to be adequately calibrated to account for dilution of nutrients. The model is calibrated as a fate model and therefore, initial validation is preformed using the fate option. The confirmation of the fate model is the best option to determine the simulation of downstream catchments for the given day. Validation 1 was performed using data from the sampling trip performed on 12/06/2012, during which flow was relatively low, but not at a low flow condition. Validation 2 was performed using data sampled on the 25/10/2012 during which the sampling was performed three days after extreme flooding of the system. During this event, the Belmont Valley WWTW had been flooded and the sewage ponds were overflowing, with sewage outflow to the river bypassing the treatment plant. Validation 3 was performed using data collected on the 26/02/2013, during which low flow conditions prevailed within the Bloukrans River. On this date, the river appeared to be at its most polluted state at Site-1 since the start of the study, with pungent smells and an abundance of grey coloured algae. Validation 4 was performed using data collected on the 26/10/2013, during which sampling was performed before and during the associated runoff event to observe and gain knowledge of the diffuse inputs during a runoff event.

The validation results for streamflow were acceptable (see Figure 6-10). Validations 1 and 4 were a very close fit to the observed values. However, the model overestimated flow during extreme low flow conditions, as observed in validation 3, and underestimated extreme high flows, as observed in validation 2.

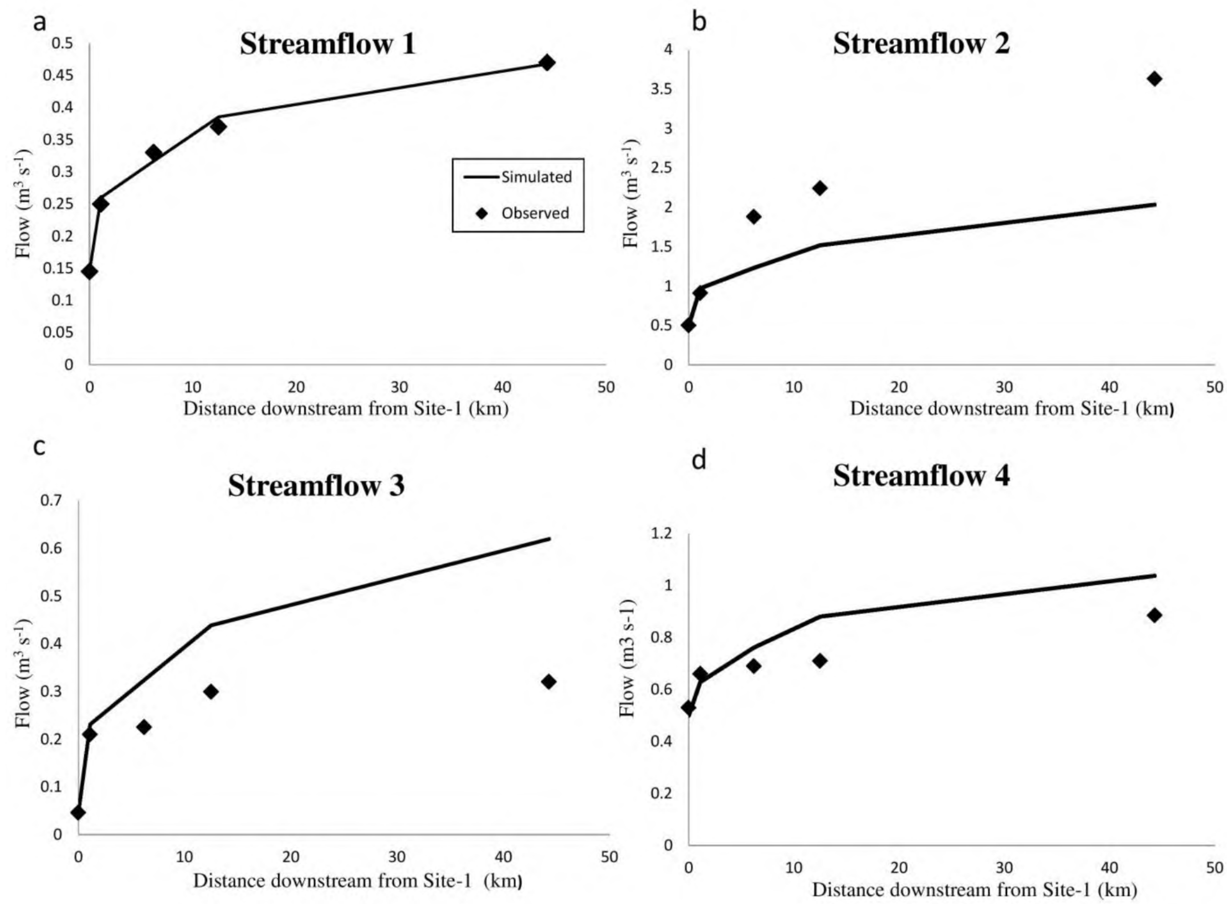

Figure 6.10: Streamflow validation results for the mass balance nutrient model (a-validation1, b-validation2, c-validation3, d-validation4).

Nitrate concentrations proved highly variable in the Bloukrans River over both temporal and spatial scales. The broad trend of the fate of nitrates was well represented by the MBN model. Validation 1 shows an underestimation of nitrates, whereas validation 2 shows an overestimation of nitrates by the model (see Figure 6-11). Validation 3 shows a relatively good fit of simulated to observed data, although the input of the point source does not increase nitrates to the levels that were observed. This could be as a result of the input of nitrates from a diffuse source in subcatchment-2 which is not simulated correctly by the model. Validation 4 has the poorest fit; however, the sampling was performed during a runoff event, and the model has simulated the general trend well, even correctly simulating the increase in nitrate concentration from diffuse sources; however the consumption of nitrates was not great enough within the model to correctly simulate the nitrates observed for validation 4.

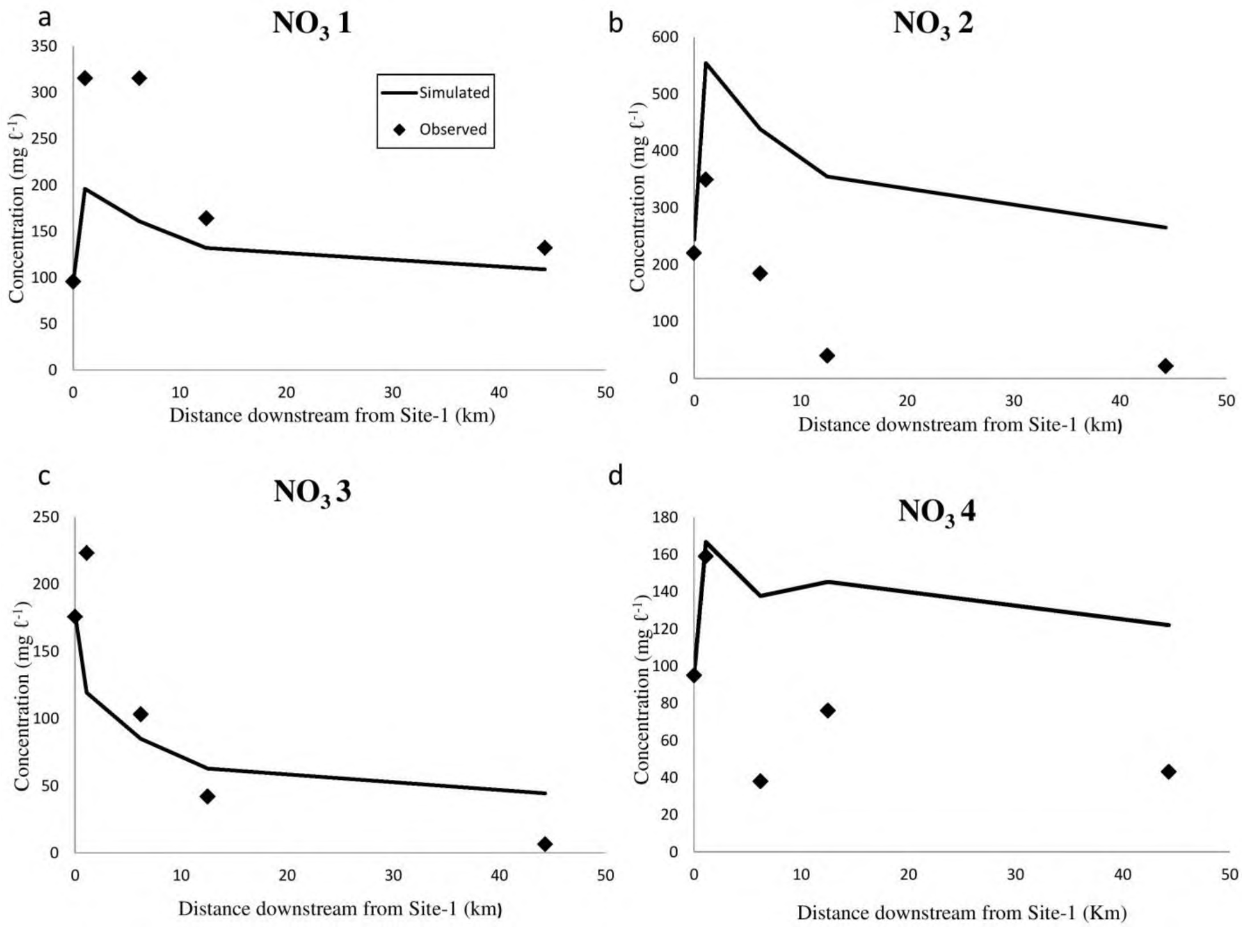

Figure 6.11: Nitrate validation results for mass balance nutrient model (a-validation1, b-validation2, c-validation3, d-validation4).

The validation results for ammonium were mixed. Validation 2 and 3 showed that the MBN model was simulating ammonium concentrations acceptably (see Figure 6.12). However, the results of validation 1 and 4 were less accurate. The diffuse input in the observed data was not simulated by the model for validation 1. Validation 4 indicated an overestimation in ammonium for the entire system; however, the simulations reflected the general trend of the observed data, showing diffuse input between 40 km and 30 km upstream, although grossly over simulated.

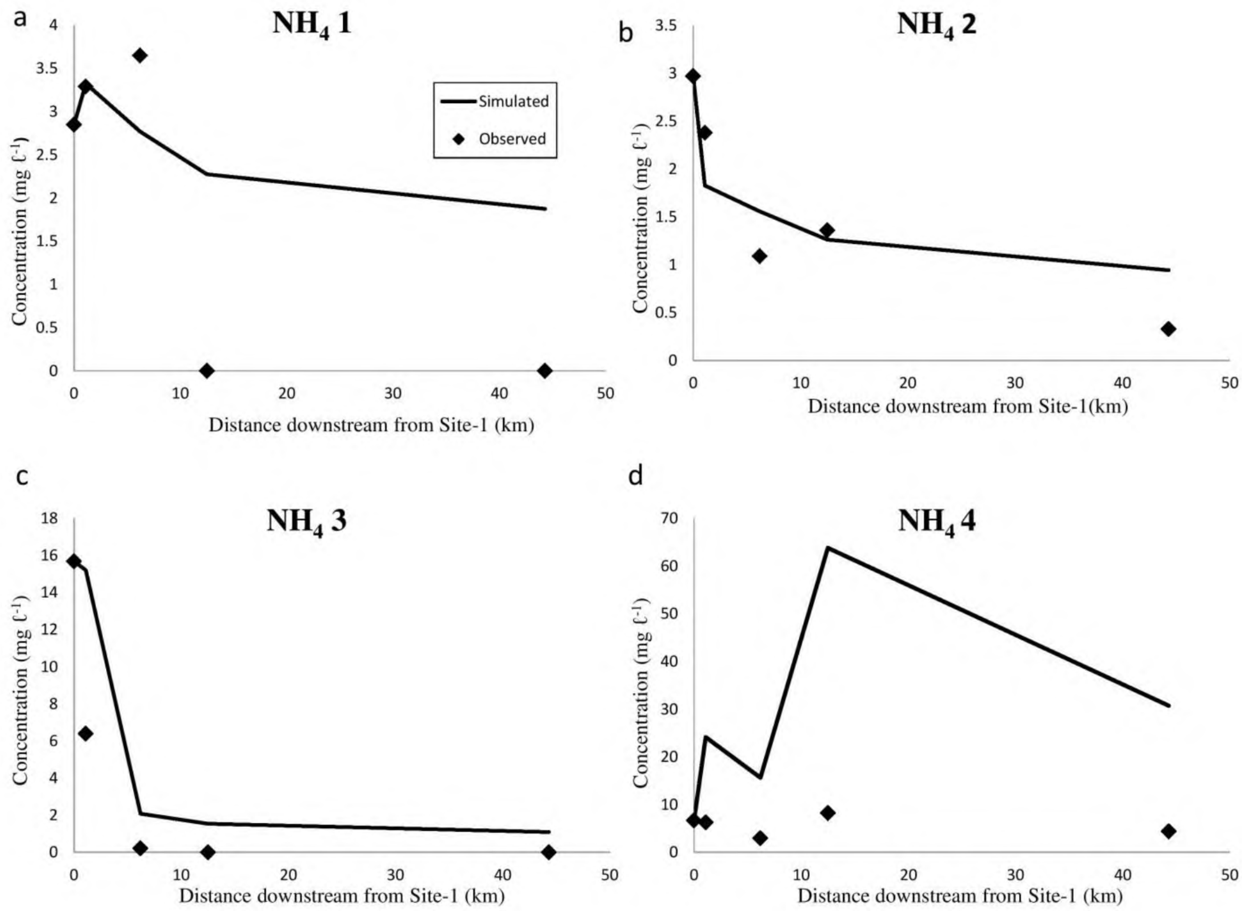

Figure 6.12: Ammonium validation results for the mass balance nutrient model (a-validation1, b-validation2, c-validation3, d-validation4).

Phosphate validation results generally showed an overestimation of phosphate concentrations (see Figure 6.13). Validation 2 shows an overestimation of phosphates. The overestimation by the model was due to the release of phosphates from decaying organic matter. Even though Figure 6.13b appears to show the model drastically overestimating phosphate concentrations, the scale of the graph must be noted: both the observed and simulated phosphate concentrations were exceedingly low, and it is unlikely that any water quality model would accurately simulate phosphate concentrations at that scale. The general trend of phosphate concentrations was well represented by validation 4, although an overall under simulation of phosphate concentrations was observed.

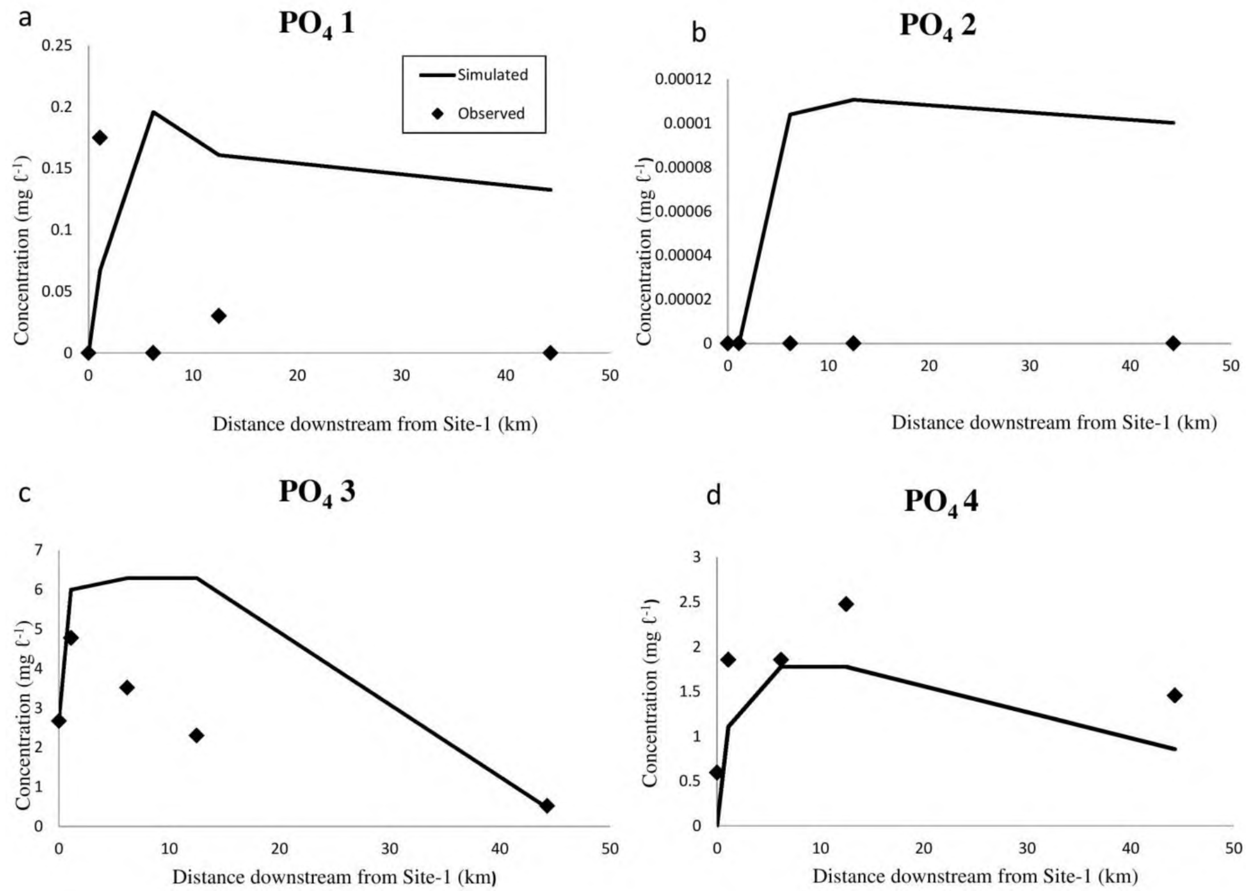

Figure 6.13: Phosphate validation results obtained for the mass balance nutrient model(a-validation1, b-validation2, c-validation3, d-validation4.

The operation of the dynamic model required the simulation of nutrient inputs from the urban area of Grahamstown, a complex system of daily changes in nutrient signatures, whereas the upstream conditions are manually input when using the model as a fate model. Daily changes in nutrient signatures are due to processes including but not limited to: leaking and overflowing sewerage pipes, leaking potable water pipes, dumping of raw sewage and nutrient containing litter. The water and sewerage infrastructure of Grahamstown is compromised, and leaks and overflowing manholes are a daily occurrence in the town; therefore, the changes in these flows and nutrient concentrations were simulated using different techniques in the MBN model.

The results from the fate model could only be shown for the days where data had been collected for the system, much the same as QUAL2K; however the observed nutrient data requirements for the MBN model are much lower.

Operating the MBN model as a dynamic model requires the simulation of input from the Belmont Valley WWTW and subcatchment-1. Using the ideas obtained through knowledge of the system, researching literature and observing trends in data, it was decided to model the inputs from the urban model as both a point and a diffuse source. The diffuse source model accounted for surface runoff and sub-surface flow transporting nutrients to the Bloukrans River. The point source model was used to represent the leaking sewerage and water pipes in Grahamstown.

The results from the MBN model for subcatchment-1 when using separate random number generators to run flow and nutrient concentrations to simulate sewerage and water leaks in the urban area showed promise, as seen in Figure 6.14. Maximum and minimum values were set for flow and each of the nutrients simulated. The random number generator is then used to obtain a value between the maximum and minimum values, with the maximum and minimum values adjusted during the calibration process. The nutrient values assigned to each maximum and minimum were higher than the observed maximum and minimum for each nutrient concentration in subcatchment-1. The elevated nutrient concentrations assigned to the subcatchment-1 point source were necessary as low flows from the impervious and pervious areas in the subcatchment dilute the nutrient concentrations from the point source. The results were satisfactory; however, the trends observed in the 1992–1995 data (Figure 3.2 and Figure 3.3) were not re-created using this method. However, this method provided the best match between simulated values and the data collected during the 2012 to 2013 period. Water Quality values collected during the sampling procedure are only an instantaneous ‘snapshot’ of what is occurring in the water body, as nutrient concentrations fluctuate constantly. It is therefore necessary to use scientific knowledge and knowledge of the system when modelling and analysing results. The phosphate results provided the best overall trend to be expected from the sub catchment, with a high variation of concentrations at the higher flows, characteristic of a diffuse input at high flows.

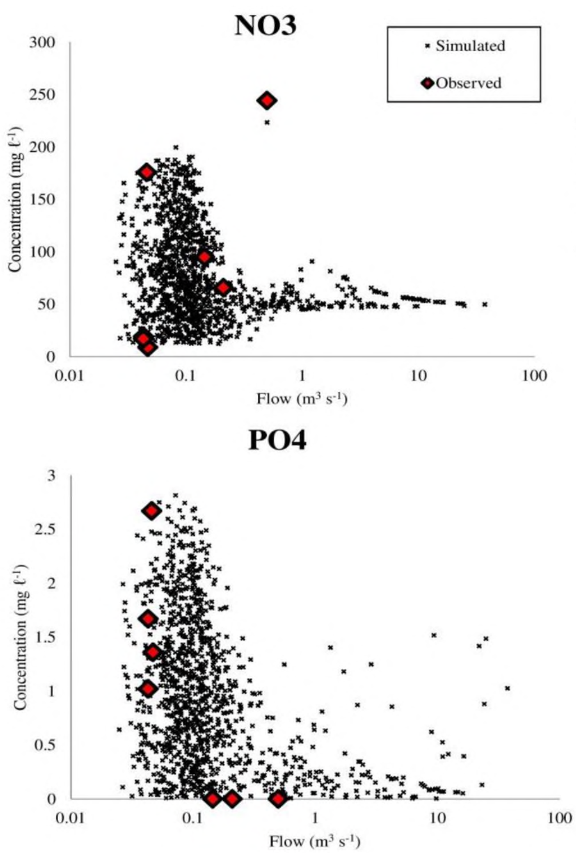

Figure 6.14: Mass balance nutrient model simulation results from subcatchment-1 simulating urban water leaks as a point source.

6.5 MBN model discussion

The MBN model is flexible and can be used as either a fate model or a dynamic model. The data requirements for the model are dependent on what the user requires. Rainfall and evaporation data, used to run the hydrological model, are relatively easy to obtain. Laboratory analyses of grab samples can be used for nutrient data, with the number of samples required dependent on the importance of the accuracy of the simulated results. As with all modelling, the observed data available is directly related to the accuracy of the simulation results. Calibration and validation of the MBN model showed the model to be acceptable within its limitations. However, as with all models, the limitations of the MBN model need to be taken into consideration. The identified limitations of the MBN model include:

- Model not simulating entire nutrient cycle
- Issues with daily averaging

- A lack of irrigation data within the site modelled

The model will be reliable for modelling changes in the Belmont Valley WWTW. Due to the simplicity of the MBN model, certain water quality processes are not modelled, the processes ignored were minor and had little effect on nutrient changes. The model, however, will not be reliable for changes in the urban area the regression used was derived from data from the catchment and will need to be re-assessed. The lack of light limitation, shading and cloud cover in the algae model may lead to incorrect algal simulations. The urban catchment has the greatest degree of uncertainty. Difficulty in measuring and monitoring nutrient sources as well as the variability of the nutrient sources within the urban area led to assumptions and created difficulties in separating the nutrient signatures from leaking sewer pipes from the nutrient signature of runoff. Therefore, it was assumed that the nutrient concentrations and flow from the leaking sewerage pipes varied, and the parameters were calibrated until simulated results were similar to observed data. Algae only grow when there is sufficient solar radiation and nutrients to facilitate growth. The algae model uses air temperature instead of solar radiation to estimate water temperature. Air temperature is not directly related to incoming solar radiation, which may lead to incorrect algal growth estimates in the model. However, the nutrient uptake by algae is very small, and this would only have a minor impact on the overall nutrient simulation. Solar radiation data are also not nearly as readily available as air temperature data, and the method used in the current study is thus a more robust method to use in modelling in data scarce areas. Nutrient concentrations in small rivers have been shown to fluctuate throughout the course of a day. Nutrient fluctuation is caused by changing rates of photosynthesis throughout the day, which affects dissolved oxygen concentrations, and thus affects shifts in nutrient forms. Ablution use patterns will affect the flow of water from sewerage leaks. The variation in flow from leaks in potable water pipes will act to dilute the nutrient concentrations being received from leaking sewerage pipes. Taking a single grab sample at each sampling site to represent a single day only allows a 'snapshot' of what is actually occurring with nutrients in the river at the given time. This method of sampling and simulation does not account for the 'first flush' effect that is observed when runoff occurs, nor does it take into account the dilution of nutrients during high flows. Using daily stream flow can cause averaging issues, as runoff is not always dependent on the total rainfall volume, but also on the intensity of the rainfall. Irrigation application will affect the contribution of nutrients to the river as well as possibly diluting concentrations of nutrients in the receiving water if return flow nutrient concentrations are lower than instream nutrient concentrations. The lack of irrigation data is not a short coming of the model, but does affect the results.

7. CONCLUSION AND RECOMMENDATIONS

A water quality model attempts to simplify a highly complex, interlinked group of processes. Although all models are a simplification of nature, some models are simpler than others. Chapter 3 outlines the advantages and disadvantages of both complex and simple models. This thesis has applied two models, one complex and one simple, using the same data. The conclusions and recommendations are provided below.

7.1 Models investigated

QUAL2K was used to represent the complex type of water quality models for the present study. The QUAL2K model is complex by water quality modelling standards and requires observed water quality data for a large number of water quality variables on fine spatial and temporal scales to set up the model. Due to the complexity of the model, an experienced modeller or someone with a thorough understanding of water quality dynamics is required to operate the model (Beck, 1987). Conducting dedicated field sampling of the data required to run QUAL2K is time consuming and expensive. QUAL2K has been used previously to simulate water quality in the Bloukrans River by Slaughter (2011) with limited success, although Slaughter (2011) only simulated low flows, whereas this study aimed to simulate water quality over a wider range of flow conditions. The results obtained in the present study using QUAL2K were poor, but the general observed patterns of the fate of nutrients from upstream to downstream were represented by the model. QUAL2K is better suited to simulating low flow conditions, or systems dominated by point sources, as calibrating and estimating diffuse inputs becomes difficult, and must be measured or estimated externally of QUAL2K as QUAL2K is an instream water quality model that does not simulate landscape processes. The Bloukrans River is a complex system; therefore, QUAL2K could not adequately simulate the wide range of flow conditions. QUAL2K is unlikely to be used for catchment wide management of water quality; however, this model is useful for determining the impact of specific point sources on downstream water quality, provided that sufficient data are available to establish appropriate parameter values.

Although the MBN model produced water quality trends that were representative of the observed data, the simulations had a poor fit; therefore, further calibration and increased observed data are required. However, it is very difficult to achieve a good model fit for nutrients which are highly variable on a daily, and even hourly time scale. The nature of this model allows the modeller to run the model using minimal water quality data and some daily climatic data that are easily obtainable and widely available. The data requirements of the MBN model are much lower than that of QUAL2K. Streamflow modelling within the water quality model is very important as dilution has the greatest influence over nutrient concentrations within the Bloukrans catchment. The Pitman low flow model has also been widely used within southern Africa and is easily calibrated. Calibration of the MBN model requires a relatively high degree of conceptual understanding of the hydrological processes that are dominant within the system being modelled. However, this is true of many hydrological models (Rouch *et al.*, 1998). The modeller is required to decide whether diffuse inputs from each subcatchment are irrigation return flow or runoff or a combination of the two, and simulate their effect in the model accordingly. When modelling an urban area such as Grahamstown where sewerage leaks are sufficiently substantial to warrant including these into the model, this creates a degree of uncertainty in the model, as measuring sewerage leaks accurately is impossible and the quality and quantity of waste water entering the river is highly variable. The uncertainty could be decreased with further information to quantify the variability of the waste water entering the river.

The MBN model could be used to extend datasets in catchments with limited data as well as scenario modelling. Datasets that are extended through modelling may not be as accurate as sampled data; however, field sampling is expensive and time consuming, and by using a model with limited field sampling, a large dataset can be produced faster and more economically. Limited data are required to run the MBN model and the model is therefore suited for modelling ungauged catchments or catchments with limited data; however, the model user is required to explicitly state the assumptions made and uncertainty within the modelling process, and the stakeholders are required to understand the uncertainty implications of limited data on model results before using the model results to aid management decisions. Long-term time series can be used to create load duration curves, which are useful in illustrating the frequency characteristics of different nutrient loads and aiding management decisions. The MBN model has both mechanistic (instream nutrient fate) and statistical (linear regression) components to the model. The instream nutrient fate is mechanistic and the water quality component of the urban runoff is statistical. The mechanistic component is suitable for scenario modelling, whereas the statistical components are better suited for interpolation, unless the relationships can be re-created for future conditions.

7.2 Answering research questions

1. Can a simple water quality model provide realistic results?

Realistic results can be achieved using the simple water quality model (Glaser and Bridges, 2007); however, the method of simulating water quality investigated in the current study, namely at a catchment scale where nutrient sources are driven by rainfall and low flow, is less accurate on a daily time step than could be achieved using an instream model (QUAL2K) where point and diffuse inputs are input into the model for the specific day. However, an instream model such as QUAL2K requires water quality and streamflow data for each day the model is run which is obtained externally from the model, and unlike the MBN model, the instream model does not automatically simulate diffuse sources. The MBN model simulated realistic results for the Bloukrans River. The model was found to be useful for extending limited datasets to provide frequency distributions of water quality loads or concentrations that can be related to the risks of exceeding management thresholds. The MBN model could be improved through a better understanding of processes occurring, which would require larger observed datasets than those used in the current thesis.

2. Can a complex model be run with limited data?

QUAL2K was able to produce simulations of water quality with the data collected that broadly represented the observed nutrient trends of nitrate, nitrite, ammonium and phosphate. Water quality variables required by QUAL2K are extensive, both in terms of range and spatial and temporal scale, and include conservative variables such as, electrical conductivity and turbidity, as well as a large range of non-conservative variables such as total nitrogen, total phosphate, periphyton and phytoplankton. The observed data may also be required on diurnal (sub-daily) scales for optimal use within QUAL2K.

3. Given similar data constraints which model is better?

South Africa has very limited water quality data, and even where data are available, there are rarely sufficient data to run a water quality model such as QUAL2K. The department of Water and Sanitation (DWS) does monitor nutrients to the same standard as those required for the MBN model. Given the limited data available for water quality in South Africa, the MBN model is more suited to modelling water quality in South Africa. The full complement of data used to run the MBN model would not be sufficient to simulate water quality in QUAL2K. QUAL2K requires a number of water quality variables to simulate water quality. These data include hourly diel variation data including total nitrogen, total phosphorus, dissolved oxygen, turbidity, electrical conductivity, periphyton and phytoplankton; however, these data are not always readily available. The climate data required by the hydrological model in the MBN model is readily available and easily accessible, even if these data are subject to uncertainties in terms of their representativeness and accuracy. The nutrient data required to calibrate the MBN model (nitrate, nitrite, ammonium and phosphate) can be collected in grab samples and sent for laboratory analysis, whereas water quality variables required by QUAL2K require extensive sampling and data loggers. The requirements of a water quality model in South Africa for management include the capacity to use the available historic data and provide information on the likely frequency distribution of water quality loads or concentrations that can be related to the risks of exceeding management thresholds, rather than models that can provide an accurate time series. The appropriate models should also be sensitive to changes in management practises that include land-use changes that affect diffuse sources, as well as WWTW operational practises, or other practises that might impact on point sources. The MBN model was found to be a more suitable model than QUAL2K for the given constraints, within the context of South African requirements for a water quality model. The minimal water quality data required to run the MBN model is very favourable for South Africa. The models differ in the output and, therefore, the use of the model. The MBN model is useful for extending limited datasets, whereas QUAL2K is useful for accurately determining the water quality processes occurring in a system. It is more useful within water quality management in South Africa to determine the frequency of concentrations or loads that exceed a threshold than having an accurate knowledge of the processes occurring in the system for a given day.

7.3 Challenges encountered during water quality modelling

Access to limited observed data is a major issue within modelling (Marsili-Libelli and Giusti, 2009). The less data available, the more difficult it is to understand the processes occurring within the system being modelled, and the more difficult it is to validate the simulated results. The method of collecting water quality data using grab samples allows only a 'snap-shot' of the water quality for that day. The concentrations of water quality variables in a system vary significantly throughout each day depending on the dynamics of the system. The sampling undertaken during runoff events is affected by the stage during which the storm hydrograph is sampled (Hughes and van Ginkel, 1994). The effluent quantity and quality of the Belmont Valley WWTW also varied considerably. Collecting and analysing water quality data is expensive and difficult. Private landowners do not readily allow access to rivers. Laboratory analysis of grab samples is expensive and time consuming. Diel data requires a sample to be taken every hour for 24 hours. The lack of data increases the uncertainty, both in the conceptualisation of the real world and the model (Chapra, 1997). Small datasets are susceptible to the introduction of bias, particularly where the representation of a range of different conditions is necessary, such as in the development of the regression curves used to link nutrient concentrations to discharge rates as in the MBN model. To avoid introducing bias in the modelling approach, an effort was made to sample a wide range of flow conditions. However, the constraints of the study meant that the dataset remained relatively small, and many uncertainties in the calibrated model parameters remain. A longer-term study with greater resources for field sampling and laboratory analysis could contribute to the reduction of these uncertainties. Such additional data may help to develop improved parameter estimates using existing model algorithms, or could point to alternative (but still relatively simple) algorithms defining the relationships between nutrients and flow. The limitations of the model and the associated uncertainties should be clearly understood by those responsible for setting up the model, as well as those who make use of the model results for making decisions.

Water quality is driven by complex and highly variable processes, and the currently accepted water quality model (QUAL2K) requires extensive data that are not readily available, particularly in developing countries. To incorporate water quality models into the water management decision making framework, it is necessary to develop models that can operate on minimal data whilst still operating at an acceptable level of uncertainty. The results from the MBN model simulations were acceptable for the limited data used to setup and calibrate the model. Further validation using greater datasets may show limitations in the model that were not identified in the current study.

References

Andersson, L., Rosberg, J., Pers, B.C., Olsson, J. and Arheimer, B. (2005). Estimating Catchment Nutrient Flow with the HBV-NP Model: Sensitivity To Input Data. *Ambio.* Vol 34. 521-532.

APHA, (1992). Standard methods for the examination of water and wastewater. American Public Health Association, Washington, DC.

Arar, E.J. and Collins, G.B. (1997). Method 445.0 In vitro determination of chlorophyll a and pherophytin a in marine and freshwater algae by fluorescence. Publication No 455. U.S Environmental Protection Agency. Cincinnati. Ohio. Available online: http://www.epa.gov/microbes/m445_0.pdf. Accessed: 20 July, 2010.

Art, H.W., (1993). Eutrophication: A dictionary of ecology and environmental science (1st ed.): New York. New York, Henry Holt and Company. 196.

Azzelino, A., Salvetti, R., Vismara, L. and 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 nutrient to surface waters. *Science of the Total Environment.* Vol 371. 214-222.

Beck, M.B. (1987). Water quality modelling: a review of the analysis of uncertainty. *Water Resources Research*. Vol 23. 1393-1442.

Beven, K. (2006). A manifesto for the equifinality thesis. *Journal of Hydrology.* Vol 320. 18-36.

Bowes, M.J., Hilton, J., Irons, G.P. and Hornby, D.D. 2005. The relative contribution of sewerage and diffuse phosphorus sources in the River Avon catchment, Southern England: Implications for Nutrient management. *Science for the Total Environment* Vol 344. 67-81.

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*. Vol 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.

Britton, D.L., Day, J.A. and Henshall-Howard, M-P. (1993). Hydrochemical response during storm events in a South African mountain catchment: the influence of antecedent conditions. *Hydrobiologia.* Vol 250. 143-157.

Britz, T.J. and Sigge, G.O. (2012). Quantitative Investigation into the Link between Irrigation Water Quality and Food Safety: Volume 1. Water Research Commission Report No. 1773/1/12. Water Research Commission. Pretoria. South Africa.

Brown, L.C. and Barnwell, T.O. (1987). The Enhanced Stream and Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual. EPA. 3-87.

Bowes, M.J., Smith, J.T., Jarvie, H.P., Neal, C. and Barden, R. (2009). Changes in point and diffuse source phosphorus inputs to the River Frome (Dorset, UK) from 1966 to 2006. *Science of the Total Environment*. Vol 407. 1954-1966.

Chapra, S. (1997). *Surface water-quality modelling*. The McGraw-Hill Companies, Inc.

Chapra, S. (2003). Engineering Water Quality Models and TMDLs. *Journal of Water Resources Planning and Management.* Vol 1291. 247-257.

Chung, S.W., Hwan Ko, I. and Kyung Kim, Y. (2008). Effect of reservoir flushing on downstream river water quality. *Journal of Environmental Management*. Vol 86. 139-147.

Cole, T.M. and Wells, S.A. (2008) CE-QUAL-W2: A Two-Dimensional. Laterally Averaged, Hydrodynamic and Water Quality Model, Version 3.6. Department of Civil and Environmental Engineering, Portland State University. Portland. Oregon. USA.

Dabrowski, J.M. and de Klerk, L.P. (2013). An assessment of the impact of different land use activities on water quality in the upper Olifants River catchment. *Water SA.* Vol 39. 231-244.

Dallas, H.F. and Day, J.A. (2004). *The Effect of Water Quality Variables on Aquatic Ecosystems: A Review*. WRC Technical Report No.224/04. Water Research Commission. Vol 224. 1-213.

Deksissa, T., Meirlaen, J., Ashton, P.J. and Vanrolleghem, P. (2004). Simplifying Dynamic Water Quality Modelling: A Case study of inorganic nitrogen dynamics in the Crocodile River (South Africa). *Water, Air and Soil Pollution.* Vol 155. 303-320.

Drolc, A. and Koncan, J.Z. (1996). Water Quality Modelling of the River Sava, Slovenia. *Water Research.* Vol 30. 2587-2592.

DWA. (2011). 2010/2011. Green Drop Report. Department of Water Affairs. Pretoria. South Africa.

DWAF. (1998). *National Water Act: No 36 of 1998*, Act edn, Republic of South Africa, Pretoria.

DWAF. (1997). *Water Services Act: No 108 of 1997*, Act edn, Republic of South Africa, Cape Town.

Evans, R.E., Grimm, V., Johst, K., Knuutila, T., de Langhe, R., Lessells. C.M., Merz, M., O`Malley, M.A., Orzack, S.H. Weisberg, M., Wilkinson, D.J., Wolkenhauer, O. and Benton, T.G. (2013). Do simple models lead to generality in ecology? *Trends in Ecology and Evolution.* Vol 1719. 1-6.

Fan, C., Ko, C. and Wang, W. (2009). An innovative modelling approach using QUAL2K and HEC-RAS integration to assess the impact of tidal effect on River Water quality simulation. *Journal of Environmental Management.* Vol 90. 1824-1832.

Fawthrop, N.P. (1994). Modelling hydrological processes for river management. *In:* Calow, P. and Petts, G.E. (Eds) *The Rivers Handbook: Hydrological and Ecological Principles.* Blackwell, Oxford, Uk.

Ferrier, R.C., Whitehead, P.G., Sefton, C., Edwards, A.C. and Pugh, K. (1995). Modelling Impacts of Land Use Change and Climate Change on Nitrate-Nitrogen in the River Don, North East Scotland. *Water Research.* Vol 29. 1950-1956.

Flügel, W.A. and Kienzle, S.W. (1989). Hydrology and salinity dynamics of the Breede River, Western Cape Province, Republic of South Africa. - In: *Regional Characterization of Water Quality*. (Proc. of the Baltimore Conference, USA, May 1989). IAHS Publ. No. 182, 221-228

Garnier, J., Billen, G. and Coste, M. (1995). Seasonal succession of diatoms and chlrophyllceae in the drainage network of the Siene River: observations and modelling. *Limnology and oceanography.* Vol 40. 750-756.

Glaser, D. and Bridges, T.S. (2007). Separating the Wheat from the Chaff: The Effective Use of Mathematical Models as Decision Tools. *Integrated Environmental Assesment and Management.* Vol 3. 442-229.

Gill, M.A. (1979). Sedimentation and Useful Life of Reservoirs. *Journal of Hydrology.* Vol 44. 9-95.

Goel, P.K. (2009). Water Pollution-Causes, Effects and Control. New Dehli. New Age International.

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.

Greenhalgh, S. and Sauer, A. (2002). Environmental Benefits and Challenges of Trading Water Quality. *Water Resources Impact.* Vol 4. 5-7.

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.* Vol 19. 975-981.

GLOBAL WATER PARTNERSHIP. (2000). Integrated Water Resources Management. GWP Catalyzing Change Series.

Hargreaves, G.H. and Samani S. (1982). Estimating potential evapotranspiration. *Journal of the Irrigation and Drainage Division*. Vol 108. 225-230.

Holm-Hansen, O. and Riemann, B. (1978). Chlorophyll determination: improvements in the methodology. *Oikos.* Vol 30. 438-447.

Hilton, K., O`Hare, M., Bowes, M.J. and Jones, J.I. (2006). How green is my river? A new paradigm of eutrophication in rivers. *Science of the Total Environment.* Vol 365. 66-83.

Horn, A.L., Rueda, F.J., Hoerman, G. and Fohrer, N. (2004). Implementing river water quality modelling issues in mesoscale watershed models for water policy demands- an overview of current concepts, deficits and future tasks. *Physics and Chemistry of the Earth.* Vol 29. 725-737.

Hongbing, L., Lin, L., Gu, H., Ping, L., Jinxiang, L., Sheng, H., Fuxiang, W., Rui, X. and Xiaoxue, H. (2009). Total pollution effect of urban surface runoff. *Journal of Environmnetal Sciences.* Vol 21. 1186-1193.

Hu, J. and Li, S. (2009). Modeling the mass fluxes and transformations of nutrients in the Pearl River Delta, China. *Journal of Marine Systems.* Vol 78. 146-167.

Huang, G.H. & Xia, J. (2001). Barriers to sustainable water-quality management. *Journal of Environmental Management.* Vol 61/1. 1-23.

Hughes, D.A. (2012). Personal Communication. Institute for Water Research. Rhodes University. Grahamstown. South Africa.

Hughes, D.A. and van Ginkel, C. (1994). Nutrient loads from developing urban areas, a simulation approach and identification of information requirements. *Water SA.* Vol 20. 139-150.

Heisler, J.M., Gilbert, P.M., Burkholder, J.M., Anderson, D.M., Cochlan, W., Dennison, W.C., Dortch, Q., Gobler, C.J., Heil, C.A., Humphries, E., Lewitus, A., Magnien, R., Marshall, H.G., Sellner, K., Stockwell, D.A., Stoecker, D.K. and Suddleson, M. (2008). Eutrophication and harmful algal blooms: A scientific consensus. *Harmful Algae.* Vol 8. 3-13.

Jackson, H.M., Gibbins, C.N. and Soulsby, C. (2007). Role of Discharge and Temperature Variation in Determining Invertebrate Community Structure in a Regulated River. *River Research and Applications.* Vol 23. 651-669.

Jewitt, G.P.W. (2002). Can Integrated Water Resources Management sustain the provision of ecosystems goods and services? *Physics and Chemistry of the Earth*. Vol 27. 887-895.

Jordan, T.E., Correll, D.L. and Weller, D.E. (1997). Relating nutrient discharges from watersheds to land use and streamflow variability. *Water Resources Research.* Vol 33. 2579-2590.

Juizo, D. and Liden, R. (2008). Modeling for transboundary water resources planning and allocation. *Hydrology and Earth System Sciences Discussions.* Vol 5. 475-509.

Kanne, P.R., Lee, S., Kanel, S.L. and Pelletier., G.J. (2005). Application of automated Qual2Kw for water quality modelling and management in the Bagmati River, Nepal. *Ecological Modelling*. Vol 202. 517.

Kennedy, M.C. and O`Hagan, A. (2001). Bayesian calibration of computer models. *Journal of Royal Statistical Society*. Vol 63. 425-464.

Kirchner, J., Moolman, J.H., du Plesis, H.M. and Reynders, A.G. (1997). Causes and Management of Salinity in the Breede River Valley, South Africa. *Hydrogeology Journal*. Vol 5. 98-108.

Lindenschmidt, K. (2006). River water quality modelling for river basin and water resources management with a focus on the Saale River, Germany. Published Phd thesis.

Lindenschmidt, K. and Fleishbein, K. (2007). Structural uncertainty in a river water quality modelling system. *Ecological Modelling*. Vol 204. 289-300.

Loucks, D.P., Van Beek, E. and Stedinger, J.R. (2005). Water Resources Systems Planning and Management: An Introduction to Methods, Models and Applications. UNESCO. Paris.

Mahamah, D.S. (1998). Simplifying assumptions in water quality modelling. *Ecological Modelling*. Vol 109. 295-300.

Malan, H.L. and Day, J.A. (2002). 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.

Marsili-Libelli, S. and Giusti, E. (2008). Water quality modelling for small river basins. *Environmental Modelling and Software*. Vol 23. 451-463.

McAvoy, D.C. Masscheleyn, P., Peng, C., Morrall, S.W., Casilla, A.B., Lim, J.M.U. and Gregorio, E.G. (2003). Risk assessment approach for untreated wastewater using QUAL2E water quality model. *Chemosphere*. Vol 52. 55-66.

McBride, G.B. and Chapra, S.C. (2005). Rapid Calculations of Oxygen in Streams: Approximate Delta Method. *Journal of Environmental Engineering*. Vol 131. 336-342.

McDiffett, 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.* Vol 179. 97-102.

McDowell. R.W., Biggs, B.J.F., Sharpley, A.N. and Nguyen, L. (2004). Connecting Phosphorus Loss from Agricultural Landscapes to Surface Water Quality. *Chemistry and Ecology.* Vol 20. 1-40.

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 modelling for targeted watershed phosphorus management II. *Agriculture, Ecosystems and Environment.* Vol 127. 223-233.

Meybeck, M. and Helmer, R. (1989). The Quality of Rivers: From Pristine Stage to Global Pollution. *Palaeogeography, Palaeoclimatology and Palaeoecology.* Vol 75. 283-309.

Mishra, S.K., and V.P. Singh. (2003). Soil Conservation Service Curve Number (SCS-CN) Methodology. Dordrecht. The Netherlands: Kluwer Academic Publishers.

Nakhaei, N. and Shahidi, A.E. (2010). Waste water discharge impact modelling with QUAL2K, case study: the Zayandeh-rood River. 2010 International Congress on Environmental Modelling and Software Modelling for the Environments Sake.

O'Keefe, J.H., van Ginkel, C.E., Hughes, D.A., Hill, T.R. and 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 (WRC) Report No. 405/1/96. Water Research Commission, Pretoria, South Africa.

Oreskes, N., Schrader-Frechette, K. and Belitz, K. (1994). Verifictaion, Validation and Confirmation of Numerical Models in Earth Sciences. *Science.* Vol 263. 641-646.

Palmer, R.W. and O`Keefe, J.H. (1989). Temperature characteristics of an impounded river. *Archives of hydrobiologia.* Vol 202. 71-83.

Park, S.S. and Lee, Y.S. (1996). A multiconstituent moving segment model for water quality predictions in steep and shallow streams. *Ecological Modelling.* Vol 89. 121-131.

Pelletier, G.J., Chapra, S.C. and Tao, H. (2006). QUAL2Kw – A Framework for modelling water quality in streams and rivers using a genetic algorithm for calibration. *Environmental Modelling and Software*. Vol 21. 419-425.

Pelmieri, V. and de Carvalho, R.J. (2006). Qual2e model for the Corumbatai River. *Ecological Modelling*. Vol 198. 269-275.

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 Report no. TT 142/01. Pretoria. South Africa.

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 streamflow draining an agricultural hill-land watershed. *Journal of Hydrology*. Vol 220. 62-73.

Quinn, P.F., Hewett, C.J.M. and Dayawansa, N.D.K. (2007). TOPCAT-NP: a minimum information requirement model for simulation of flow and nutrient transport from agricultural systems. *Hydrological Processes*. Vol 22. 2565-2580.

Ranalli, A.J. and Macalady, D.L. (2010). The importance of the riparian zone and in-stream processes in nitrate attenuation in undisturbed and agricultural watersheds- A review of the scientific literature. *Journal of Hydrology*. Vol 389. 406-415.

Rouch, W., Henze. M., Koncsos, L., Reichert, P., Shanahan, P., Somlyody, L. and Vanrolleghem, P. (1998). River Water Quality Modelling: 1 State of The Art. Proceedings of the IAWQ Biennial International Conference. Vancouver. Brittish Columbia. Canada. 21-26 June 1998.

Reckhow, K.H. and Chapra, S.C. (1999). Modelling excessive nutrient loading in the environment. *Environmental Pollution*. Vol 100. 197-207.

Refsgaard, J.C., van der Sluijs, J.P., Hojberg, A.L. and Vanrolleghem, P.A. (2007). Uncertainty in the environmental modelling process- A framework and guidance. *Environmental Modelling and Software*. Vol 22. 1543-1556.

Rist, S., Chidambaranathan, M., Escobar, C., Wiesmann, U. and Zimmermann, A. (2007). Moving from sustainable management to sustainable governance of natural resources: The role of social learning processes in rural India, Bolivia and Mali. *Journal of Rural Studies*. Vol 23. 23-37.

Rivers-Moore, N.A., Jewitte, G.P.W., Weeks, D.C. and O'Keeffe, J.H. (2004). Water Temperature and Fish Distribution in the Sabie River System: Towards the Development of an Adaptive Management Tool. WRC Report No. 1065/1/04. *Water Research Commission*. Pretoria, South Africa.

Rivers-Moore, N.A., Hughes, D.A., Mantel, S. and Hill, T.R. (2008). First steps in the development of a water temperature framework for refining the ecological Reserve in South African rivers. *Water SA*. Vol 34. 585-595.

Robarts, R.D. and Zohary, T. (1987). Temperature effects on photosynthetic capacity, respiration and growth rates of bloom forming cyanobacteria. *New Zealand Journal of Marine and Freshwater Research.* Vol 21. 391-199.

Royer, T.V., Tank, J.L. and David, M.B. (2004). Landscape and Watershed Processes: Transport and Fate of Nitrate in Headwater Agricultural Streams in Illinois. *Journal of Environmental Quality.* Vol 33. 1296-1304.

Salvai, A. and Bezdan, A. (2008). Water Quality Model QUAL2K in TMDL Development. *BALWOIS*. Vol 27. 1-8.

Schulze, R. E., Schmidt, E. J., and Smithers, J. C. (1992). PC-based SCS design flood estimates for small catchments in Southern Africa. Department of Agricultural Engineering. University of Natal.

Shanahan, P., Henze, M., Koncsos, L., Rauch, W., Reichert, P., Somlyody, L. and Vanrolleghem, P. (1998). River Water Quality Modelling: 2 Problems of the Art. IAWQ Biennial International conference.

Slaughter, A.R. (2011). Modelling the relationship between flow and water quality in South African rivers. Unpublished PhD thesis. Rhodes University. Grahamstown. South Africa.

Slaughter, A.R. and Hughes, D.A. (2013). Simple model to separate point and diffuse nutrient signatures in stream flows. *Hydrology Research.* Vol 44. 538.

Smith, V.H. (2003). Eutrophication of Freshwater and Marine Ecosystems, A Global Problem. *Environmental Science and Pollution Research.* Vol 10. 126-139.

Simon, N.S. (1989). Nitrogen Cycling between Sediment and the Shallow-Water Column in the Transition Zone of the Potomac River and Estuary. II. The role of Wind-Driven Resuspension and Absorbed Ammonium. *Estuarine, Coastal and Shelf Science.* Vol 28. 531-547.

Stirzaker, S., Biggs, H., Roux, D. and Cilliers, P. (2010). Requisite Simplicities to Help Negotiate Complex Problems. *AMBIO.* Vol 39. 600-607.

Strahler, A.N. (1957). Quantitative Analysis of Watershed Geomorphoplogy. *American Geophysical Union Transactions.* Vol 38. 913-920.

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.* Vol 42. 4249-4260.

Tao, Y., Wei, M., Ongley, E., Zicheng, L. and Jingsheng, C. (2010). Long-term variations and casual factors in nitrogen and phosphorus transport in the Yellow River, China. *Estuarine, Coastal and Shelf Science.* Vol 86. 345-351.

Thomann, R.V. (1998). The Futrure "Golden Age" of Predictive Models for Surface Water Quality and Ecosystems Management. *Journal of Environmental Engineering.* Vol 124. 94-103

Triska, F.J. and Higler, L.W.J. (2012). Fresh Surface water Volume II: Biogeochemical processes in river systems. EOLSS. http://www.eolss.net/sample-chapters/c07/e2-07-04-01.pdf.

Van der Westhuizen, A.J. and Eloff, J.N. (1985). Effect of the temperature and light on the toxicity and growth of the blue-green algae *Microcystis aeruginosa* (UV-006)*. *PLANTA.* Vol 163. 55-59.

Van Orden, G.N. and Uchrin, C.G. (1993). The study of dissolved oxygen dynamics in the Whippany River, New Jersey using the Qual2e model. *Ecological Modelling.* Vol 70. 1-17.

Yuceer, M., Karadurmas, E. and Berber, R. (2006). Simulation of river streams: Comparison of a new technique with QUAL2E. *Mathematical and Computer Modelling.* Vol 46. 292-305.

Walmsley, R.D., Walmsley, J.J. and 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:/www.environment.gov.za/Enviro-Info/sote/nsoer/issues/water/index.htm.

Walmsey, R.D. and Butty, M. (1980). Limnology of some selected South African impoundments. Special Report. Water Research Commission. Pretoria. 229.

Wang, H. and Wang, H. (2009). Mitigation of lake eutrophication: Loosen nitrogen control and focus on phosphorus abatement. *Progress in Natural Science.* Vol 19. 1445-1451.

Wang, L., Wei, J., Huang, Y., Wang, G. and Maqsood, I. (2011). Urban non-point source pollution buildup and washoff models for simulating storm runoff quality in the Los Angeles County. *Environmental Pollution.* Vol 159. 1932-1940.

Watkins, K. (2009). "Human Development Report 2006-Beyond scarcity: Power, poverty and the global water crisis". *United Nations Development Programme.* Retrieved November 14, 2012 from http://hdr.undp.org/en/media/HDR06-complete.pdf

Wei, Q., Zhu, G., Wu, P., Cui, L., Zhang, K., Zhou, J. and Zhang, W. (2010). Distributions of typical contaminant species in urban short-term storm runoff and their fates during rain events: a case of Xiamen City. *Journal of Environmental Sciences.* Vol 22. 533-539.

Wimberley, F. and Coleman, T. (2005). Water Quality Modelling for Planning. Department of Water Affairs Report no: 7028-6631-1-E, Pretoria, South Africa.

Withers, P.J.A. and Jarvie, H.P. (2008). Delivery and cycling of phosphorus in rivers: A review. *Science of the Total Environment.* Vol 400. 379-395.

Appendices

Number of Headwaters	1																
Headwater 0 (Mainstem)																	
Headwater label	Reach No	Flow	Elevation	Weir				Rating Curves				Manning Formula					Prescribed
		Rate		Height	Width	adam	bdam	Velocity		Depth		Channel	Manning	Bot Width	Side	Side	Dispersion
		(m^3/s)	(m)	(m)	(m)			Coefficient	Exponent	Coefficient	Exponent	Slope	n	m	Slope	Slope	m2/s
Mainstem headwater	1	0.145	502.000	0.0000	0.0000	1.2500	0.9000	0.0000	0.000	0.0000	0.000	0.089	0.1000	2.00	0.00	0.00	0.00
Water Quality Constituents	Units	########	######	2:00 AM	3:00 AM	4:00 AM	5:00 AM	6:00 AM	7:00 AM	8:00 AM	9:00 AM	10:00 AM	11:00 AM	12:00 PM	1:00 PM	######	3:00 PM
Temperature	C										6.50						
Conductivity	umhos										1120.00						
Inorganic Solids	mgD/L																
Dissolved Oxygen	mg/L										8.20						
CBODslow	mgO2/L																
CBODfast	mgO2/L										10.72						
Organic Nitrogen	ugN/L										20000.00						
NH4-Nitrogen	ugN/L										2220.00						
NO3-Nitrogen	ugN/L										1010.00						
Organic Phosphorus	ugP/L										1020.00						
Inorganic Phosphorus (SRP)	ugP/L										0.00						
Phytoplankton	ugA/L										0.39						
Internal Nitrogen (INP)	ugN/L																
Internal Phosphorus (IPP)	ugP/L																
Detritus (POM)	mgD/L																
Pathogen	cfu/100 mL																
Alkalinity	mgCaCO3/L	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Constituent i																	
Constituent ii																	
Constituent iii																	
pH	s.u.	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	8.37	7.00	7.00	7.00	7.00	7.00	7.00
Headwater 1 (Tributary 1)																	
Headwater label	Reach No	Flow	Elevation	Weir				Rating Curves				Manning Formula					Prescribed
		Rate		Height	Width	adam	bdam	Velocity		Depth		Channel	Manning	Bot Width	Side	Side	Dispersion
		(m^3/s)	(m)	(m)	(m)			Coefficient	Exponent	Coefficient	Exponent	Slope	n	m	Slope	Slope	m2/s

QUAL2K | Time Zones | Headwater | Downstream | Reach | Reach Rates | Air Temperature | Dew Point Temperature | Wind Speed

Screen shot of Headwater page from Qual2K.

		ISS	Slow CBOD		Fast CBOD	Organic N		Ammonium	Nitrate		Organic P		Inorganic	Phytoplankton					Bottom Algae			
Reach	Prescribed	Settling	Hydrolysis	Oxidation	Oxidation	Hydrolysis	Settling	Nitrification	Denitri	Sed Denitri	Hydrolysis	Settling	Settling	Max Growth	Respiration	Excretion	Death	Settling	Max Growth	Respiration	Excretion	Death
Label	Reaeration	Velocity	Rate	Rate	Rate	Rate	Velocity	Rate	Rate	transfer coeff	Rate	Velocity	Velocity	Rate	Rate	Rate	Rate	Velocity	Rate	Rate	Rate	Rate
	/d	m/d	/d	/d	/d	/d	m/d	/d	m/d	m/d	/d	m/d	m/d	/d	/d	/d	/d	m/d	mgA/m2/d or /d	gA/m2/d or	gA/m2/d or	gA/m2/d o
Site 1	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	1.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010
Site 6	0.05		1.0000	1.0000	1.0000	0.5000	0.0000	2.0000	1.0000	0.0000	0.5000	5.0000	1.0000	9999.0000	0.5000	0.0100	0.0100	0.0000	9999.0000	0.5000	0.0100	0.010

QUAL2K | Time Zones | Headwater | Downstream | Reach | Reach Rates | Air Temperature | Dew Point Temperature | Wind Speed

Screen shot of Reach Rates page from Qual2k

Prescribed downstream boundary?	Yes														
Downstream Boundary Water Quality (optiona	*Units*	*12:00 AM*	*1:00 AM*	*2:00 AM*	*3:00 AM*	*4:00 AM*	*5:00 AM*	*6:00 AM*	*7:00 AM*	*8:00 AM*	*9:00 AM*	*10:00 AM*	*11:00 AM*	*12:00 PM*	*1:00 PM*
Temperature	C														9.50
Conductivity	umhos														1467.00
Inorganic Solids	mgD/L														
Dissolved Oxygen	mg/L														10.30
CBODslow	mgO2/L														
CBODfast	mgO2/L														
Organic Nitrogen	ugN/L														
NH4-Nitrogen	ugN/L														0.00
NO3-Nitrogen	ugN/L														29870.00
1120	ugP/L														1120.00
Inorganic Phosphorus (SRP)	ugP/L														0.00
Phytoplankton	ugA/L														0.38
Internal Nitrogen (INP)	ugN/L														
Internal Phosphorus (IPP)	ugP/L														
Detritus (POM)	mgD/L														
Pathogen	cfu/100 mL														
Alkalinity	mgCaCO3/L														
Constituent i															
Constituent ii															
Constituent iii		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
pH	s.u.	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.00	8.94	7.00	7.00	7.00	7.00

Screen shot of Downstream page from Qual2K