Detergent Phosphorus in South Africa: Impact on Eutrophication with Specific Reference to the Umgeni Catchment

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ABSTRACT

The contribution of detergent phosphorus to eutrophication and the economic and water quality consequences of eliminating detergent phosphorus were assessed in the Umgeni catchment, in KwaZulu-Natal, South Africa.

The following computations and investigations formed part of the assessment:

- calculation of the phosphorus loading arising from urban and rural detergent consumptions,
- quantification of phosphorus loadings on the four major impoundments in the Umgeni catchment and the contribution made by detergent phosphorus,
- development of a predictive equation relating phosphorus loading to algal production in the impoundment and using it to determine the impact of detergent phosphorus elimination on algal production,
- investigation of the fate of phosphorus compounds in an impoundment, using the MINTEQA2 geochemical equilibrium speciation model,
- a cost-benefit assessment of detergent reformulation.

The results indicated that detergents contributed significantly to the environmental phosphorus loading, with rural inputs (46 %) being slightly less than urban inputs (54 %).

The phosphorus loading on the Inanda impoundment was found to be significantly greater than that on the other impoundments, primarily due to the large urban and rural populations residing in the catchment area. Three scenarios for obtaining the catchment loading showed detergents to comprise between 26 and 53 % of the loading on the impoundment.

A phosphorus-loading/algal-production model was successfully developed for the Inanda impoundment and was used to assess the impact of the reduced loading corresponding to detergent phosphorus elimination. For the most probable reduction scenario of 53 %, the algal count was predicted to reduce by 75 %.

Examination of the phosphorus species distribution using the MINTEQA2 model showed that precipitation and adsorption processes dominate over soluble complex formation and leave only a small amount of phosphorus in solution for algal uptake.

An investigation of the costs and benefits of eliminating detergent phosphorus indicated that the costs associated with proscribing detergent phosphorus outweighed the benefits.

To my dear family, for their steadfast support, encouragement and enduring patience.

PREFACE

I declare that this thesis has not been submitted to any other university or institution and unless stated in the text, is my own work.

This research was carried out in terms of a Water Research Commission (*WRC*) project entitled *Detergent Phosphorus in South Africa: Impact on Eutrophication with Specific Reference to the Umgeni Catchment.*

Professor C A Buckley of the University of Natal, Pollution Research Group supervised this project, most of which was undertaken at Umgeni Water in Pietermaritzburg.

The style of this thesis is based on the University of Natal, Faculty of Engineering *Style Guide for Theses and Dissertations* [Wright & Broadhurst, 1991].

M Pillay December 1994

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LIST OF SYMBOLS, ACRONYMS AND ABBREVIATIONS

l	litre
μg	microgram
cells.m ℓ^{-1}	cells per millilitre
kg	kilogram
mg	milligram
ACRU	Agricultural Catchments Research Unit
ADP	Adenosine diphosphate
ATP	Adenosine triphosphate
CCWR	Computing Centre for Water Research
DWAF	Department of Water Affairs and Forestry
EDTA	Ethylenediamine tetraacetic acid
ESD	Enumerative subdistrict
GIS	Geographic Information System
Lever Bros	Lever Brothers (Pty.) Ltd.
NTA	Nitrilotriacetic acid
OECD	Organisation for Economic Co-operation and Development
RWQO's	Receiving Water Quality Objectives
South Africa	The Republic of South Africa
STPP	Sodium tripolyphosphate
UK	United Kingdom
USA	United States of America
USSR	former Union of Soviat Socialist Republic
WRC	Water Research Commission
WWW	Wastewater Works

GLOSSARY

- *Cyanophycae* Commonly referred to as blue-green algae. *Cyanophycae* is often the dominant algal class in eutrophic impoundments often causing severe water quality problems.
- Destratification Refers to the mixing of water in an impoundment resulting from the breakdown of thermal stratification.
- Epilimnion The upper layer of water in an impoundment, which in a stratified water body is warmer and less dense than the lower water layers.
- Eutrophic A term applied to a water body which has high nutrient concentrations resulting in excessive plant growth.
- Eutrophication In this report, eutrophication is an increase in the nutrient supply or loading, over and above the basic supply from the natural environment or from its former state.
- Hypolimnion Refers to the deep, colder and relatively undisturbed region of a stratified water body.
- Life Cycle Life cycle assessment is a new and developing discipline which Assessment evaluates the environmental performance of products and processes on a *cradle to grave* basis.
- Macrophyte Large aquatic plants, macroscopic in size.
- Non-point orRefers to the discharge of pollutants from distributed or dispersedDiffuse Sourcesources, which enter the receiving water body *via* surface or
subsurface flow and also atmospheric depositions.
- Oligotrophic A term applied to a water body which has low concentrations of plant nutrients resulting in low productivity.
- Point Source Refers to the discharge of pollutants from a known discrete source, such as a wastewater works.

- Productive In this report, productive refers to the manufacture of organic material, such as algae.
- Stratification Thermal stratification is the layering of the water mass as a consequence of a thermally induced density gradient over the water column. A water body may also be stratified with respect to chemical constituents. In this report stratification refers to thermal stratification.

CHAPTER ONE Introduction

In 1986, Heynike & Wiechers of the Water Research Commission (*WRC*) undertook an investigation into detergent phosphorus and its impact on eutrophication in the Republic of South Africa (*South Africa*). Their study showed that detergents comprised between 35 and 50 % of the total phosphorus loading on domestic wastewaters and presented a significant source of phosphorus to the environment. An assessment of the implications of banning detergent phosphorus, however, showed that the costs associated with eliminating detergent phosphorus outweighed the benefits. The authors indicated that there was lack of suitable data for the study and some of the calculations were based on assumptions. They therefore recommended:

- more accurate data be collected to improve the computations,
- the Water Research Commission continue to keep a watching brief on the subject of detergent phosphorus,
- the South African detergent industry continue to test and implement cost effective substitutes for phosphate builders [Heynike & Wiechers, 1986].

Towards the latter part of 1990, Lever Brothers (Pty.) Ltd. (*Lever Bros*) had approached the University of Natal, Pollution Research Group (*PRG*) and the University of Cape Town (*UCT*) and discussed sponsoring an investigation into the effect of substitute detergent builders on wastewater treatment. This study commenced at *UCT* in 1991 as a Masters research project. Following on from this, a meeting was held in 1991 with representatives of the *WRC*, *Lever Bros*, the *PRG* and Umgeni Water where it agreed that the *PRG* in collaboration with Umgeni Water would undertake to update the Heynike & Wiechers study on the impact of detergent phosphorus on eutrophication. The latter investigation funded by the *WRC* commenced in 1992, with the principal researcher stationed at Umgeni Water in Pietermaritzburg.

The Umgeni catchment was chosen as the study area, since it was relatively well known by the researcher, was easily accessible, and water quality data had been collected for the catchment as part of the Umgeni Water routine monitoring programme. The Umgeni catchment also constitutes a major developmental region in *South Africa* and serves the water needs of three major urban centres, namely, Pietermaritzburg, Pinetown and Durban, as well as surrounding small towns and rural areas.

The research on detergent phosphorus and its contribution to eutrophication, i.e. nutrient enrichment, is particularly relevant to *South Africa* where many impoundments have become eutrophic or are threatened by eutrophication. For example, Walmsley & Thorton [1982] reported on the trophic status of 31 impoundments in *South Africa* and indicated that 9 were eutrophic and 13 bordering on eutrophication.

The major consequence of eutrophication is prolific growth of algae or certain rooted macrophytes. This may result in severe water quality problems, including, unpleasant tastes and odours, deoxygenation and fish kills, which may affect all recognized users of the water. The Department of Water Affairs and Forestry (*DWAF*) defined the five users of water as potable, industrial, agricultural, recreational and the environment [*DWAF*, 1990]. In the case of the potable user, eutrophication has resulted in considerable expense due to the requirement of sophisticated treatment measures such as the use of powdered activated carbon to treat taste and odour problems [Umgeni Water, 1993].

Eutrophication may be controlled by the reduction of the nutrient supply to the impoundment. Phosphorus is frequently the nutrient limiting aquatic plant growth and is therefore often singled out for reduction in eutrophication control programmes.

Phosphorus sources include point sources such as domestic and industrial wastewaters and diffuse sources such as agricultural wastes and fertilizers. In detergents, phosphorus serves as a builder which works in synergy with the surfactant to perform the cleaning function. Phosphorus arising from detergent consumption is usually in the form of orthophosphate - the bioavailable phosphorus form, and is therefore a suitable option for control. Various authors [e.g. Heynike & Wiechers, 1986; Sas, 1989; Edmondson, 1991] have indicated that about half the phosphorus contained in domestic wastewaters may arise from laundry detergents, which could in turn contribute significantly to the phosphorus loading on impoundments. Should this be the case in the Umgeni catchment, elimination of detergent phosphorus could contribute to improving water quality, especially of impoundments.

Over the years following the Heynike and Wiechers [1986] study, additional data and information have become available, including more detailed water quality and landuse data, particularly for the Umgeni catchment, as well as more accurate data and information on the costs and implications of treating water drawn from eutrophic impoundments. In addition, the proportion of the phosphorus loading attributable to non-point sources appears to have increased as well as the number of eutrophic impoundments. For example, the Nagle impoundment on the Umgeni system, previously classified as oligotrophic [Walmsley

1.2

& Thornton, 1982] has since 1989 displayed recurring blooms of *Cyanophycae* (or bluegreen algae), resulting in severe water treatment problems [Umgeni Water, 1984a]. In the light of these developments, the contribution of detergent phosphorus to eutrophication of water bodies has been re-examined in the Umgeni catchment.

1.1 OBJECTIVES

The objectives of the study were:

- To assess the contribution of detergent phosphorus to eutrophication in the Umgeni catchment.
- To determine the economic and water quality consequences of eliminating detergent phosphorus.
- To provide a methodology for studies in other catchments.

1.2 STUDY AREA

The area of study, shown in **Figure 1.1**, extended from the headwaters of the Umgeni at the foothills of the Drakensberg, to the Umgeni outflow from the Inanda impoundment. The total study area comprised 4 078 km².

The study catchment lies in the summer rainfall region of *South Africa* and receives 800 to 1 200 mm of rainfall per annum. Four major impoundments lie on the Umgeni system, namely the Midmar, Albert Falls, Nagle and Inanda impoundments. The Umgeni river, its tributaries and impoundments, all serve to satisfy the water demands of the greater Pietermaritzburg and Durban areas, the surrounding rural areas as well as the recreational and environmental requirements of the Umgeni catchment [*DAWF* & Umgeni Water, 1994].

Landuse practices in the upper three subcatchments, namely, Midmar, Albert Falls and Nagle, is predominantly agricultural with some informal settlements, a few small towns and a fair amount of rural subsistence settlements. The lower lying Inanda subcatchment is the largest and most developed and supports the city of Pietermaritzburg with an urban population of *ca*. 275 000 people [**Appendix A**] as well as surrounding industrial, rural and informal areas.



Various point sources are located throughout the Umgeni catchment, the largest being the Darvill Wastewater Works, in the Inanda subcatchment, serving the greater Pietermaritzburg area.

Water quality in the Inanda impoundment is expected to be affected the greatest as a result of the large catchment size and nature of the landuse practices.

1.3 TIME PERIOD

Initial calculations assessing the mass of detergents used in rural and urban areas and the percentage contribution to the environmental loading, were undertaken for one year, namely October 1990 to September 1991, and made use of the population data collected during the census in 1991. However, for the development of phosphorus-eutrophication models and the estimation of the impact of detergent phosphorus elimination on water quality, data collected for a four-year period, namely, February 1990 to January 1994, were used.

1.4 **REPORT STRUCTURE**

This thesis comprises five chapters, of which *Chapter One* provides a broad introduction detailing the background, purpose and extent of the study and previous work undertaken.

Chapter Two is a review of the literature and comprises a critical discussion of three key aspects, namely, *Phosphorus Chemistry, Eutrophication* and *The History of Detergent Legislation and Formulation*. The section on *Phosphorus Chemistry* discusses the behaviour of phosphorus in the aquatic environment and provides insight into the fate of phosphorus compounds discharged. Definitions, consequences, causes and control measures are discussed under the topic of *Eutrophication*. *The History of Detergent Legislation and Formulation*, provides information on the bans and restrictions on detergent phosphorus in other countries, the various types of substitute builders employed and the impact of detergent phosphorus bans and reformulations on water quality.

Chapter Three describes the procedures employed for data acquisition and processing. Various calculation procedures are described, including, quantification of phosphorus loadings from detergent consumption in urban and rural areas, point source phosphorus loadings on the environment, phosphorus loadings on impoundments and the proportion of detergent phosphorus in the Inanda impoundment loading. The processes leading to the development of a predictive equation, relating phosphorus loading to algal production in the

impoundment, and the use of this equation to estimate the impact of detergent phosphorus elimination on algal production, is thereafter described. This is followed by an outline of the use of the MINTEQA2 geochemical speciation model to investigate the fate of phosphorus compounds discharged to the impoundment. Finally the method of assessing the costs and benefits of detergent reformulation is described.

Chapter Four presents the results of the various computations in text, tabular and graphical form, and discusses the key findings. Conclusions reached from the work undertaken and recommendations for future work are provided in *Chapter Five*.

CHAPTER TWO Literature Review

This literature review comprises a critical discussion of three key aspects, namely, *Phosphorus Chemistry, Eutrophication* and *The History of Detergent Legislation and Formulation.* The section on *Phosphorus Chemistry* discusses the behaviour of phosphorus in the aquatic environment and provides insight into the fate of phosphorus compounds discharged. Definitions, consequences, causes and control measures are discussed under the topic of *Eutrophication. The History of Detergent Legislation and Formulation*, provides information on the bans and restrictions on detergent phosphorus in other countries, the various types of substitute builders employed and the impact of detergent phosphorus bans and reformulations on water quality.

2.1 PHOSPHORUS CHEMISTRY

Phosphorus compounds discharged to the aquatic environment will be distributed between dissolved, precipitated and adsorbed phases, as a result of physical, chemical and biological processes. An understanding of these processes is useful when investigating the impact of phosphorus reduction measures on eutrophication, as it provides insight into the fate of phosphorus compounds discharged and the species that are likely to be available for algal uptake.

2.1.1 Phosphates

Most of the phosphorus compounds present in nature or used commercially are in the form of phosphate salts or organic and inorganic derivatives of them [Van Wazer, 1973]. The phosphate anion PO_4^{3-} consists of a central phosphorus atom surrounded by four oxygen atoms. Compounds with a single phosphate group are called orthophosphates, while a chain of phosphate molecules is referred to as a condensed phosphate or polyphosphate. The simplest condensed phosphate is pyrophosphate $P_2O_7^{4-}$ and comprises two phosphate groups bonded together, while the tripolyphosphate $P_3O_{10}^{5-}$ is a three chain phosphate compound. Cyclic phosphates also occur and are generally referred to as cyclic metaphosphates. [Van Wazer, 1973; Snoeyink & Jenkins, 1980].

Examples of inorganic phosphates that are used commercially on a large scale include tripolyphosphates (detergents and water conditioners), and calcium and ammonium orthophosphates and polyphosphates (fertilizers). Organic phosphates used commercially include those in insecticides, plasticizers and surfactants. In the environment both

inorganic and organic phosphorus compounds are degraded biologically and chemically to orthophosphate - the ultimate degradation product. [Shen & Morgan, 1973; Austin, 1984].

2.1.2 Phosphorus forms in the aquatic environment.

In the aquatic environment, phosphorus may be present in organic or inorganic form. A major portion of the phosphorus occurs in organic form, the main sources of which were identified by Hooper [1973], as:

- organic compounds of living and dead particulate suspended matter including plants and animals,
- dissolved organic compounds,
- organic phosphorus present in bottom sediments.

Decay of settling plant and animal matter will result in particulate organic phosphates being converted to dissolved inorganic phosphates. Orthophosphate is the phosphorus form that is biologically mobile and the main form in which phosphorus is exchanged among biological components [Hooper, 1973; Sonzogni, et al., 1982]. Sonzogni, et al. [1982] reported that, at the pH of most natural waters, $H_2PO_4^-$ and HPO_4^{2-} were the directly bioavailable inorganic forms.

Analytically, orthophosphate in a water sample may be measured by filtering the sample through a 0.45 μ m filter. However, other phosphorus compounds that pass through a 0.45 μ m filter, such as polyphosphates, dissolved organic phosphates and fine particulate phosphorus, may also be included in the orthophosphate measurement. Although these fractions are often small compared to the orthophosphate fraction, they are accounted for by referring to the phosphorus fraction that passes through a 0.45 μ m filter as *soluble reactive phosphorus*. [APHA, et al., 1985; Sonzogni, et al., 1982].

The total phosphorus that is present in a water sample, is measured after acid digestion of an unfiltered sample. This would provide a measure of the sum of all the phosphorus fractions present, including, dissolved inorganic phosphates (orthophosphates and polyphosphates), dissolved organic phosphates and particulate inorganic and organic phosphates including adsorbed fractions. [APHA, et al., 1985; Harwood & Hatting, 1973].

2.1.3 Properties of phosphates

The key chemical and physical properties of phosphates that are of environmental interest were defined by Van Wazer [1973] as the following :

• The formation of soluble complexes with metal ions (sequestration):

Both orthophosphate and polyphosphate anions form soluble complexes with metal ions. (This property of polyphosphates has also proved important commercially, for example, in the detergent industry tripolyphosphates are employed *inter alia* as agents for complexing the calcium Ca^{2+} and magnesium Mg^{2+} ions present in the wash water, which would otherwise interfere with the cleaning process).

- Adsorption on surfaces and precipitation to form low solubility compounds: Both adsorption and precipitation are important processes governing the distribution of phosphorus in aquatic systems. These are expanded on in the following section. Van Wazer [1973] pointed out that for the phosphate concentrations present in natural waters, precipitation and adsorption processes will dominate over the formation of soluble complexes.
- Degradation of esters and condensed phosphates:
 In the environment, organic and condensed inorganic phosphorus compounds, will over a period of time, degrade by chemical and biological action to orthophosphates.

2.1.4 Processes influencing phosphorus distribution in an impoundment.

Various physical, chemical and biological processes govern the mass distribution of phosphorus in an impoundment. These include, turnover and stratification, soluble complex formation, precipitation and dissolution, adsorption and desorption, redox processes and biological uptake and mineralization. [Snoeyink & Jenkins, 1980]. Some of these processes are illustrated in **Figure 2.1**.

Precipitation, adsorption and biological uptake are processes removing phosphorus from solution. Stratification of the impoundment also aids phosphorus removal by promoting sedimentation of particulate phosphorus material. Formation of soluble complexes, dissolution, desorption and mineralisation are processes supplying phosphorus to the system. Destratification or turnover will promote phosphorus supply to the impoundment epilimnion.

While all of the above processes are interrelated in a complex manner, an attempt is made to describe their influence on the phosphorus distribution in an impoundment, using examples from the literature where appropriate.

2.1.4.1 Stratification and destratification

Stratification and destratification of the impoundment are brought about by seasonal changes in temperature and can influence the distribution of phosphorus in the water

column. In summer when the impoundment is stratified, the phosphorus distribution will be non-uniform with higher concentrations in bottom waters. However, during winter when the impoundment is uniformly mixed, phosphorus may be homogeneously distributed throughout the water column [Golterman, 1973].

The stratification and mixing of impoundments will also influence phosphorus compounds entering in the inflowing water. In winter, when the impoundment has destratified, the inflowing water will be assimilated into the impoundment water mass. In summer the surface of an impoundment may be warmer, and therefore less dense than the inflowing water, causing the colder inflowing water to sink to a depth in the impoundment which has water of the same density. However, as water flows through the length of the impoundment it may become increasingly dispersed into the bulk of the water mass [Thomas, 1973].

Figure 2.1: The fate of phosphorus in an impoundment. Modified after Golterman [1975], cited in Dallas & Day [1993].



2.1.4.2 Precipitation, adsorption and sedimentation

In summer higher phosphorus concentrations are noted in the impoundment hypolimnion and may be attributed to the sinking of particulate phosphorus material, which may arise from processes occurring in the impoundment and phosphates supplied to the impoundment in the inflowing water.

The types of inorganic phosphate precipitates entering an impoundment will depend on their origin and may enter as minerals of iron, aluminium, calcium and fluoride [Hesse, 1973; Golterman, 1973]. Iron and aluminium phosphates were reported by Hesse [1973] to be associated with finer soil particles and were thus transported to the deeper parts of the impoundment before settling, while calcium phosphates were associated with

the coarse particles and were deposited in the shallower water. Phosphates entering the impoundment in dissolved form will also readily form precipitates. Brown [1973] stated that hydroxyapatite $Ca_5(PO_4)_3OH$ is the least soluble of the calcium phosphate precipitates, but in practice it has been found that two hydrated salts, monetite $CaHPO_4.H_2O$ and octacalciumphosphate $Ca_8H_2(PO_4)_6.5H_2O$ are the salts that precipitate. The presence of fluoride ions in the impoundment will result in the formation of fluorapatite $Ca_{10}(PO_4)_6(F,OH)_2$, which has been reported to be markedly less soluble than hydroxyapatite [Brown 1973; Altschuler, 1973]. Golterman [1973] and Marsden [1989] both reported that calcite $CaCO_3$ formation in an impoundment may also co-precipitate phosphate ions.

Soluble phosphorus compounds that enter the impoundment appear to rapidly disappear from solution. Hesse [1973] stated that this was partly due to biological uptake but largely due to adsorption of the phosphate onto particulate material. Phosphates may also enter the impoundment already adsorbed onto clays and organic complexes. The chemistry of adsorption processes appears to be complex. In the literature, the most frequently quoted adsorbent is $Fe(OH)_3$ [e.g. Golterman, 1973]. Another system for phosphate adsorption was given as the clay minerals, such as kaolinite and montmorillonite for which various possible mechanisms were proposed including: binding of phosphate anions ($H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}) by displacement of OH^- ions in the clay lattice; chemical bonding of phosphate anions to positively charged edges of clays; and adsorption of phosphates onto clays through clay/humic acid/phosphate complexes [Golterman, 1973].

Whether precipitated or adsorbed, however, the tendency of particulate phosphates would be sedimentation in the impoundment and therefore epilimnetic depletion.

2.1.4.3 Redox processes, dissolution and desorption

In summer when an impoundment is stratified, decay of organic matter may result in low oxygen concentrations in the hypolimnion, causing reducing conditions in the sediments. This may cause precipitated and adsorbed phosphorus compounds to be released back into the water column [Ryding, 1985]. The sediment phosphorus pool is generally dominated by inorganic phosphorus compounds such as mineral phosphates of iron, calcium and aluminium [Golterman, 1973]. The reduction of Fe^{3+} solids to soluble Fe^{2+} ions or ionic complexes has been suggested by many authors [Golterman, 1973; Hesse, 1973; Ryding 1985] as an important mechanism for phosphorus release. Hesse [1973] reported that calcium phosphates and aluminium phosphorus complexes are not influenced

by electrochemical reduction. Phosphate absorbed onto montmorillonite has also been reported to be indifferent to redox potential [Serruya, 1971, cited in Golterman, 1973]. Reduced iron species have been found in sediment layers with redox potential below 200 mV (sic) [Golterman, 1973]. Marsden [1989] reported that the presence of oxygen in the water will rapidly re-oxidize Fe^{2+} ions migrating up from the sediments and precipitate them as Fe^{3+} hydroxide. The $Fe(OH)_3$ in turn has a high sorptive capacity for phosphate and will thus limit its release into the water column [Marsden, 1989]. Golterman [1973] also indicated the presence of an oxidised crust $Fe(OH)_3$ overlying other sediment layers, which could inhibit the movement of molecules and ions.

Phosphorus migration into the water column may still occur, as a result of processes limiting phosphorus adsorption onto iron compounds. These include, high concentrations of silica which would selectively adsorb onto iron compounds, hydrogen sulphide which will precipitate ferrous sulphide, and the presence of organic acids which chelate iron and other cations. The capacity of iron to adsorb phosphorus also decreases with increasing pH value due to selective adsorption of OH^- . [Marsden, 1989]. Golterman [1973] reported on the work of Thomas [1968], who put forward a strong argument against the reduction of iron leading to phosphate release into water. Thomas [1968] proved that $FePO_4$ does not solubilise under anaerobic conditions in activated sludge and suggested the precipitation of vivianite $Fe(PO_4)_2$ as an explanation [Golterman, 1973].

The release of phosphorus from the bottom sediments into the water column has been reported by Ryding & Rast [1989] to be a complicated process involving the interaction of physical, chemical and biological mechanisms. These include the redox condition, mineralisation, gas bubble formation, bioturbation, effects of algae and macrophytes, pH value, diffusion and wind turbulance. Ryding & Rast [1989] also indicated that in the initial state of lake eutrophication the remobilization of phosphorus is often retarded by the sorption and chemical bonding of phosphate to bottom sediments. However, phosphorus release can become significant once the sediments are saturated with phosphate.

In a deep productive impoundment with a large anaerobic zone, the phosphorus released under anaerobic conditions would be diluted in a large hypolimnion. In addition, increasing distance away from the sediments will result in a small phosphorus concentration gradient across the thermocline [Marsden, 1989]. Within the epilimnion of such impoundments, phosphorus will be depleted during summer by algal uptake and eventually sink into the hypolimnion with dead algae. Autumn turnover may cycle phosphorus from the hypolimnion back into the photic zone but blooms of algae may then be limited by light and temperature.

Unused phosphorus may remain in the water column until the spring, by which time sedimentation and flushing may reduce the amount available to algae [Marsden, 1989].

2.1.4.4 Soluble complex formation

Many authors [e.g. Snoeyink & Jenkins, 1980; Ryding, 1985] show that inorganic and organic phosphates have the ability to form soluble complexes and chelates with many metal ions. If these processes were to dominate in an impoundment, high phosphorus concentrations could be maintained in solution and made available to algae. Examples of soluble complexes with orthophosphate include $MgHPO_4$ (aq), $FeHPO_4^+$ and $CaH_2PO_4^+$ species. The extent of the complex or chelate formation will depend on the concentration of phosphates and metal ions, the pH value of the water and the presence of other ligands [Snoeyink & Jenkins, 1980]. Van Wazer [1973] reported that at the concentrations present in natural waters, precipitation and adsorption processes will dominate over the formation of soluble complexes.

2.1.4.5 Biological uptake and mineralisation

Phosphorus uptake by algae is reported by various authors [e.g. Hooper, 1973; Rigler, 1973] to occur predominantly in the dissolved inorganic orthophosphate form. The quantity of phosphate required by algae differs for different genera. Mackenthun [1973] reported on work done by Chu [1943] on nutrient uptake. For the organisms studied Chu [1943] found that optimum growth was obtained at phosphorus concentrations in the range 0.09 to 1.8 mg. ℓ^{-1} , while a limiting effect occurred at phosphorus concentration below 0.09 mg. ℓ^{-1} Mackenthun [1973].

Experience has shown that when the external phosphate concentration is high, algae can absorb more than is required for growth and utilize it when the external supply becomes scarce [O'Kelly, 1973; Sawyer, 1973]. Dissolved orthophosphate entering the impoundment will therefore be rapidly immobilized by algae. However, other phosphate removal processes occurring simultaneously in the impoundment suggest that algae would have to compete for the orthophosphate in solution. It follows that larger influxes of dissolved orthophosphate would make more phosphorus available to algae and is therefore likely to sustain larger algal standing crops.

The phosphate taken up by algae may be utilized in three overlapping ways. Firstly, for conversion of adenosine diphosphate (ADP) to adenosine triphosphate (ATP) to be used as a chemical energy store for later use; secondly, phosphorus is used as a component of some electron carriers mediating biological redox reactions; and finally, phosphorus plays an important role in other plant metabolism [Jagendorf, 1973]. Hodson [1973] reported that phosphorus found in living systems may be present as orthophosphates, polyphosphates (of various molecular weights), phosphoproteins, phosphonates, various orthophosphate and polyphosphate esters and complex nucleoproteins.

During mineralisation, orthophosphate is liberated from organic compounds by the enzymes and organic acids produced by micro-organisms [Ryding, 1985]. Organic phosphorus formed in the impoundment and organic particulate phosphorus entering the impoundment as partially and undecomposed plant and animal material are expected to follow the same decomposition route. Hesse [1973] stated that micro-organisms liberate the inorganic portion of the organic phosphorus, but the remaining organically bound phosphorus (e.g. nucleic acids, phosphoesters, and phytin) are resistant to mineralization and will eventually deposit at the bottom of the impoundment. This was supported by Scharpf, Jr. [1973] who pointed out that about 30 % of the phosphorus material of algae and associated organisms was resistant to degradation and formed refractory material in the sediments within impoundments. Golterman [1973] and Levine & Schindler [1989] found that phosphorus recycling is rapid, occurring in a few hours, compared to carbon and nitrogen cycling which takes a few days. Golterman [1973] also suggested that phosphate mineralization takes place primarily in the epilimnion of impoundments.

2.1.4.6 Summary

- The normal phosphorus balance of an impoundment, appears to be rapid removal of phosphorus from solution by sedimentation and algal uptake.
- Phosphorus sedimentation may occur in the form of:
 - ⇒ precipitated phosphates as minerals of calcium, iron, aluminium and fluoride;
 - ⇒ phosphates adsorbed onto surfaces such as iron hydroxide precipitates or clays;
 - ⇒ non-biodegradable phosphorus associated with dead organic matter.
- Phosphorus uptake by algae occurs as dissolved inorganic orthophosphate and can take place from phosphorus entering the impoundment in dissolved form or recycled from decaying organic material.
- While a proportion of the phosphorus of dead algae may be rapidly recycled for further uptake, only additional incoming phosphates would be able to maintain prolonged algal blooms since about one-third of phosphorus from the decay of organic matter will always be lost from the system.
- Desorption and dissolution of phosphorus from sediments in deep impoundments is a slow process relative to sedimentation. In the initial state of lake eutrophication the remobilization of phosphorus is often retarded by the sorption and chemical bonding of phosphate to bottom sediments. However, phosphorus release can become significant once the sediments are saturated with phosphate.

• Without new inputs to the impoundment, the net result of phosphorus sedimentation and algal uptake would appear to be an epilimnetic deficiency of phosphorus.

2.2 EUTROPHICATION

2.2.1 Definition

The term eutrophication is regularly used in the literature, but different authors have ascribed different and often conflicting meanings to it.

The Organisation for Economic Cooperation and Development [*OECD*, 1982] described eutrophication as,

"the response in water to overenrichment by nutrients,"

while Ryding & Rast [1989] reported eutrophication as,

"the state of a waterbody which is manifested by an intense proliferation of algae and higher aquatic plants, and their accumulation in the waterbody in excessive quantities."

Ryding & Rast [1989] proceeded to discuss natural and cultural eutrophication, where the former is the natural aging process of an impoundment and the latter arising from anthropogenic activity. Marsden [1989], on the other hand, described eutrophication as,

"the biological reaction of aquatic systems to nutrient enrichment, the eventual consequence of which is the development of primary production in nuisance proportions."

Edmondson [1991] was generally not in favour of definitions of a given phenomenon, which included the processes associated with the phenomenon and described eutrophication simply as,

"an increase in the nutrient supply or loading, over and above the basic supply from the natural environment or from its former state."

Edmondson [1991] stated that confusion of terminology arose when the definition of eutrophication included a description of its consequences. Edmondson [1991] also differentiated between natural and cultural eutrophication, where the latter would refer to nutrient enrichment as a result of anthropogenic discharges, e.g. wastewater effluents and

agricultural runoff, while an example of the former could be an increase in nutrients from a newly exposed soluble rock formation.

Edmondson's definition of eutrophication, i.e. " *increase in nutrient supply or loading ... from its former state*," was considered to be meaningful and well thought out and was therefore adopted for use in this thesis. Increased production of algae and macrophytes, were therefore regarded as the consequences of eutrophication.

2.2.2 Consequences of eutrophication

The most significant consequence of eutrophication is excessive algal or macrophyte production in an impoundment. Eutrophication is often characterised by the dominance of *Cyanophycae* or blue-green algae, which tend to be more of a nuisance than other algae. *Cyanophycae*, also referred to as cyano-bacteria, are autotrophic like other algae and liberate oxygen as a by-product of photosynthesis, but they have a cellular structure identical to bacteria. Some genera of *Cyanophycae* (e.g. *Anabaena*) can fix atmospheric nitrogen. In addition, unlike most other algae which occur as single cells or relatively small groups or colonies, they tend to form larger colonies and are consequently more visible. [Edmondson, 1991].

Possible ways in which excessive algal production, particularly *Cyanophycae*, can interfere with the uses of the water resource are provided below [Thomas, 1973; Edmondson, 1991] :

- Taste and odour problems may arise in raw water inflows to water treatment works requiring sophisticated and expensive water treatment processes to be used.
- Excessive algal growths are highly visible and therefore aesthetically unpleasant.
- Dense growths of algae can significantly reduce water transparency as well as interfere with water sports and other activities involving water contact.
- Some algal species are capable of producing toxins, thus posing a health hazard to humans and other animals that drink the water.
- Excessive oxygen depletion which occurs when algae die and sink to the bottom of impoundments can result in mortality of fish and other aquatic life.
- Low oxygen levels may result in the presence of electrochemically reduced species of iron and manganese in the water, which increase the cost of water treatment.

2.2.3 Causes of algal proliferation: limiting factor

Edmondson [1991] reported that about twenty elements have been found to be essential for algal growth. The major inorganic ions such as calcium, magnesium, sodium, potassium, chloride and sulphate are present in much higher concentrations (milligram. ℓ^{-1}) than needed for growth, while elements such as nitrogen and phosphorus are present in much smaller concentrations (microgram. ℓ^{-1}) and therefore may not always be available for algal uptake. The constituent that limits production to the greatest extent as a result of its scarcity is referred to as the limiting constituent. Typically, phosphorus and nitrogen are the most common elements that limit growth but carbon has also been suggested as a possible growth limiting element [Brown, 1973; Ryding & Rast, 1989]. Light may also be a growth limiting factor in very turbid impoundments [Umgeni Water, 1994b].

The only method by which algae can obtain phosphorus is by absorption of phosphate ions from the water, while nitrogen is obtained from nitrate, nitrite or ammonia, but can also be extracted from the atmosphere by certain algal genera. Carbon is usually obtained from carbon dioxide or bicarbonate. Ryding & Rast [1989] stated that carbon only becomes limiting when the water is saturated with both phosphorus and nitrogen and when light availability and temperature are high and carbon dioxide transport from the atmosphere to the water is slow.

Phosphate more often than nitrogen is present in low concentrations in water. This may be attributed to, natural inflows containing little phosphate but large amounts of nitrate, fewer phosphates than nitrogenous compounds being washed off agricultural lands, and rainwater containing large quantities of nitrogenous compounds that can be utilised by plants [Thomas, 1973]. Consequently, phosphorus is most often the constituent that limits growth. However, when phosphorus is present in very high concentrations due to significant anthropogenic activity, and is not the limiting element, it can be made to limit growth since it is still the most easily controllable element [Golterman, 1973].

2.2.4 Control of eutrophication

Many authors, [e.g. Levine & Schindler, 1989; Edmondson, 1991], indicated that production in most impoundments is determined primarily by the quantity of nutrients that enter with the inflowing water. While it is found that part of the nutrient supply to the impoundment is recycled, dense algal blooms can usually not be attributed to nutrient recycling alone [Edmondson, 1991]. Consequently, the most effective long-term strategy for controlling eutrophication has been found to be the reduction of the incoming nutrient supply.

In order to reduce the inputs of phosphorus to the aquatic environment the most significant and readily controllable sources are usually identified. Phosphorus sources may be both natural and cultural and are usually categorized as point and non-point (or diffuse). Phosphorus discharges from wastewater works and industries are examples of point sources, while natural inputs and runoff from agricultural lands, rural and informal settlements are described as non-point or diffuse sources.

Phosphorus arising from the various sources may occur in both soluble and particulate form. The soluble fraction is generally considered easily utilized by algae and is termed the bioavailable fraction. Consequently sources high in bioavailable phosphorus are especially attractive as control targets. Diffuse phosphorus sources are not readily controllable as they enter the water with rainfall events, and in many instances the phosphorus arising from these sources is predominantly in a particulate form. Bath & Marais [1991], measured the soluble and particulate phosphorus fractions in runoff from an agricultural catchment in the Berg river, and showed that more than 80 % of the phosphorus was present in particulate form. Point sources such as wastewater effluents, on the other hand, discharge largely bioavailable phosphorus and are therefore the most important sources considered in eutrophication control programmes.

2.2.4.1 Water quality management policies, approaches and practices in SA

Precautionary approach

The Department of Water Affairs and Forestry (*DWAF*) has adopted a precautionary approach to management of water quality in South Africa, in which positive steps are taken to prevent or minimise undesirable impacts on the environment. The precautionary approach is applied in all water resources decisions made by the *DWAF* and requires the probable impacts on public health and the environment to be predicted when developments are being considered. [*DWAF*, 1995]

Special Phosphate Standard

In South Africa legislation exists and is implemented, for limiting the phosphorus content of wastewater discharges in so called *sensitive* catchment areas. Seven such *sensitive* catchment areas have been identified in South Africa, of which the Umgeni river upstream of the influence of tidal water is one. Existing legislation requires that wastewater works discharging in these catchment areas comply with a 1 mg. ℓ^{-1} orthophosphate discharge standard. [*DWAF*, 1984].

The Special Phosphate Standard forms part of the current Special Effluent Standard which together with a General Effluent Standard serve as the minimum standards that have to be

complied with in the country. The impact of effluent discharges on the receiving water's fitness for use will be assessed against receiving water quality objectives (see below) and may lead to revision of the effluent standard which may sometimes be stricter than the minimum effluent standards. [*DWAF*, 1995]

Receiving water quality objectives

An approach based on water quality objectives for the receiving water has been proposed by the *DWAF* for controlling the entry of non-hazardous pollutants, such as phosphorus, to the water environment. This approach, the Receiving Water Quality Objectives (*RWQO's*) approach, focuses on the quality of the receiving water instead of the quality of the emissions from a pollution source in decisions concerning pollution control.

It involves the specification of water quality requirements for the receiving water based on the users of the water, and proposes control of point and non-point (or diffuse) sources of pollution to meet these water quality requirements [Van der Merwe & Grobler, 1990]. The *RWQO's* approach assesses the assimilative capacity of the receiving water and determines the extent to which the pollution can be absorbed without detriment to the accepted users of the water.

Changes to existing effluent discharge practices can be effected by carrying out a *RWQO's* study. Pollution from point sources is controlled by setting site specific effluent standards which take into account the contribution of non-point sources and the objectives set for the receiving water [Van der Merwe & Grobler, 1990].

2.2.4.2 Detergents as a phosphorus control measure

The use of phosphorus in detergents has been debated globally for at least three decades. In countries of North America, Western Europe and in Japan, detergent phosphorus bans and restrictions have been in place since the late 1960's. Currently no restrictions on detergents are imposed in South Africa.

In *South Africa*, laundry detergents are used in both urban and rural areas and enter the environment with wastewater. While wastewater from urban areas generally undergoes treatment which *inter alia* reduces the phosphorus content, wastewater from rural and informally settled areas passes untreated into the environment. The phosphorus contained in detergents is in the form of a condensed or polyphosphate which when exposed to water treatment or the environment will degrade to orthophosphate - the bioavailable form of
phosphorus. Eliminating detergent phosphorus therefore appears to be an attractive option for further control of both point and non-point bioavailable phosphorus inputs to the environment.

2.2.5 Phosphorus removal at WWW

Phosphorus may be removed from WWW by both chemical and biological processes. Biological phosphorus removal is widely implemented in South Africa and may be supplemented by chemical processes. Large wastewater works such as the Darvill WWW in the Umgeni catchment, employ the activated sludge process whereby phosphorus is stripped by micro-organisms. Phosphorus removal may also be achieved by using artificial reed-beds. As effluent flows through the reed-bed, the reeds absorb phosphorus while bacteria decompose organic matter. Chemical phosphorus removal is achieved by addition of salts of iron or aluminium (usually iron or aluminium sulphate) which readily form insoluble precipitates with phosphate and may then be removed by sedimentation.

Sludge containing phosphorus generated at a WWW may be incinerated, land-filled and less often, used as agricultural fertilizer.

Landbank Environmental Research & Consulting [1994] reported on two relatively new technologies for phosphate recovery in a form in which it could be recycled for use in artificial fertilizers, animal-feeds, industrial grade phosphates and in food and pharmaceutical applications. The two technologies described are the Smit Nymegen magnetic water treatment system and the Crystalactor. The Smit Nymegen system, developed in Holland has been described as one of the most effective forms of wastewater treatment available and removes phosphorus by utilizing a magnetic carrier material. The Crystalactor is a compact fluidised-bed reactor and will provide high-grade phosphate for use in a wide variety of phosphate and phosphoric acid products. [Landbank Environmental Research & Consulting, 1994].

2.3 HISTORY OF DETERGENT LEGISLATION AND FORMULATION

2.3.1 Definition

A detergent is a synthetic cleaning compound, which derives its cleaning ability from its dual water-attracting (hydrophilic) and water-repelling (hydrophobic) properties. When detergents are introduced into water these properties cause the detergent molecules to aggregate into spherical clusters called micelles with the hydrophilic components in the water and the hydrophobic components in air or dissolved in fatty soils (dirt). This causes a

reduction in interfacial tension which when combined with the mechanical action of washing causes dirt molecules to be easily removed from the fabric and into the wash water. [Austin, 1984; United Nations, 1992]. **Figure 2.2** illustrates the processes by which detergents remove dirt particles from fabrics.

Figure 2.2: Illustration of the mechanism by which detergents remove dirt particles from the surface of fabrics. Modified after Berth, et al., [1987].



2.3.2 Composition of laundry detergents

Laundry detergents constitute a major portion of detergent products. The functionality of laundry detergents is derived from the combined action of a surfactant, builder, bleach and various additives, as described below.

• Surfactant or tenside

The surfactant or surface active ingredient performs the primary cleaning in detergents through the reduction of interfacial tension. This consists of completely wetting the dirt and surface of the item being washed, removing the dirt from the surface, and maintaining the dirt in solution [Austin, 1984]. The surfactants frequently used can be classified as anionic or non-ionic, which refers to the charge that results when the surfactant dissociates in water. Alkyl benzene sulphonate and alkyl sulphates are the most widely used anionic surfactants, while commonly used non-ionic surfactants are reaction products of alcohols with ethylene oxide [United Nations, 1992].

• Builder

Detergents can generally be classified as built or un-built. The builder is a compound which works in synergy with the surfactant and is generally employed in domestic laundry detergents. Un-built detergents require the surfactant to perform the cleaning unaided and are mostly utilised by industries for washing of hard surfaces. [Department of the Environment, 1991]. The function of the builder is inactivation of the hardness ions (calcium and magnesium, which would otherwise interfere with the cleaning), by sequestration, precipitation or ion-exchange [United Nations, 1992]. Builders also counteract soil redeposition and provide pH buffering in the wash liquor [Department of the Environment, 1991]. The detailed properties and characteristics of detergent builders were reported by Morgenthaler [1987] as the following:

Functional properties:

Control of hardness and heavy metal ions; source of alkalinity; provision of pH buffering; capability to deflocculate, emulsify and solubilise and prevent redeposition.

Formulation and processing properties:

Compatibility with other ingredients; suitability for use in agglomerated products, drymixed products, spray-dried products, liquid products and slurry products; contribution to detergent processing; and contribution to product properties.

Environmental and safety properties:

Safe for humans; and environmentally acceptable.

Bleach

Bleaching agents are employed in laundry detergents to remove unwanted discolouration on fabrics and return fabrics to their original whiteness [Department of the Environment, 1991]. Examples include sodium perborate and sodium percarbonate [Ecover, 1990].

Additives

Additives are used to improve the performance of the detergent and include antiredeposition agents, bleach stabilizers, enzymes, fabric-whitening agents, foam controllers, corrosion inhibitors, perfumes and colourants [Austin, 1984; United Nations, 1992]. **Table 2.1**, reproduced from Writh [1987] provides examples of typical North American phosphate and phosphate-free detergent formulations. In practice however, considerable variation of the types and amounts of the listed components occur.

Table	2.1 :	Composition	of	phosphate-built	and	phosphate-free	laundry
deterge	ents [after Writh, 198	37].				

Component	Composition (%)		
	Phosphate-built	Phosphate-free	
Alkyl Benzene Sulphonate	13	17	
Alcohol	0.5	0.5	
Sodium Tripolyphosphate	24	0	
Zeolite A	0	20	
Sodium Carbonate	5	18	
Polymer	0 to 3	0 to 3	
Sodium Silicate	7	5	
Sodium Sulphate	Made up to 100	Made up to 100	

2.3.3 History of detergent phosphorus legislation

The most efficient and cost effective builder used in laundry detergent formulations has been pentasodium triphosphate $Na_5P_3O_{10}$ commonly referred to as tripolyphosphate or *STPP* [Kandler, 1987]. Reasons for its extensive use are provided in *Section 2.3.4*. In wastewater works and in the aquatic environment *STPP* hydrolyses readily to orthophosphate and is therefore a source of bioavailable phosphorus. This has resulted in its use in detergents being a subject of controversy for at least 3 decades. Criticism started in the late 1960's when eutrophication of lakes became a problem. Detergent manufactures in North America, including Canada and many of the states in the USA, Japan and Europe were required to exclude or limit the use of phosphorus in detergents through either legislative or voluntary agreements [Andree et al., 1988].

In North America, concern over eutrophication primarily in the Great Lakes region was first expressed in 1967 and led to the introduction of detergent phosphate legislation during the early 1970's. Canada is reported to be a pioneer in limiting the phosphorus input to the Great Lakes [Edmondson, 1991]. In the USA, bans were generally imposed in those states bordering on the Great Lakes or which had many small lakes. Factors put forward by the United States Environmental Protection Agency in support of the ban were [Alexander, Jr., 1978]:

- the confirmation of the role of phosphorus as the limiting nutrient for eutrophication in the Great Lakes;
- high phosphorus loadings and accelerated eutrophication in some locations in all the Great Lakes;
- inability of wastewater works to always achieve design phosphorus removal levels and slower construction of wastewater works than was planned;
- costly removal of phosphorus by chemical treatment and increased sludge handling costs and increased discharge of total dissolved solids;
- difficulty in controlling the atmospheric phosphorus load which comprised up to 20 % of the loading in some areas;
- difficulty in controlling non-point source or diffuse phosphorus loading;
- experience with detergent bans in other areas indicated that they were accepted by consumers, had reduced the costs of wastewater treatment and in certain waters had been followed by reduced algal growth;
- banning phosphorus in laundry detergents would enable phosphorus to be reduced immediately and at the least cost.

Detergents are currently banned in *ca.* 28 % of the USA [Alhajjar, 1990]. In non-ban areas the popularity of phosphate free liquid detergents, which procured 30 % of the detergent market in the 1980's, resulted in further reduction in *STPP* usage in the USA [Bressan, 1987].

In Western Europe statutory limits and voluntary legislation were imposed in 1975 and resulted in a decline in *STPP* consumption. Further legislation enforced the limit of laundry detergent phosphorus in Switzerland and Italy to less than 1 % [Bressan, 1987]. In France, where restrictions are voluntary, detergent manufacturers had agreed to produce at least one phosphate-free brand, while in The Netherlands, which also has voluntary restrictions, 95 % of the detergents are phosphate-free.

Apart from Western Europe and the USA the only other detergent phosphate restrictions are in Japan, where the detergent industry voluntarily agreed on a maximum of 4.3 %

phosphorus. In 1987, however, Andree et al. reported that more than 90 % of all Japanese household laundry detergents were phosphate free and zeolite-built, while in 1992 the United Nations reported that complete replacement of *STPP* by zeolite A had taken place in Japan. Mori [1987] stated that the successful switching from phosphate to phosphate-free detergents in Japan was due to the maintenance of washing performance by the new formulations.

In the United Kingdom (*UK*) no detergent phosphate restrictions are imposed but about one-fifth of detergent products are phosphate-free. The *UK* Soap and Detergent Industry Association stated that the phase-out of phosphates in detergents was not planned for the future, as the environmental benefits were not evident and the most effective method of reducing the environmental phosphate load was phosphate stripping at wastewater works [Patel, 1991]. Ecover, a *green* detergent manufacturer, reported that pollution by toxic blue-green algae was widespread in the *UK*, where 30 % of the phosphorus load entering receiving waters, was reported to arise from washing powders. However, only 9 out of the 2 000 *UK* wastewater works had phosphate stripping capabilities. Ecover proposed removal of phosphates from detergents as a first step towards cleaner water [Ecover, 1991]. In 1989 Ecover produced a handbook, providing details of the ingredients of its laundry detergents [Bines & Marchand, 1989], while in 1990 a *Green Paper* was published where step-wise changes to *UK* detergent formulation were proposed to minimize the threat to the environment [Ecover, 1990].

A detailed list of countries and states which currently have detergent phosphorus restrictions or bans is provided in **Table 2.2**.

Country	Year	Status	% Phosphorus
Switzerland	1986	Legislative	banned 1,2,3
Germany	1984	Legislative	5.5 ¹ , 5.0 ³
Austria	1987	Legislative	5.5 ¹ , 5.0 ³
The Netherlands	1983	Voluntary	5.5 ¹ , 5.0 ³
Sweden	1970	Voluntary	7.5 1,3
France		Voluntary	5.0 ³
Finland	1970	Legislative	7.0 ^{1,3}
Italy	1986	Legislative	2.5 ¹ , 1.0 ^{2,3}
Norway	1986	Legislative	3.0 ¹ , banned ³
Japan (Shiga and Tokyo)		Legislative	banned ^{3,5}
Japan	1978	Legislative	4.3 ¹ , 2.5 ³
Venezuela		Legislative	banned ³
Canada	1973	Legislative	2.3 ¹ , 2.2 ³
USA States			
Connecticut	1972	Legislative	8.7 ^{3,4}
Florida	1972	Legislative	8.7 ^{1,3,4}
Maine	1972	Legislative	8.7 1,3,4
Indiana	1973	Legislative	banned 1,3
Maryland	1985	Legislative	banned ^{1,3}
Michigan	1977	Legislative	banned ^{1,3}

Table 2.2: List of countries which impos	e detergent phosphorus restrictions or bans.
------------------------------------------	----------------------------------------------

Literature Review

Minnesota	1979	Legislative	banned 1,3
New York	1973	Legislative	banned 1,3
Vermont	1978	Legislative	banned 1,3
Wisconsin	1984	Legislative	banned 1,3
Virginia		Legislative	banned 1,3
North Carolina		Legislative	banned ³
South Carolina	1991	Legislative	0.5 4
Oregon	1991	Legislative	0.5 4
USA Selected Counties			
Dade county		Legislative	8.7 ³
Idaho		Legislative	banned ⁴
Montana		Legislative	banned ⁴
Ohio		Legislative	banned ⁴
Texas	1992	Legislative	banned ⁴
USA Municipalities			
Washington DC	1986	Legislative	banned ^{1,3}
Chicago		Legislative	banned ³
Akron		Legislative	banned ³
Portland		Legislative	banned ⁴
Ore		Legislative	banned ⁴
Spokane		Legislative	banned ⁴
Washington		Legislative	banned ⁴
USA Communities			
Illinois		Legislative	banned ⁴
New Hampshire		Legislative	banned ⁴
Idaho		Legislative	banned ⁴

1 Andree et al., 1987

2 Department of the Environment, 1991

3 United Nations, 1992

4 Ainsworth, 1992

5 Houston, 1987

2.3.4 History of laundry detergent formulation

Sodium tripolyphosphate (*STPP*) has been used in detergent formulations for longer than thirty years. Morgenthaler [1987] reported that *STPP* was the preeminent detergent builder since the introduction of built detergent formulations in the 1940's. The properties and characteristics that detergent builders are required to have were described in *Section 2.3.2*, and *STPP* is reported to provide more of these than any other single component. The three main factors that have been responsible for its popularity are, high performance, low cost and non-toxicity and as yet, no other builder is *alone* able to meet these conditions as efficiently as *STPP* [Kandler, 1987; United Nations, 1992].

Restrictions on the use of phosphate resulted in the development of a range of multicomponent builder systems to replace *STPP* formulations. Substitutes that have been considered as builders or co-builders include :

Zeolite A Nitrilotriacetic Acid (NTA) Silicates

Citrates Carbonates Carboxylic Acids Soaps Ethylenediamine Tetraacetic Acid (EDTA)

The attributes of these builders and co-builders including *STPP* are discussed below, detailing *performance, availability, usage* and *environmental and health impacts*.

2.3.4.1 Sodium tripolyphosphate (STPP)

Performance

Technical reasons favouring the use of *STPP* as a detergent builder are summarized below [Kandler, 1987; United Nations, 1992] :

- efficient sequestration of hardness ions, namely calcium and magnesium;
- disintegration of soil encrustation's on the fibre and washing machines;
- dispersion of pigment soils, in particular oxidic pigment soils;
- prevention of soil redeposition;
- buffering of wash liquor pH value;
- chemical stability during storage;

Availability

Phosphate rock is the primary source of raw material for phosphorus [Jones, 1973]. Emigh, [1973] reported that the known reserves of phosphate rock are extremely large and practically unlimited (sic). The USA is the world's largest producer of phosphate rock, followed by the former USSR and Morocco, but it is also produced in smaller quantities in many other countries.

Usage

Prior to legislation in 1973 laundry detergent formulations in Canada and the USA were very similar, typically using between 40 and 45 % *STPP*. Since then use has been restricted or banned with Canada using formulations containing 8 % *STPP* and the USA using none in ban areas and 35 % in restricted areas. In Japan, although legislation permits the use of about 12 % *STPP*, most detergents are phosphate free. [Murata, 1987; Morgenthaler, 1987; Andree et al., 1987]. *STPP* is still likely to be the principal builder in countries which do not restrict the use of phosphate in detergents. *Lever Bros* reported that all laundry detergents in South Africa are phosphate-built [*Lever Bros*, 1993].

Environmental and Health Impacts

Structurally *STPP* is a condensed phosphate or polyphosphate comprising a chain of 3 phosphate molecules. In the aquatic environment and at a neutral pH value *STPP* degrades by hydrolysis to orthophosphate which is non-toxic. The only environmental concern with regard to the use of *STPP*, is eutrophication. In wastewater treatment more than 90 % of the *STPP* hydrolyses to orthophosphate and in biological treatment plants hydrolysis is practically complete. Contribution of detergent phosphorus to the total phosphorus load to wastewater works varies and in the UK was reported to be between 25 and 50 % [Department of the Environment, 1991]. In South Africa, Wiechers & Heynike [1986] estimated the load to be between 35 and 50 %.

2.3.4.2 Nitrilotriacetic Acid (NTA)

NTA was the first potential *STPP* substitute considered when the need arose to reformulate detergents and it has been investigated for many years as a partial or total substitute.

Performance

NTA has much better sequestering properties than *STPP* (the most important builder property [Houston, 1987]), but does not have all the desirable properties of an effective builder. **Table 2.3**, reproduced from Houston [1987] shows the performance of *NTA* relative to *STPP*.

Properties	NTA	STPP
Solubility	Excellent	Fair
Sequestering	Excellent	Good
Detergency	Fair	Good
Peptization	None	Good
Buffering	Poor	Good
Lime soap dispersion	Fair	Good

Table 2.3 : Performance of NTA versus STPP (after Houston [1987]).

During the wash process *NTA* forms complexes with the hardness ions thereby enabling the surfactant to function efficiently. However, effective formation of these complexes require alkaline conditions throughout the wash process which *NTA* is unable to provide. *NTA* therefore has to be used as a co-builder with other builders, such as zeolite A [Department of the Environment, 1991]. *NTA* also does not have similar soil suspending or anti-redeposition properties to *STPP* [United Nations, 1992].

Availability

NTA can be chemically prepared from hydrogen cyanide which is relatively expensive. Production of *NTA* can however be made economically feasible, if hydrogen cyanide were to be obtained as a by-product from other production processes (e.g. production of polyacrylonitrile) [United Nations, 1992].

Usage

Attitudes over the use of *NTA* in detergents vary from country to country. Wendt et al. [1988] stated that it had been accepted for use in 16 countries, while in New York city it is banned. *NTA* is used in limited quantities in domestic detergent formulations in Germany, The Netherlands, Sweden and Switzerland. The acceptable *NTA* level in German and Dutch formulations is *ca.* 4 %, while the Swiss government has set a maximum limit of 5 %.

As a result of the restriction on the quantity of *NTA*, insufficient amounts are available to totally replace phosphate builders, since *ca*. 14 to 18 % *NTA* is the equivalent level required to replace the traditionally used 20 to 25 % *STPP* [United Nations, 1992]. In Canada, high levels of *NTA*, namely *ca*. 15 to 20 %, have been used in detergent formulations for the past 20 years [Morgenthaler, 1987; United Nations, 1992]. *NTA* became established in Canadian laundry detergents when legislation restricting phosphate usage came into place [Morgenthaler, 1987], and is used in combination with the maximum permitted level of polyphosphate and more recently with zeolite A.

In the USA, *NTA* was introduced into detergent builders in the late 1960's. In the 1970's its use was discontinued due to what were later shown to be erroneous safety testing results [Edmondson 1991]. After ten years of intensive safety testing the USA Environmental Protection Agency notified the detergent industry that it saw no reason to take regulatory action against the resumed use of *NTA* in detergents in the USA. In New York however, opposition was met with *NTA* usage from a safety viewpoint based on a small portion of the safety test results and a ban was imposed in 1984. This had the effect of limiting the widespread use of *NTA* in the USA [Morgenthaler, 1987].

Environmental and Health Impacts

Dywer, et al. [1990] reported that *NTA* can be used as a substitute for *STPP* with respect to washing performance, but unfavourable reports with respect to toxicology, chelating effects and inconsistent removal efficiencies from wastewaters are likely to preclude its widespread use. These findings were mostly supported by the Department of the Environment [1991] and the United Nations [1992]. Houston [1987] reported that studies on rodents had shown *NTA* to be potentially carcinogenic, while the World Health Organization [WHO, 1990, cited in United Nations, 1992] classified *NTA* as possibly carcinogenic to humans.

NTA removal in wastewater treatment takes place primarily as a result of biodegradation. Efficient biodegradation requires prior acclimatization of the bacteria and adverse influent conditions, such as high *NTA* loadings and rainfall will result in inefficient removal until acclimatization has been re-established. In addition, cold weather (i.e. temperatures below 5 to 7°C) and low oxygen levels (below 0.5 mg. ℓ^{-1}) considerably reduces biodegradation. *NTA* has a strong affinity for metal ions, apart from calcium and magnesium, and in the event of incomplete biodegradation may increase the concentration of dissolved heavy metal complexes in the environment. [Department of the Environment, 1991; Dwyer, et al., 1990].

Fairly extensive monitoring in Canada, where between 15 and 20 % *NTA* is used, have indicated no adverse effects [Houston, 1992]. Wendt et al. [1987] also reported the findings of a 4-year monitoring programme from 25 sites in the vicinity of Indianapolis, Indiana where 3.8 % *NTA* has been used in detergent formulations. From this research it was concluded that the use of *NTA* did not significantly increase *NTA* levels in rivers and final waters and did not affect metals removal in wastewater treatment or in rivers and drinking water. *NTA* removal averaged 91 % at activated sludge plants and 65 % at trickling filter plants. However, Giger [1990] (cited in Department of the Environment, 1991) reported that in Switzerland, where *NTA* is used in domestic laundry detergents, zinc carry over occurred in wastewater treatment works and *NTA* accumulation was found in Swiss and German groundwaters.

2.3.4.3 Zeolite A

Zeolite A is a water-insoluble sodium aluminosilicate and is one of the many types of sodium aluminium silicates that is applicable for use in detergents. Zeolite A has been known in nature since 1756 [Schweiker, 1987], and its discovery for use in detergents has been a milestone in the search for phosphate substitutes [Andree et al., 1987].

Performance

Zeolite removes Ca ions in water by ion exchange. Since zeolite A is water insoluble and ion exchange occurs in heterogeneous phase, with other water soluble sequestering agents transporting the metal ions through the aqueous medium and releasing them to the zeolite ion exchanger.

The United Nations [1992] reported that zeolites have no buffering capacity and therefore do not match the detergency of *STPP*. However, Andree et al. [1987] pointed out that non-phosphate zeolite-based detergents can be formulated with performance equaling that of phosphate-built detergents by utilizing zeolite A in combination with co-builders such as

nitrilotriacetic acid (NTA), polycarboxylates, carbonates and citrates. A three builder system could, for example, consist of zeolite A, sodium carbonate and a polycarboxylate. The zeolite A would soften water by ion exchange, removing the hardness ions and increasing solids suspension, while the polycarboxylate would prevent the build up of calcite deposits and solids redeposition. The sodium carbonate would serve to buffer the wash water and also sequester part of the hardness ions [Andree et al., 1987]. Some typical compositions of binary and ternary builder systems used in European formulations are shown in **Table 2.4**, reproduced from Gresser, [1987].

Builder	STPP (%)	Zeolite (%)	NTA (%)	Additive (%)
All STPP systems	20 to 40			
Binary systems				
STPP/zeolite	15 to 30	15 to 30		
STPP/NTA	15 to 30		3 to 6	
STPP/additive	15 to 30			0.5 to 3
Zeolite/NTA		25 to 40	3 to 6	
Zeolite/additive		30 to 40		0.5 to 3
Ternary systems				
STPP/zeolite/NTA	15 to 25	25 to 25	3 to 6	
STPP/zeolite/additive	15 to 25	15 to 25		0.5 to 3
STPP/NTA/additive	15 to 25		3 to 6	0.5 to 3
Zeolite/NTA/additive		20 to 35	3 to 6	0.5 to 3

Table 2.4: Typical builder systems in European detergent formulations (after Gresser, [1987]).

Andree et al. [1987] reported that low phosphate zeolite based type laundry detergents have been accepted for use by the consumer without objection. This is substantiated by the United Nations [1992] who reported that in Europe, the USA and the Far East, there are no serious reservations regarding complete replacement of *STPP* by zeolite A. Mori [1987] gave the reason for consumer satisfaction in Japan, as maintenance of washing performance at the same level as the phosphate-built detergents. The United Nations [1992] also reported that the utilization of zeolite A as a constituent in powdered laundry detergent formulations had thus far not caused any major manufacturing problems.

Non-phosphate zeolite-built detergents were reported to be slightly more expensive than phosphate-built detergents due to more costly production technology but were retailed at the same price [Andree et al., 1987].

Availability

The United Nations [1992] stated that with regard to natural resources and future production capacities, there were no serious restrictions against total replacement of *STPP* by zeolite A in Europe, the USA and the Far East. Moreover, Oxlade [1990] reported that zeolites cost less than phosphates.

Usage

The single largest use of zeolites throughout the world is in commercially-built detergents [Schweiker, 1987]. Concern over eutrophication of lakes led to replacement of phosphate detergents with zeolites in Japan, North America and most Western European Countries. Andree et al., [1987] reported that in Japan more than 90 % of detergents had been reformulated with zeolite A, while in 1992 the United Nations [1992] reported that *STPP* had been replaced completely by zeolite A in Japan and some countries of Western Europe and parts of the United states.

Environmental and Health Impacts

Replacement of *STPP* by zeolite A requires that zeolite shows no adverse effects on water treatment and degrades easily in the environment. The United Nations [1992] reported that intensive investigation using model and actual wastewater treatment systems showed no deleterious effects even at high concentrations and in many instances the use of zeolite improved performance, possibly due to increased sludge retention time. These findings were supported by studies undertaken by Kaschula, et al., [1993] for biological wastewater works in South Africa. The United Nations [1992] reported that tests on biological wastewater treatment works containing both activated sludge and trickling filters gave zeolite elimination as 90 to 95 %, while in chemical wastewater treatment practically quantitative removal was indicated. The use of zeolite, however, results in increased sludge production. In addition, heavy metal retention may be expected in the presence of zeolite.

Thorough research into the ecotoxicology of zeolite A in laboratory and field studies have shown no antagonistic effects towards the environments exposed to. Available data indicate that zeolite A would weather to natural aluminosilicate halloysite and gibbsite, while a bioaccumulation experiment indicated that no significant bioaccumulation of zeolite A was anticipated in living aquatic organisms [United Nations, 1992]. Zeolite A is thus characterised as an inert dust, harmless to living organisms.

2.3.4.4 Sodium silicate

Sodium silicate is used in laundry detergent formulation to provide alkaline buffering and for corrosion control [Morgenthaler, 1987].

Performance

Silicate has no effect on water softening or redeposition, but is a source of alkalinity in the wash water.

Availability

In Europe an over-capacity of silicates exists and if complete replacement of *STPP* were to occur, demand could easily be met. If *STPP* were to be replaced by zeolite, the amounts of silicates directly used would decrease as a result of incompatibility with zeolite, while the amount of silicate employed in the form of zeolite would increase [United Nations, 1992].

Usage

Sodium silicate was used in early detergent formulations but was largely replaced by *STPP*. With the introduction of *STPP* restrictions, its use was increased but subsequently decreased in both phosphate and phosphate-free formulations containing zeolite, due to interference with the ion exchange properties of zeolite [Morgenthaler, 1987].

Environmental and Health Impacts

The United Nations [1992] reported that sodium silicate is an alkaline irritant to the eyes and skin. No bioaccumulation occurs in the environment.

2.3.4.5 Sodium citrate

Sodium citrate is used largely in liquid detergents as a result of its hydrolytic stability, safety and excellent biodegradability [Morgenthaler, 1987; United Nations, 1992]. Recent powder formulation also contain large amounts of citrate [United Nations, 1992]. However, Morgenthaler [1987] reported that compared to *STPP* it is inferior from both a cost and performance perspective.

Performance

Sodium citrate has three basis functions in laundry detergents [United Nations, 1992]:

- Water softening by removal of calcium and magnesium ions.
- Disintegration of fibre bound soil by formation of complexes with calcium and magnesium ions.
- Aiding emulsification and dispersion of soil particles.

At lower temperatures (<60°C) the calcium binding capacity of sodium citrate exceeds *STPP* but decreases rapidly at higher temperatures. Improved performance is achieved at higher temperature when used in combination with zeolite [United Nations, 1992].

Availability

Sodium citrate is manufactured from all renewable resources such as starch hydrolysates, sugar, can molasses and beet molasses [United Nations, 1992].

Usage

Early use of sodium citrate was very limited, but use increased in the USA when a major liquid brand reformulated to an entirely citrate composition in the 1980's [Morgenthaler, 1987]. In the USA sodium citrate has no competition in liquids, but a leading liquid brand that is built with citrate in the USA is built with *NTA* in Canada [Morgenthaler, 1987].

Environmental and Health Impacts

Morgenthaler [1987] reported that sodium citrate is safe and environmentally acceptable. This is substantiated by the United Nations [1992] who reported that citric acid and its salts are widespread in living organisms and is absorbed and metabolized immediately.

2.3.4.6 Carbonates

Sodium carbonate is used in both phosphate and phosphate-free detergent formulations largely due to its low cost and other properties, notably alkaline buffering [Morgenthaler, 1987].

Performance

Sodium carbonate softens the wash water by precipitation of hardness ions. In practice it is less effective than *STPP* in that, the hardness ions are deposited and not maintained in suspension, the extent of removal is less, and its foam stability is inferior to that of *STPP*. The salt deposits that occurs with sodium carbonate also results in decreased life-span of fabrics and machine parts, but can be reduced or eliminated by incorporating *STPP* in the detergent formulation [United Nation. 1992]. When used as the sole builder, sodium carbonate also has poorer powder structure and the formulation is prone to caking in bulk storage. To produce free-flowing powders carbonates have to be used together with silicates [United Nations, 1992].

Availability

Sodium carbonate does occur naturally, but the naturally occurring source is unsuitable for use in detergents. Commercial sodium carbonate is manufactured from sodium chloride and carbon dioxide.

Usage

Sodium carbonate was used in detergent formulations as a builder prior to *STPP* but was swiftly and totally replaced when *STPP* was introduced into the detergent market [Morgenthaler, 1987]. Phosphate restrictions during the early 1970's led to some new manufacturers introducing high concentrations of sodium carbonate (up to 75 %) into the formulation. This led to concern over human safety as well as encrustation onto fabrics and washing machines. Subsequent non-phosphate formulations used 20 to 30 % sodium carbonate with higher levels of silicates. Currently in the USA, non-phosphate formulations contain 20 to 30 % sodium carbonate without the higher levels of silicates and some products are combined with zeolites and a polymer.

Environmental and Health Impacts

Sodium carbonate occurs naturally and no adverse effects on the environment have been established [United Nations, 1992]. Its alkaline nature can cause temporary irritation to the skin, mucous membrane and the eyes and if swallowed can cause nausea, vomiting and diarrhea.

2.3.4.7 Carboxylic acids

Two compounds that were considered for use in detergents in the 1970's were carboxymethyltartrate and carboxymethylsuccinate. These compounds displayed potential for use in both powdered and liquid detergents [Morgenthaler, 1987].

Performance

Polycarboxylates are used in formulations as co-builders to disperse dirt particles and precipitates which would cause greying and encrustation on washing machine parts and fabrics [United Nations 1992]. Polycarboxylates are unable to substitute *STPP* completely because they possess insufficient complexing capability, but their use during detergent manufacture are of considerable economic advantage as they result in better homogenization and stabilization.

Availability

Polycarboxylates are used at such low levels in detergent formulations that availability is not of primary concern [United Nations, 1992]. They are manufactured by homopolymerization of acrylic acid but may be modified as desired by copolymerization of acrylic acid and maleic anhydride.

Usage

Polycarboxylates are used at levels of 1 to 4 % especially in low-phosphate and phosphatefree formulations [United Nations, 1992].

Environmental and Health Impacts

Polycarboxylates display low toxicity and do not produce irritation of the skin or mucous membranes [United Nations, 1992]. During wastewater treatment polycarboxylate removal is favoured by precipitation with calcium and physico-chemical adsorption onto sludge. Biodegradation plays only a limited role as polycarboxylates resist degradation [Dwyer, et al., 1990]. In the environment adsorbed polycarboxylates do not desorb.

2.3.4.8 Soaps

Soaps are salts of long chain carboxylic acids and have been used for thousand of years for washing.

Performance

Soaps are generally very good water softeners, but are less efficient than *STPP*. They generally give good overall results under normal soil conditions, but are not suitable for heavily soiled fabrics. They can therefore only be incorporated in very limited amounts in detergents.

Availability

Soaps are manufactured from renewable and readily available resources, namely, oils and fats.

Environmental and Health Impacts

In the environment soaps undergo rapid biodegradation but increase the biochemical oxygen demand [United Nations, 1992]. Increased use may therefore place an additional load on wastewater treatment. Prolonged contact of soap solution with skin causes irritation, and contact with the eyes causes a stinging sensation.

2.3.4.9 Ethylenediamine tetrataacetic acid (EDTA)

EDTA has powerful chelating abilities. In detergents EDTA is used in low concentrations to control the levels of free metal ions in the wash water and thereby increases bleaching efficiency. For various reasons including cost, EDTA is not likely to be used as a replacement for *STPP* [United Nations, 1992].

2.3.5 Liquid detergents

The first successful liquid laundry detergent was introduced in the late 1960's. Tetrapotassium pyrophosphate was used as the builder instead of sodium tripolyphosphate as it was considerably more water soluble although more expensive [Houston, 1987]. Solubility problems were eventually overcome, enabling *STPP* to be used. However in the late 1970's restrictions on the use of phosphate resulted in liquid detergents being reformulated with sodium citrate. Sodium citrate has fair sequestering properties compared to *STPP* but loses some of its effectiveness at high temperatures. The preferred surfactants in liquid detergents are soap and alcohol ethoxylates [Oxlade, 1990].

Ainsworth [1992] reported that banning and restriction of laundry detergent phosphorus had led to growth of phosphate-free laundry liquids. In the USA states where detergent phosphorus is banned, liquid detergents comprise more than 50 % of detergent sales, while in non-ban areas liquid detergents comprise 30 % of the detergent market [Greek 1991]. Oxlade [1990] reported that the success of phosphate-free liquid products could be partially attributed to better performance than phosphate-free powdered detergents. Un-built liquid formulations however, use a higher concentration of surfactant to achieve acceptable performance, as a result, profits made on liquid detergents are less than those on powdered formulations [Greek, 1991].

2.3.6 Life cycle assessment

In January 1994, Landbank Environmental Research & Consulting undertook a life cycle study to evaluate the environmental impacts of two builders used in *UK* laundry detergent formulations, namely, *STPP* and zeolite A co-built with a polycarboxylic acid (PCA). It was concluded that on a life cycle basis with equivalence of performance taken into account, there was no real difference between the environmental impacts of these two builder systems. *STPP* was found to have a slightly greater impact than the zeolite-PCA in the production phase, but marginally less impact in the disposal phase.

As a final stage of the life cycle Landbank Environmental Research & Consulting [1994] made recommendations for improving the environmental performance of phosphate. These

included recycling of phosphogypsum waste from phosphoric acid plants, conservation of energy during the *STPP* manufacturing process, phosphate recovery from WWW for recycling into detergents using the latest phosphate stripping techniques and resource saving by formulation of compact detergent powders.

2.3.7 Impact of reformulation on the life of washing machines and fabrics

The literature contains very little information on the impact of phosphate substitutes on the life of washing machines and fabrics, but the general suggestion is that incorrectly formulated detergents would cause deposits to occur, leading to premature greying of fabrics.

In the 1970's when restrictions were placed on the use of *STPP* in detergent formulations, some manufacturers reformulated with very high concentrations of sodium carbonate (up to 75 %) which *inter alia* caused encrustation on washing fabrics and washing machines [Morgenthaler, 1987]. The salt deposits that occur with using sodium carbonate result in decreased life-span of fabrics and machine parts, but can be reduced or eliminated by incorporating some *STPP* into the detergent formulation.

Writh [1987] stated that the use of small amounts of organic polymers in detergent formulations lengthened the life of textiles and washing machines. This effect is particularly pronounced in low-phosphate or phosphate-free formulations. The polymers that have been studied up to now are readily removed during wastewater treatment and are toxicologically harmless.

Wiechers & Heynike [1986] reported that no extra wear and tear on fabrics and washing machines results from detergents reformulated with zeolite and *ca*. 2 % NTA.

2.3.8 Impact of detergent phosphorus bans and reformulation on water quality

Detergent phosphates are banned or reduced in order to lower the phosphorus loading on impoundments. Various studies have shown that a reduction in the external phosphorus loading on impoundments could lead to a decrease in algal production in the impoundment. For example, Edmondson reported that Lake Washington, known as the success story of lake restoration, displayed a reduction in algal growth for every reduction in phosphorus input to the lake. Sas [1989] reported that restoration measures, which comprised reduction in the external nutrient loading, applied to 18 eutrophic impoundments in Western Europe, resulted in 16 impoundments showing clear signs of improvement.

Edmondson [1991], indicated that not all impoundments are expected to respond to a reduction in the phosphorus loading. For some hypereutrophic impoundments the reduction may not be significant enough to cause a response in the production, while

shallow impoundments with small inflows could maintain a eutrophic state for a longer period of time due to recycling of sediment phosphorus. Lee & Jones [1986] stated that impoundments which derived the bulk of their phosphorus loading from domestic wastewater, would show the greatest improvement following a detergent phosphorus ban. Following the banning of detergent phosphorus in the Great Lakes regions, various studies were undertaken to assess the impact of the bans on water quality. Some of these are described below.

Michigan detergent phosphorus ban

Two studies to assess the impact of detergent phosphorus bans on wastewater treatment chemical costs were undertaken in Michigan, one by Hartig & Hovath [1982] and the other by Hartig et al. [1982]. In both studies significant cost savings were reported due to reduction in chemical usage with decrease in the influent phosphorus loading. An improvement in environmental quality was implied, although not substantiated with data, and it was concluded that in Michigan, the phosphorus detergent ban was an effective tool for pollution control [Hartig et al., 1982].

In 1986, however, Booman & Sedlak reported that although a statistically significant reduction in influent phosphorus occurred as a result of the Michigan detergent phosphorus ban, no significant change in effluent phosphorus was observed. Booman & Sedlak [1986] asserted that at wastewater works where chemical phosphorus removal was practiced, the effluent phosphorus concentration would be largely determined by the operator who would adjust the process to achieve the desired concentration. This suggests that in order for the benefits of a detergent ban to be transferred to the environment, the ban would have to be coupled with more stringent effluent phosphorus control.

Indiana, New York, Minnesota and Wisconsin

Maki et al., [1984] reported on various case studies undertaken in the USA to assess the impact of detergent phosphorus reductions on water quality. In Indiana, Bell & Spacie [1977] were reported to have assessed the water quality of 15 lakes, four years after a detergent ban was implemented. The investigation was reported to show no water quality improvement as a result of the ban and was attributed to the small contribution of detergent phosphorus to the lake loading compared to other sources of phosphorus. Etzel et al., [1975] (cited in Maki et al., [1984]), also examined the phosphorus concentration in some of the Indiana rivers and found several hundred

micrograms per litre of phosphorus to be present. The receiving water phosphorus concentrations were reported to be so high that no benefit could be derived from a detergent phosphorus ban.

In New York, Sharfstein et al., [1977] reported that following a detergent ban, reductions in influent wastewater phosphorus loading ranged from 12.5 % to 59 %. However, these were found to result in only a small improvement in the water quality of the receiving water [Maki et al., 1984].

Maki et al., [1984] also reported on lake studies in Minnesota and Wisconsin and again reported that detergent bans resulted in only a very small change in phosphorus loading and no significant water quality effects could be related to these bans.

Ohio

Hartig et al. [1990] reported on the rationale behind the 1988 detergent phosphorus ban in Ohio, which lies in the catchment area of Lake Eerie. In 1972 an agreement was signed between the United States and Canada to reverse eutrophication in the Great Lakes by various measures, including, limiting the quantity of phosphorus in laundry detergents [Hartig et al., 1990]. By 1979 all Great Lake states had implemented detergent phosphorus restrictions with the exception of Ohio and Pennsylvania. Over the years following the bans, the total phosphorus loading to Lake Eerie was reported to have decreased from 28 000 tonnes to 12 000 tonnes with a corresponding improvement in water quality in the lake. However, to achieve the target load of 11 000 tonnes, further reductions were needed, hence the detergent phosphate ban in Ohio [Hartig et al., 1990].

The Ohio ban is expected to benefit water quality threefold, namely, by assisting noncompliant wastewater works to achieve compliance with the 1 mg. ℓ^{-1} effluent phosphorus standard, by limiting phosphorus input to the environment from combined sewer overflows, and also by limiting input from homes which employed septic tank wastewater treatment systems [Hartig et al., 1990].

• Septic tank systems

Alhajjar et al. [1990] carried out research into phosphate and phosphate-free detergents in an area served by septic tank systems. His findings were that phosphate-free detergents built with carbonate, increased the concentration of nitrate in groundwater and recommended that phosphate bans be lifted in non-sewered areas.

Chesapeake Bay

Water quality data collected between 1984 and 1991 in the Chesapeake Bay area showed a phosphorus reduction of about 19 %, attributed to the enactment of phosphate detergent legislation in the states around the bay [Blakenship, 1993]. However, this reduction was not significant enough to improve the adverse conditions in the bay, primarily low oxygen concentrations. Blakenship [1993] reported that recent computer modeling work undertaken for the area, indicated that anoxic conditions were likely to worsen if further nutrient reductions (both phosphorus and nitrogen) did not occur.

Italy

The Scientific Committee on Phosphates, Tassin, France [1991] reported that the detergent phosphorus restriction in Italy had failed to improve water quality. While the ban was reported to have reduced the phosphorus loading on Italian waters from 59 000 tonnes to 49 000 tonnes, it failed to improve water quality due to the much larger load emanating from agriculture, industry and urban wastewaters.

Germany

The phosphate content of detergents in the former Federal Republic of Germany was reduced in 1975 and by 1990 detergents were reported to be 95 % phosphate-free [De Jong et al., 1989; United Nations, 1992]. Monitoring of the river Rhine at Düsseldorf for phosphorus between 1979 and 1989 indicated that a 64 % decrease in the phosphorus load had occurred. This corresponded to a reduction in detergent phosphorus consumption from 69 000 tonnes in 1979 to only 5 000 tonnes in 1989. In addition, phosphorus removal at wastewater works increased from 25 % in 1979 to 40 % in 1989. De Jong [1989], stated that about 60 % of the phosphorus input to the river Rhine arose from wastewater effluents. The observed reduction in phosphorus load was therefore attributed to a combination of reduced use of phosphate in detergents and more efficient wastewater treatment [United Nations, 1992].

Surfactants

Zoller [1993] reported that reformulated detergents used larger concentrations of surfactants, which could also impact negatively on the environment. Alcohol ethoxylates and alkyl phenol ethoxylates were reported to be the major non-ionic surfactants in usage, of which alcohol ethoxylates were easily biodegradable (soft), and alkyl phenol ethoxylates non-biodegradable (hard) [Zoller, 1993]. The use of the non-biodegradable alkyl phenol ethoxylates is generally limited in western industrialized countries, but large quantities were reported to be used in Israel. This posed a threat to the environment as metabolites of alkyl phenol ethoxylates are known to be highly toxic

[Zoller, 1993]. It was also reported in ENDS [1993] that alkyl phenol ethoxylate usage has been implicated in male reproductive disorders leading to sterility. Two possible solutions were proposed by Zoller [1993], namely, a ban on the use of the non-biodegradable alkyl phenol ethoxylates in detergent formulations and more effective removal of both hard and soft detergents at wastewater works.

CHAPTER THREE Method

To satisfy the identified objectives, namely:

- to assess the contribution of detergent phosphorus to eutrophication in the Umgeni catchment,
- to determine the economic and water quality consequences of eliminating detergent phosphorus,
- to provide a methodology for studies in other catchments,

the following calculations were deemed necessary:

- calculation of the phosphorus loading arising from urban and rural detergent consumptions,
- quantification of phosphorus loadings on the four major impoundments in the Umgeni catchment and the contribution made by detergent phosphorus,
- development of a predictive equation relating phosphorus loading to algal production in the impoundment and using it to determine the impact of detergent phosphorus elimination on algal production,
- investigation of the fate of phosphorus compounds in an impoundment, using the MINTEQA2 geochemical equilibrium speciation model,
- a cost-benefit assessment of detergent reformulation.

As described in *Chapter 1*, the Umgeni system comprises four major subcatchments corresponding to the Midmar, Albert Falls, Nagle and Inanda impoundments. Loading calculations were performed in each subcatchment and the contribution of detergent phosphorus to the loadings on each impoundment computed.

3.1 RURAL AND URBAN DETERGENT PHOSPHORUS LOADINGS

An assessment of detergent phosphorus loadings from both urban and rural areas required a knowledge of the amount of detergent consumed and its pathway to the environment.

A market survey was carried out by Lever Brothers (Pty.) Ltd. (*Lever Bros*) in both rural and urban areas in KwaZulu-Natal, which provided data to calculate the per capita detergent consumptions for both rural and urban areas. This is described in *Section 3.1.1* below. The per capita detergent consumptions were translated to per capita phosphorus

consumptions by calculating the mean phosphorus content of the detergent products (*Section 3.1.2*). Population data were obtained for rural and urban areas in the Umgeni catchment and coupled with the per capita data to calculate the total detergent loadings from rural and urban areas (*Section 3.1.3*).

3.1.1 Rural and urban per capita detergent consumption

In 1988, *Lever Bros* undertook a survey of washing practices in major urban and rural areas of *South Africa*. Data collected for KwaZulu-Natal are shown in **Table 3.1** and included the mass of product dosed per wash load, the number of wash loads carried out per day, the number of people washed for and other relevant details.

Table 3.1: Data on washing practices, obtained from a survey undertaken by *Lever*

 Bros in urban and rural areas in KwaZulu-Natal [Palmer, 1993].

Parameter		Urban		Rural	
Number of wash loads per day.	1	2	3	1	2
Mass of product dosed per wash load, in	104	111	128	79	70
grams.					
Number of people undertaking one and	124	19	4	61	1
more than one wash.					
Average mass of product dosed per wash		105.6		78	8.9
day, in grams.					
Average number of loads washed per day.		1.18		1.	.02
Number of wash days per week.		3.71		2.	.53
Number in family.		33 have 1 to 4 persons		27 have 1 to 4 persons	
	178 have 5 to 8 persons		85 have 5 to 8 persons		
	92	have 9+ pe	rsons	41 have 9-	+ persons
Average number of persons per family.		6.8		6.5	5

The data in **Table 3.1** were used to calculate the annual per capita detergent consumption, as indicated below.

Average annual mass of detergent consumed per family [kg.(family.annum)⁻¹] :

 average number of wash loads per family per day x average mass (in grams) of detergent dosed per load x number of wash days per week x 52 weeks per annum ÷ 1000 kilograms per gram

Annual per capita detergent consumption [kg.(person.annum)⁻¹]:

 Annual mass of detergent consumed per family ÷ average number of persons per family.

3.1.2 Phosphate content of South African laundry detergents

To relate detergent consumption to phosphorus consumption, the phosphorus content of detergents was calculated using data on phosphate builder content and detergent sales, provided by *Lever Bros.* As shown in **Table 3.2** the percentage of phosphate builder, namely, sodium tripolyphosphate (*STPP*), in the various laundry detergent products varied from 16 % to 35 % with most products containing 26 %. An average value was calculated, as described below, using the fraction of sales of the product as a weight.

Table 3.2: STPP content and fraction of sales of laundry detergent products in KwaZulu-Natal during 1992 [Palmer, 1993].

Product	% STPP	Fraction of sales
Omo	26	0.44
Skip	26	0.07
Skip Micro	35	0.02
Surf	26	0.41
Gcf Regular	16	0.04
Gcf Auto	26	0.02

Average STPP content of detergents :

= {% STPP in Omo x Fraction sales Omo} + {% STPP in Skip x Fraction sales Skip} +
 ... + {% STPP in Gcf Auto x Fraction sales Gcf Auto}.

Average phosphorus content of detergents :

= Average STPP content of detergents x molecular weight phosphorus molecular weight STPP

Therefore, the annual per capita detergent phosphorus consumption [kg.(person.annum)⁻¹]:

 Annual per capita detergent consumption (Section 3.1.1) x Fraction of phosphorus in detergents.

For the above calculation, it was assumed that the builder content of competitor's products did not differ significantly from *Lever Bros* products. *Lever Bros* estimated that they supplied 80 % of the detergent market in *South Africa*, suggesting that if competitor's products deviated from *Lever Bros* products, it would not significantly alter the calculation results.

3.1.3 Rural and urban population

Population data for the Umgeni catchment were obtained from the Institute of Natural Resources and comprised the unverified 1991 census data for the region. The data were

provided in spreadsheet format per enumerative sub-district (*ESD*) and the location of *ESD* boundaries were displayed on a map. The rural population was obtained by manually overlaying the subcatchment boundaries in the area of study onto the *ESD* boundaries, to obtain the *ESD*'s or portions of *ESD*'s that fell into each subcatchment of interest. The population per subcatchment was then estimated by summing the populations in the appropriate *ESD*'s or fractions of *ESD*'s. An example of this is shown in **Table 3.3** and **Figure 3.1** for the Midmar-Lions subcatchment. The Urban population for each subcatchment was obtained by summing the population for each subcatchment was obtained by summing the population in towns in the subcatchment.

ESD	Total Population per	Fraction of ESD	Fraction of Population
Code	ESD	in Lions River Area	in Lions River Area
4203	854	100	854
4214	1 324	17	221
4217	1 138	64	724
4218	1 110	100	1 110
4219	1 192	78	927
4220	1 439	100	1 439
4221	927	3	28
4222	863	82	711
4223	1 493	100	1 493
4225	763	100	763
4226	1 062	42	443
4229	1 386	100	1 386
Total population for the Lions subcatchment			10 099

Table 3.3 : Example of ESD's and population in the Midmar-Lions subcatchment.

Figure 3.1 : An example of an overlay of enumerative sub-districts and catchment boundary for the Midmar-Lions subcatchment.



Population data from the above calculations were combined with the per capita detergent phosphorus consumption obtained from *Section 3.1.2*, to give the detergent phosphorus loadings for urban and rural areas.

3.1.4 Pathway of rural and urban detergent phosphorus to the environment

Generally in KwaZulu-Natal, urban wastewaters are treated at wastewater works, while a portion of rural wastewaters may be discharged directly to water bodies.

3.1.4.1 Rural detergent load

Data on washing practices in rural areas, indicating the percentage of the rural population that washed laundry directly at a water course, were obtained from a survey undertaken by *Lever Bros* in KwaZulu-Natal [Palmer, 1993]. For rural areas it was assumed that only laundering done directly at a water course, i.e. a river or dam, will reach the impoundment and be of consequence to water quality.

3.1.4.2 Urban detergent load

To quantify the detergent phosphorus loading from urban areas, the contribution of detergents to wastewater work's influents had to be calculated, and the phosphorus loading of the wastewater works on the aquatic environment had to be quantified.

Apart from detergent consumption, the other major sources of **soluble phosphorus** in wastewater influents were assumed to be the urine portion of human excreta and industrial discharges. The phosphorus loading from urine was obtained in a similar manner to the urban detergent phosphorus component by combining population data and the per capita phosphorus content of urine obtained from the literature, namely, 600 milligram per capita per day (or 0.219 kilogram per capita per annum) [Machlin, 1973]. The industrial phosphorus loading was quantified using data from the Umgeni Water routine trade effluent monitoring programme. The detailed data set is shown in **Appendix B**.

Information on point sources in the Umgeni catchment and water quality data for the discharges were obtained from the Umgeni Water routine point source monitoring programme. Flow data were generally obtained directly from the point source discharger. For the largest point source in the catchment area, namely, the Darvill Wastewater Works (*WWW*), daily flow and quality data were used to perform a detailed phosphorus load calculation which also included an estimate of the overflow loading during periods of high rainfall. The detailed calculation procedure is described in **Appendix C**. For smaller *WWW's* such as the Mpophomeni *WWW*, daily flow and weekly quality data were used to estimate the phosphorus loading, while for the minor point sources only monthly or annual

estimates of flow and at most monthly quality data were used. [Point sources in the Umgeni catchment are shown in **Figure 3.2**].



3.2. PHOSPHORUS LOADINGS ON IMPOUNDMENTS AND CONTRIBUTION BY DETERGENTS

3.2.1 Phosphorus loadings on impoundments

The phosphorus loadings on the four impoundments in the Umgeni system were quantified by combining inflow volumes and phosphorus concentrations using the Flux Model, developed by Walker [1987] for loading calculations [**Appendix D**]. Inflow sites corresponded to Umgeni Water monitoring sites for which water quality data were available at weekly frequency. Site locations are shown in **Figure 3.2**. Flow data were acquired from streamflow gauging undertaken by *DWAF*, or where not measured, calculated from impoundment water balances or estimated using the Agricultural Catchments Research Unit (*ACRU*) hydrological model. Details of the methods used for obtaining flow data are provided in **Appendix E**.

3.2.2 Percentage detergent phosphorus in the total environmental soluble phosphorus loading.

The sum of the urban and rural detergent phosphorus loadings, was compared to the total soluble phosphorus loading from the catchment area. Three scenarios were considered for estimating the total **soluble** phosphorus loading for the catchment, namely :

- Scenario 1 : The only sources of **soluble** phosphorus were wastewater effluents and detergents that entered from rural laundering carried out directly at the water course.
- Scenario 2 : In addition to the loading from wastewater effluents and rural laundering, non point sources (e.g. agricultural lands, informal settlements) contributed 20 % to the catchment **soluble** phosphorus loading.
- Scenario 3 : In addition to the loading from wastewater effluents and rural laundering, non point sources (e.g. agricultural lands, informal settlements) contributed 50 % to the catchment **soluble** phosphorus loading.

The percentage of detergent phosphorus in the inflow loading to impoundments was calculated for each scenario to assess the contribution of detergent phosphorus to eutrophication.

The sequence of calculations leading to the assessment of the contribution of detergent phosphorus to eutrophication is summarized in **Figure 3.3** using the Inanda subcatchment as an example.



Figure 3.3 : Sequence of calculations leading to the assessment of the contribution of detergent phosphorus to eutrophication in the Inanda subcatchment.

3.3. PHOSPHORUS-LOADING/ALGAL-PRODUCTION RELATIONSHIPS AND THE IMPACT OF DETERGENT PHOSPHORUS ELIMINATION.

3.3.1 Soluble phosphorus/algal-production models

Examination of the results of the phosphorus loading calculations for each impoundment *Chapter 4, page 4.6,* indicated that the Inanda impoundment had the most significant loading. All further work therefore concentrated on the Inanda impoundment.

Eliminating detergent phosphorus would be expected to result in a reduced phosphorus loading to the impoundment and possibly a decrease in algal production. In order to predict the impact of a reduced loading, the relationship between phosphorus entering the impoundment and algal production in the impoundment had to be established.

One of the most widely used phosphorus-eutrophication models for impoundments are the Vollenweider and Organisation for Economic Co-operation and Development (*OECD*) models.

Vollenweider [1976] [cited in Foy, 1992] proposed a loading model which related the mean total phosphorus concentration in the impoundment (P_{dam}) to the mean inflow total phosphorus concentration (P_{in}) and the water retention time in the impoundment (t_w):

$$\frac{P_{dam}}{P_{in}} = \frac{1}{1 + \sqrt{t_w}} \qquad \dots \dots 3.1$$

This model provided the basis of the OECD loading models, namely:

To relate total phosphorus concentration to algal production the OECD proposed the following chlorophyll (CHL) - phosphorus (P) models [cited in Walmsley & Thornton, 1984]:

OECD general	CHL =0.37 P ^{0.79}	3.4
OECD reservoirs	CHL =0.54 P ^{0.72}	3.5

These models are the result of investigations of nutrient loading and its trophic reaction [OECD, 1982]. The model parameters were derived from a study of lakes in various

countries, including, Europe, Canada and the USA. The *OECD* indicated that these models were not universal and would have to be evaluated for each geographical area.

Walmsley & Thornton [1984] applied the OECD phosphorus-chlorophyll models to Southern African impoundments and arrived at the following parameters:

$$CHL = 0.416 P^{0.675}$$
 (r = 0.84, n = 16)3.6

Application of the Vollenweider, *OECD* and Walmsley & Thornton models to the Inanda impoundment, significantly underestimated the total phosphorus and chlorophyll *a* concentrations that were found to be present. Predictions have been included in **Table 3.4.**

Table 3.4: Application of published phosphorus and chlorophyll models to the

 Inanda impoundment. (These models were developed using annual phosphorus loads).

Loading model		Predicted P_{dam}	Measured P_{dam}
Vollenweider ¹	$\frac{P_{dam}}{P_{in}} = \frac{1}{1 + \sqrt{t_w}}$	56	103
OECD general ²	$P_{dam} = 1.55 \bigoplus_{i=1}^{i} \frac{P_{in}}{+\sqrt{t_w}} \bigoplus_{i=1}^{i}$	42	(P _{in} meas =92)
OECD reservoirs ²	$P_{dam} = 1.02 $	35	$(t_w \text{ annual} = 0.40)$
Phosphorus-Chlorophyll Model		Predicted CHL	Measured CHL
OECD general ³	$CHL = 0.37 P^{0.79}$	14	58
OECD reservoirs ³	$CHL = 0.54 P^{0.72}$	15	
Walmsley & Thornton ⁴	$CHL = 0.416P^{0.675}$	10	$(P_{dam} \text{ meas} = 103)$

1 Vollenweider, [1976] cited in Foy, [1992].

2 OECD, [1982], cited in Foy, [1992].

3 OECD, [1982], cited in Walmsley & Thornton, [1984].

4 Walmsley & Thornton, [1984].

It was therefore resolved not to use the published models but to derive new relationships for the Inanda impoundment. In development of both the *OECD* and Walmsley & Thornton models, data for a range of impoundments were combined to yield regression parameters. However, for the Inanda impoundment weekly monitoring data were available since its completion in 1989, providing 4 full years of data for investigating nutrient-loading/algal-production relationships.

Examination of phosphorus loadings on the Inanda impoundment and algal count in the impoundment on a monthly scale, suggested that the external phosphorus loading is primarily responsible for algal production. These relationships are shown in **Figures 3.4** and **3.5**. The algal data shown is the monthly average of weekly algal measurements on a integrated sample (0 to 5m) collected from the main basin of the impoundment near the wall. The monthly soluble phosphorus loadings were calculated from weekly phosphorus measurements and daily flows for the Umgeni river inflow to the impoundment located *ca*. 16 km river distance away from the main basin site. Closer examination of the data indicated that the peaks in phosphorus loading appeared to precede the peaks in algal production and a forward shift of the monthly phosphorus loading by one month offered a much better visual correlation as shown in **Figure 3.6**.

In impoundments the magnitude of the total algal count and more particularly the type of algal genus found, determines whether problems (e.g. water treatment, aesthetic, etc.) are likely to be experienced or not. Data collected from other impoundments in the Umgeni system have shown that taste and odour problems in potable waters only occur when the total count is exceptionally high and when the algal genera is dominated by the blue-green genus, *Anabaena*. [Umgeni Water, 1994a].

All published models use chlorophyll *a*, to establish the relationships, largely because chlorophyll *a* is a simple measurement and more likely to be measured than algal count or genus. Chlorophyll *a* is used as a general indication of algal biomass. However, for an impoundment that shows seasonal variation in algal genera, chlorophyll *a* may not always be appropriate to use, since different algal genera have different chlorophyll *a* concentrations. More particularly, the nuisance blue-green algae (e.g. *Microcystis, Anabaena*) which proliferate when the nutrient loading to the impoundment is high, have a much lower chlorophyll *a* content than the less problematic green algae (e.g. *Chlorella*) which dominate when nutrients are scarce (such as in winter and drought periods). [Umgeni Water, 1994b].

As shown in Figure 3.7, the Inanda impoundment clearly displays seasonal variation in genera. In 1991 the nuisance blue-green genera dominated in spring, summer and autumn, while the green genera dominated in winter. Figure 3.8 shows that chlorophyll a is not a consistent indication of algal numbers as 6 000 cells m ℓ^{-1} Chlorella gave the same amount of chlorophyll a as 144 000 cells.m ℓ^{-1} Microcystis. On the algal scale (Figure 3.9) 6 000 cells.m ℓ^{-1} Chlorella is insignificant. In addition, 144 000 cells.m ℓ^{-1} Microcystis will result in serious water treatment problems while 6 000 cells.m ℓ^{-1} Chlorella can be easily treated. Consequently, using chlorophyll a as an indicator of problems would result in a poor model. As a result of this, the total algal count in the impoundment and not the preferentially chlorophyll reading, was modeled with the soluble а

phosphorus loading on the impoundment, to obtain the relationship between bioavailable phosphorus loading and algal production.

The best correlation between measured soluble phosphorus loading and algal numbers, was obtained by averaging weekly algal data and monthly soluble phosphorus loadings over two consecutive months, with the soluble phosphorus loading shifted forward by one month to compensate for the observed lag in algal count. A total of 24 data points were obtained for the period February 1990 to January 1994, as shown in **Table 3.5**. The Inanda impoundment reached full supply level for the first time (since the dam wall was completed) in February 1990 and remained close to full supply level for most of the study period. Phosphorus loading and algal count data collected prior to February 1990 was not considered representative of the impoundment under normal operating conditions and was therefore excluded from the regression. The data sets, being environmental data, were found to be skew. Logarithms were therefore taken prior to the regression analysis, to yield more normally distributed data sets. The relationship between algal count and water retention time was also investigated, as was done with some of the models presented in the literature.

Time period over which	Average SRP Loading	Average Algal Count	Partial Water Retention
data were averaged	(Advanced 1 month)	cells.mℓ ⁻¹	time
	kg		months
Feb90-Mar90	1 177	30 599	22
Apr90-May90	4 064	50 139	8
Jun90-Jul90	600	8 349	32
Aug90-Sep90	1 127	18 356	22
Oct90-Nov90	1 164	32 138	15
Dec90-Jan91	1 224	69 259	5
Feb91-Mar91	4 099	159 577	2
Apr91-May91	1 717	115 946	10
Jun91-Jul91	327	18 511	21
Aug91-Sep91	721	12 571	20
Oct91-Nov91	2 354	67 179	8
Dec91-Jan92	1 599	50 325	17
Feb92-Mar92	698	19 381	14
Apr92-May92	935	15 866	25
Jun92-Jul92	589	4 398	54
Aug92-Sep92	745	11 013	50

 Table 3.5 : Soluble phosphorus loading, algal count and partial water retention time for

 the Inanda impoundment for the period February 1990 to January 1994.

Figure 3.4 : Monthly total algal count in an integrated sample (0-5m) taken from the



Inanda impoundment main basin site near the wall.

Figure 3.5 : Monthly SRP loadings calculated for the Umgeni river inflow to the Inanda impoundment, located ca. 16 km river distance away from the main basin site.







Gioser examination of the data indicated that the peaks in phosphorus loading appeared to lag the peaks in algal production and a forward shift of the monthly phosphorus loading by one month offered a much better visual correlation (**Figures 3.4** and **3.6**).

Figure 3.7: Algal species composition in an integrated sample (0-5m) taken from the Inanda main basin near the wall.



Figure 3.8 : Weekly Chlorophyll a reading (μ g.I-1) in the Inanda main basin near the wall.





Figure 3.9 : Weekly total algal count (cells.ml-1) in the Inanda main basin near the wall.
Chapter Three

Table 3.5 continued : Soluble phosphorus loading, algal count and partial water retention time for the Inanda impoundment for the period February 1990 to January 1994.

Time period over which data were averaged	Average SRP Loading (Advanced 1 month) kg	Average Algal Count cells.m ℓ^{-1}	Partial Water Retention time months
Oct92-Nov92	399	6 439	35
Dec92-Jan93	468	8 469	29
Feb93-Mar93	599	3 482	31
Apr93-May93	575	3 022	17
Jun93-Jul93	268	1 530	16
Aug93-Sep93	502	922	16
Oct93-Nov93	547	1170	18
Dec93-Jan94	621	1677	17

Preliminary scatter plots of the data, shown in **Figures 3.10** and **3.11**, indicated that a good correlation (r = 0.79) existed between algal count and SRP loading but could be significantly improved (r = 0.91) by deleting a single outlier. The correlation between algal count and water retention time was fair (r = 0.58) but improved to good (r = 0.71) if the square root of water retention time was taken.



Figure 3.10 : Scatter plot of SRP loading with algal count.





3.3.2 Impact of detergent phosphorus elimination on algal growth

The contribution of detergents to the phosphorus loading on the Inanda impoundment was estimated for the different scenarios described in *Section 3.2.2, page 3.7.* These results were used to reduce the phosphorus loading to the impoundment by the amount corresponding to detergent phosphorus elimination. The reduced algal count corresponding to detergent phosphorus elimination was then predicted using the phosphorus-loading/algal-production model developed.

3.4 THE FATE OF PHOSPHORUS COMPOUNDS IN THE AQUATIC ENVIRONMENT

3.4.1 Investigation of phosphorus speciation using the MINTEQA2 model

In the aquatic environment, phosphorus may be present in organic or inorganic form and in both categories the individual phosphorus species may be present in either dissolved, precipitated or adsorbed phases. Interchange between the various categories is possible as a result of physical, chemical and biological action.

As suggested by the literature in *Chapter 2*, *Phosphorus Chemistry*, a knowledge of the various types of phosphorus species and their relative distribution, is important in understanding the fate of phosphorus in the environment. A more discerning assessment of the impact of phosphorus control measures on eutrophication and the quantity of phosphorus available for algal uptake, may be obtained from a study of chemical speciation data and the interaction between the various physical, chemical and biological processes which govern the speciation.

The distribution of phosphorus between the various phases, was examined in the Inanda impoundment using MINTEQA2. MINTEQA2 is a geochemical speciation program developed by the US Environmental Protection Agency for environmental risk assessment [Allison, et al., 1990]. The model contains a large database of thermodynamic equilibrium constants. The user supplies water quality information describing the concentrations of the water quality variables that may undergo reaction, together with system parameters such as temperature, pH or partial pressure of gases. MINTEQA2 computes the equilibrium distribution between dissolved and solid phases and has provision for modeling surface adsorption phenomena.

MINTEQA2 was used to examine the distribution of phosphorus species in the Inanda impoundment in an attempt to determine which chemical processes may be operative. The chemical modeling was accomplished in 3 stages :

Chapter Three

Soluble complex formation and precipitation

Firstly, soluble complex formation and precipitation were investigated to determine their relative contributions to the phosphorus speciation. This is the simplest of the modeling scenarios where the phosphate speciation is controlled by a precipitation process.

Adsorption

Following this, the effect of adsorption processes on the species distribution was examined using the Diffuse Layer Model for a range of phosphorus concentrations.

The generally observed decrease in the soluble phosphorus concentration in water entering an impoundment, is believed to be due to biological uptake, precipitation and to a greater extent, adsorption of the phosphate onto particulate material [Hesse, 1973]. In the previous modeling run, iron was predicted to precipitate as hematite (**Appendix F**). More realistically, due to kinetic considerations, the iron would probably be precipitated as a ferric hydroxide (goethite) [Kerr, 1993, pers. comm]. The predicted precipitation of ferric hydroxide from the water would provide surface adsorption sites for phosphate binding. MINTEQA2 provides a separate database file, FEO-DLM.DBS, which contains surface reactions that are applicable to the Diffuse Layer Model for adsorption of some metals and ligands onto an amorphous iron oxide surface.

Amorphous iron oxide surfaces were assumed to be present at a solids concentration of $3.422 \text{ g.}\ell^{-1}$ and with an amorphous iron concentration of 0.721 mg.g^{-1} . These values are based on average porosity, dry density and amorphous iron concentrations of some aquifer materials encountered by the EPA in their work [Kerr, 1993, pers. comm.]. Using these values the effect and extent of adsorption on these surfaces was examined. Precipitation was allowed to occur if required by equilibrium conditions, so that the competitive effect of adsorption versus precipitation processes could be evaluated.

Impact of pH and redox condition on the desorption

Finally, the impact of pH and redox condition of the water on the desorption of phosphate ions from a ferric hydroxide surface was investigated.

Normal sediment settling processes in an impoundment would remove phosphate bound onto ferric hydroxide particles from the surface waters, to the bottom sediments. The establishment of anaerobic conditions, and the resultant transformation of Fe^{3+} solids to soluble Fe^{2+} ions or ionic complexes, has been suggested as a mechanism for the release of phosphate from the adsorbed to the aqueous phase by various authors [e.g. Golterman, 1973]. Marsden, [1989] has however suggested that this process may be self limiting, as

the soluble ferrous ions will be reconverted to insoluble ferric compounds on contact with oxygenated water (see Chapter 2, page 2.6). Furthermore, the rate of sediment phosphorus release is reported to be slow, compared to sedimentation, so that desorption constitutes a negligible phosphorus source [Marsden, 1989; Levine & Schindler, 1989]. Thomas [1965], (cited in Golterman, 1973) provided a strong argument against the reduction of iron leading to phosphate release under anaerobic conditions and suggested the low solubility of $Fe(PO_4)_2$ (vivianite) as an explanation.

Desorption could not be modeled directly with the Diffuse Layer Model and the FEO-DLM.DBS database, as the presence of the ferric oxide surface is implicit in this model. [Kerr, 1993, pers. comm.]. However an examination was made of the conditions under which ferric hydroxide would no longer be precipitated and thus no longer be available to provide adsorption sites.

The input dataset to MINTEQA2 comprised the results of a chemical analysis on a water sample taken from the impoundment surface in summer (December 1990), and served as a basis for chemical modeling.

WATER QUALITY	CONCENTRATION		
VARIABLE	mg.ℓ ⁻¹	moles.ℓ ⁻¹	
Calcium (Ca)	10.4	2.595E-4	
Magnesium (Mg)	5.6	2.304E-4	
Sodium (Na)	20.9	9.092E-4	
Potassium (K)	2.4	6.138E-5	
Total Iron (Fe)	0.48	8.596E-6	
Chloride (Cl)	26.2	7.391E-4	
Fluoride (F)	0.15	7.949E-6	
Sulphate (SO ₄)	12.2	1.270E-4	
Total Phosphorus (PO ₄)	1.28	1.348E-5	
Carbonate (CO ₃)	29.1 9.615E-4		
Temperature	29.2 °C		
рН	8.3 pH units		

Table 3.6: Input dataset to MINTEQA2, comprising results of a chemical analysis on a single water sample taken from the Inanda impoundment in December 1990, at a site close to the inflow.

Initial MINTEQA2 runs indicated that the water was oversaturated with respect to a number of solid species. As several of these species involved ions such as silica, aluminium and chromium which are unlikely to be of primary influence on the phosphorus concentration and speciation, they were removed from the equilibrium calculations. Preliminary modeling

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runs also indicated that the water was essentially in equilibrium with carbon dioxide and oxygen in the atmosphere. Consideration of the effect of these gas phases on the aqueous chemistry was neglected in subsequent model runs. The simplified water composition used is given in **Table 3.6**.

The total carbonate concentration was calculated from an alkalinity value, taking account of the carbonate speciation. Total phosphorus includes soluble orthophosphate and particulate phosphate.

3.5 THE COSTS AND BENEFITS OF DETERGENT REFORMULATION

3.5.1 Costs of reformulating detergents

Estimates of cost increases as a result of reformulating phosphate built detergents with zeolite A (the most popular substitute), were provided by *Lever Bros.* The estimates included the increased cost of raw materials, as a result of importation, and plant modifications to the laundry detergent plant in Boksburg to accommodate the new raw materials in the manufacturing process. The cost (1993) was reported in rand per kilogram of detergent and was used to calculate the cost increase to consumers in the Umgeni catchment using the per capita detergent consumption values (kg per capita) and the total population in the catchment.

3.5.2 Cost savings at wastewater works

The Darvill Wastewater Works is the major works discharging effluent in the Umgeni catchment. Estimated costs savings to the works arising from a reduced influent phosphorus load were provided by Umgeni Water Process Services [De Haas, 1993].

Phosphorus removal at the Darvill works is accomplished by a combination of biological removal and alum dosing. The works is in the process of being upgraded to improve biological phosphorus removal, which would result in a lower alum dose being required in future. De Haas [1993] provided two projections of cost savings that would occur with and without the upgrade.

A review of the literature on detergent bans and reformulation (*Chapter 2, Section 2.3*) indicated that the benefits of a detergent phosphorus ban is generally not expected to benefit both the wastewater works and environment simultaneously. This is the case, particularly if wastewater phosphorus loadings comprise a more significant percentage of the catchment loading than rural laundering. The benefits of a detergent phosphorus ban

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can only be effectively transferred to the environment if there is a corresponding reduction in the phosphorus loading from the wastewater works.

3.5.3 Cost savings at water treatment works.

The presence of algae in water may result in colour, taste, odour, undesirable organic compounds and toxins in potable waters. These problems are minimised by various treatment technologies, but ultimately powdered or granular activated carbon would have to be employed to eliminate severe tastes and odours.

The Inanda impoundment has only recently (July 1994) been put on-line for water treatment and therefore has no water treatment history with regard to costs. Water treatment costs were therefore predicted for the Inanda impoundment by extrapolating data from the upstream Nagle impoundment, which occasionally had to be treated for taste and odour problems at the Durban Heights Water Works.

3.5.4 The cost of reduced life of washing machines and fabric.

Heynike & Wiechers [1986], reported that the life-time of washing machines and the value of fabrics decreased as a result of using non-phosphate built detergents. However, in the survey of literature on the history of detergent legislation and reformulation, no references were made to this in countries that had reformulated to other builders. The literature instead suggests that reduction in the life-time of washing machines and fabrics occurs when detergents are incorrectly formulated. Nevertheless, cost estimates associated with the deterioration in washing machines and fabrics were made for the current study, using the Heynike & Wiechers values for 1983 and inflation rates since 1983.

CHAPTER FOUR Results & Discussion

The results are provided under 5 main section headings corresponding to those in *Chapter Three*, with breakdown into sub-sections where necessary. A summary of the findings is provided at the end of the *Chapter*. Most results were conducive to tabular presentation, but final results were presented graphically.

4.1 RURAL AND URBAN DETERGENT PHOSPHORUS LOADINGS

4.1.1 Rural and urban per capita detergent consumption

For rural areas :

Average annual mass of detergent consumed per rural family in kg.(family.annum)⁻¹

- average number of wash loads per family per day x average mass (grams) of detergent dosed per load x number of wash days per week x 52 weeks per annum ÷ 1000 kilograms per gram
- 1.02 loads per family day x 78.9 gram per load x 2.53 wash days per week x 52 weeks per annum ÷ 1000 kilograms per gram
- = 10.541 kilograms per family per annum

Annual rural per capita detergent consumption in kg.(person.annum)⁻¹

- = Annual mass of detergent consumed per family ÷ average number of persons per family.
- = 10.541 kilograms per family per annum ÷ 6.5 persons per family.
- = 1.63 kilograms detergent per rural capita per annum

For urban areas :

Average annual mass of detergent consumed per urban family in kg.(person.annum)⁻¹

- average number of wash loads per family per day x average mass (grams) of detergent dosed per load x number of wash days per week x 52 weeks per annum ÷ 1000 kilograms per gram
- = 1.18 loads per family day x 105.6 grams per load x 3.71 wash days per week x 52 weeks per annum ÷ 1000 kilograms per gram
- = 24.105 kilograms per family per annum

Annual urban per capita detergent consumption:

- = Annual mass of detergent consumed per family ÷ average number of persons per family.
- = 24.105 kilograms per family per annum ÷ 6.8 persons per family.
- = 3.53 kilograms detergent per urban capita per annum

4.1.2 Phosphate content of South African laundry detergents

Average STPP content of detergents :

- = {% STPP in Omo x Fraction sales Omo} + {% STPP in Skip x Fraction sales Skip} + ... + {% STPP in Gcf Auto x Fraction sales Gcf Auto}.
- = $\{26 \times 0.44\}$ + $\{28 \times 0.07\}$ + $\{35 \times 0.02\}$ + $\{26 \times 0.41\}$ + $\{16 \times 0.04\}$ + $\{26 \times 0.02\}$.
- = 26% STPP

Average phosphorus content of detergents :

= Average STPP content of detergents x molecular weight phosphorus

= 26% STPP x
$$\frac{93 P}{397 STPP}$$

= 6.5% P

Therefore, the annual per capita detergent phosphorus consumption:

For rural areas:

- = Annual per capita detergent consumption x Fraction of phosphorus in detergents.
- = 1.63 kilograms detergent per capita per annum x 0.065 phosphorus.
- = 0.106 kilograms detergent phosphorus per capita per annum.

For urban areas:

- = 3.53 kilograms detergent per capita per annum x 0.065 phosphorus.
- = 0.229 kilograms detergent phosphorus per capita per annum.

4.1.3 Rural and urban population

The total population per subcatchment is shown in **Table 4.1** for urban and rural areas. A more detailed population breakdown is provided in **Appendix A**.

Subcatchment	Iment Rural population Urban population	
Midmar	16 678	16 370
Albert Falls	16 514	10 624
Nagle	82 493	2 007
Inanda	494 786	274 848
Total	610 471	303 849

 Table 4.1 : Rural and urban population per subcatchment

The total detergent phosphorus loadings based on the above population and the per capita detergent phosphorus consumptions is shown in **Table 4.2**, for rural and urban areas.

areas.

Subcatchment	Detergent pho tonnes.	sphorus loading annum ⁻¹
	Rural	Urban
Midmar	1.8	3.8
Albert Falls	1.7	2.4
Nagle	8.7	0.5
Inanda	52.4	63.1
Total	64.5	69.7

4.1.4 Pathway of detergent phosphorus to the environment

4.1.4.1 Rural detergent load

Data on washing practices in rural areas, are shown in **Table 4.3**, and were obtained from a survey undertaken by *Lever Bros* in KwaZulu-Natal. The survey indicated that 16 % of the rural population washed laundry directly at a water course.

Location	Rural %
Just outside home	65
Inside home/bathroom	5
By river/dam	16
Near central or community bore-hole/ command top	12

 Table 4.3 : Washing practices in rural areas [Lever Brothers (Pty.) Ltd., 1993]

It was therefore assumed that only 16 % of rural detergent phosphorus will reach the impoundment and be of consequence to water quality. The revised rural detergent loadings are shown in **Table 4.4**.

Table 4.4 : Revised rural detergent loading	assuming	only 16	% o	f rural
detergents enter watercourse.				

Subcatchment	Detergent phosphorus loading tonnes.annum ⁻¹		
	Total rural loading	16 % of rural loading	
Midmar	1.8	0.28	
Albert Falls	1.7	0.28	
Nagle	8.7	1.4	
Inanda	52.4	8.4	
Total	64.5	10.3	

4.1.4.2 Urban detergent load

(a) Contribution of detergents to wastewater works influents.

The major sources of soluble phosphorus in wastewater influents were assumed to be detergents, urine and industrial discharges. These phosphorus components are shown in **Table 4.5**.

The phosphorus loading from urine was calculated from the population and a per capita phosphorus urine value of 0.219 kilogram per capita per annum [Machlin, 1973], while the industrial phosphorus loading was quantified using data from the Umgeni Water routine trade effluent monitoring programme. An analysis of the trade effluent data (shown in **Appendix B**) indicated that four industries were largely responsible for the bulk of the industrial phosphorus loading. The nature of these industries suggested that the loading was due to industrial processes and not detergent consumption. Therefore, in computing the percentage detergent phosphorus, it was assumed that the industrial phosphorus loading did not have a detergent component.

		Phosphorus Load in tonnes per annum				
Subcatchment	Urban	Urban	Urine	Industry	Total	% detergent
	population	detergents				phosphorus
Midmar	16 370	3.8	3.6	0	7.3	51
Albert Falls	10 624	2.4	2.3	0	4.8	51
Nagle	2 007	0.5	0.4	0	0.9	51
Inanda	274 848	63.1	60.2	47.9	171.1	37
Total	303 849	69.7	66.5	47.9	184.1	

Table 4.5 : Urban wastewater influent phosphorus loadings arising from detergents, urine and industrial discharges.

The total soluble phosphorus loading on wastewater works was obtained by summing the detergent, urine and industrial components. The percentage soluble phosphorus attributable to urban detergents could thus be obtained and ranged from 37 to 51 %. These results are similar to that found by Heynike & Wiechers [1986] who indicated a range of 35 to 50 %.

(b) Phosphorus loadings of point sources on the environment .

Results of point source phosphorus loading calculations are shown in **Table 4.6**. Flow and concentration details are provided in **Appendix G**.

Catchment and point source	SRP load tonnes. a ⁻¹	Catchment total tonnes.a ⁻¹
Midmar		1.09
Mpophomeni WWW	1.09	
Albert Falls		4.18
Howick Mid Hospital	0.27	
Howick WWW	0.55	
Sarmcol 1	0.52	
Sarmcol 2	2.10	
Mountain Home	0.01	
Midmar WWW	0.50	
Cedara	0.09	
Ladsworth	0.01	
Hilton College	0.15	
Golden Pond	0.001	
Nagle		0.55
Albert Falls 1	0.02	
Albert Falls 2	0.04	
Cool Air WWW	0.50	
Inanda		24.90
Cato Ridge	0.47	
Darvill treated	14.99	
Darvill overflow	7.70	
Feralloys	0.003	
Camperdown	0.08	
Sevontein Prison New	1.03	
Lynnfield Park	0.14	
Enthembeni Hospital	0.49	

 Table 4.6 : Point source soluble phosphorus loadings on the environment.

The urban detergent phosphorus loading on the environment (**Table 4.7**) was obtained by applying the percentage detergent phosphorus calculated for the influent (**Table 4.5**) to the effluent loadings.

0			0
Subcatchment	Phosphorus loadings	% detergent	Urban detergent
	of wastewater works	phosphorus in	phosphorus loading
	on environment	wastewater	on environment
	tonnes.annum ⁻¹		tonnes.annum ⁻¹
Midmar	1.09	51	0.56
Albert Falls	4.18	51	2.14
Nagle	0.55	51	0.28
Inanda	24.90	37	9.17

Table 4.7 : Detergent component of point source phosphorus loadings .

4.2 PHOSPHORUS LOADINGS ON IMPOUNDMENTS AND CONTRIBUTION BY DETERGENTS

4.2.1 Phosphorus loadings on impoundments

The phosphorus loadings on the four impoundments on the Umgeni system are shown in **Table 4.8**. The loads shown are the measured soluble phosphorus loads emanating from the major and minor catchment areas of the impoundment per annum. Details of loading per season and corresponding flow and concentration data are provided in **Appendix H**.

	Flow	River or stream loadings	Catchment total
Site	10 ⁶ .m ³	tonnes.annum ⁻¹	tonnes.annum ⁻¹
Midmar			3.89
Umgeni inflow	242.1	2.81	
Umthinzima inflow	3.6	0.65	
Kwagqishi inflow	8.1	0.14	
Nguku inflow	3.1	0.02	
Direct inflow	12.9	0.26	
Albert Falls			2.57
Umgeni inflow	399.0	2.37	
Doringspruit inflow	3.5	0.13	
Nculwane inflow	7.9	0.03	
Direct inflow	12.7	0.04	
Nagle			3.10
Umgeni at weir	463.5	3.10	
Inanda			20.05
Umgeni inflow	596.1	19.9	
Total trib and direct inflow	11.6	0.35	

Table 4.8 : Phosphorus loadings on the four major impoundments in the Umgeni system.

The above results indicate that In the Umgeni system, the phosphorus loading on the Inanda impoundment, is the most significant.

4.2.2 Percentage detergent phosphorus in the total environmental soluble phosphorus loading

The sum of the urban and rural detergent phosphorus loadings from each of the four impoundments is shown in Table 4.9.

U			
Subcatchment	Rural	Urban	Total
Midmar	0.28	0.56	0.84
Albert Falls	0.28	2.14	2.42
Nagle	1.40	0.28	1.68
Inanda	8.38	9.17	17.56
Total	10.34	12.15	22.49

Table 4.9: Total detergent phosphorus loading, arising from urban and rural laundering.

The scenarios for estimating the total **soluble** phosphorus loading for the catchment is shown in **Tables 4.10** to **4.12**.

The percentages of detergent phosphorus in the catchment loading calculated for the above scenarios, were applied to the phosphorus loadings measured at the inflows to impoundments, to provide estimates of the contribution of detergent phosphorus to eutrophication.

Table 4.10 : Scenario 1 - Catchment soluble phosphorus loading, assuming the only sources of soluble phosphorus were wastewater effluents and detergents that entered from rural laundering carried out directly at the water course.

Subcatchment		%			
	Point	Rural detergent	Total catchment	Total detergents	detergents
Midmar	1.09	0.28	1.37	0.84	61
Albert Falls	4.18	0.28	4.46	2.42	54
Nagle	0.55	1.40	1.95	1.68	86
Inanda	24.90	8.38	33.28	17.56	53

Table 4.11 : Scenario 2 - Catchment soluble phosphorus loading, assuming that in addition to the loading from wastewater effluents and rural laundering, non-point sources (e.g. agricultural lands, informal settlements) contributed 20% to the catchment soluble phosphorus loading.

Subcatchment		Soluble phosphorus loading in tonnes						
	Point	Rural detergent	Other non point	Total catchment	Total detergents	detergents		
Midmar	1.09	0.28	0.34	1.72	0.84	49		
Albert Falls	4.18	0.28	1.11	5.57	2.42	43		
Nagle	0.55	1.40	0.49	2.43	1.68	69		
Inanda	24.90	8.38	8.32	41.6	17.56	42		

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Table 4.12 : Scenario 3 - Catchment soluble phosphorus loading, assuming that in addition to the loading from wastewater effluents and rural laundering, non- point sources (e.g. agricultural lands, informal settlements) contributed 50% to the catchment soluble phosphorus loading.

Subcatchment	Soluble phosphorus loading in tonnes						
	Point	Rural detergent	Other non point	Total catchment	Total detergents	detergents	
Midmar	1.09	0.28	1.37	2.75	0.84	31	
Albert Falls	4.18	0.28	4.46	8.92	2.42	27	
Nagle	0.55	1.40	1.95	3.90	1.68	43	
Inanda	24.90	8.38	33.28	66.57	17.56	26	

4.2.3 Summary

Figure 4.1 summarizes the phosphorus loading emanating from the Midmar, Albert Falls, Nagle and Inanda subcatchments for Scenario 1, while **Figure 4.2** shows the detailed results set for the Inanda subcatchment.

Figure 4.1: Soluble phosphorus loadings emanating from the Midmar, Albert Falls, Nagle and Inanda subcatchments for Scenario 1. The distribution of the loading between rural detergents, urban detergents and other urban phosphorus inputs is indicated.





Figure 4.2 : Schematic showing the detailed results set for the Inanda subcatchment.

4.3 The relationship between soluble phosphorus loading and algal count in the Inanda impoundment

4.3.1 Results of the regressions

Results of the regressions between soluble phosphorus loading and average algal count are shown in (a) and (b) below. The results of regression (b) which included the water retention time showed that water retention time did not improve the regression and the coefficient was not significant. This indicated that it was not a major factor influencing algal production in the main basin of the Inanda impoundment.

(a) Log (algal count) vs. Log (SRP loading)

Regression Statistics					
Multiple R	0.80				
R Square	0.64				
Adjusted R Square	0.63				
Standard Error	0.39				
Observations	23				

Analysis of variance	Degrees of freedom	Sum of squares	Mean square	F statistic
Regression	1	5.78	5.78	37.8
Residual	21	3.21	0.15	
Total	22	8.99		
Parameter	Coefficients	Standard error	t statistic	
Intercept	-1.26	0.87	-1.45	
Log (SRP loading)	1.83	0.30	6.15	

(b) Log (algal count) vs. Log (SRP loading) & Log (1 + $\sqrt{t_W}$)

Regression Statistics					
Multiple R	0.80				
R Square	0.64				
Adjusted R Square	0.61				
Standard Error	0.40				
Observations	23				

Analysis of variance	Degrees of freedom	Sum of squares	Mean square	F statistic
Regression	2	5.78	2.89	18.02
Residual	20	3.21	0.16	
Total	22	8.99		
Parameter	Coefficients	Standard error	t statistic	
Intercept	-1.18	1.53	-0.77	
Log (SRP loading)	1.82	0.41	4.41	
Log (1 + √t _w)	-0.02	0.35	-0.06	

The resulting soluble phosphorus-loading/alga-production model for predicting the algal count in the Inanda main basin impoundment is therefore presented below.

	Log (Algal Count)	=	1.83 Log (SRP loading) - 1.26	4.1
	or Algal Count	=	0.055 SRP Loading ^{1.83}	4.2
Where	SRP Loading =	avera monti	age SRP loading on the impoundment over two cons hs, in kilograms per month	secutive
	Algal Count =	Predi mont	icted average count over two consecutive mont h after the SRP loading	hs one

A plot of observed and predicted algal count is shown in Figure 4.3.



Figure 4.3 : Plot of observed and predicted algal count for the Inanda main basin.

4.3.2 Impact of detergent phosphorus elimination on algal production

Based on the three scenarios for soluble phosphorus loadings from the catchment, detergents could comprise 53, 42 or 26 % of the phosphorus loading on the Inanda impoundment. To assess the impact of detergent phosphorus elimination on algal production, the measured loading on the impoundment was sequentially reduced by these percentages and the resulting algal count predicted using the model developed. The reduced phosphorus loadings and corresponding algal counts are shown in **Table 4.13**.

Date	Reduction in SRP Loading			Predict	ted Reducti	on in Algal (Count	
	None	1(26%)	2(42%)	3(53%)	0%	1(42%)	2(64%)	3(75%)
Feb-90	1 177	871	671	553	23 717	13 651	8 457	5 936
Jun-90	600	444	342	282	6 878	3 959	2 453	1 722
Aug-90	1 127	834	642	530	21 886	12 597	7 804	5 478
Oct-90	1 164	862	664	547	23 242	13 378	8 287	5 817
Dec-90	1 224	906	697	575	25 458	14 653	9 077	6 372
Feb-91	4 099	3 033	2 336	1 927	23 3897	134 624	83 399	58 542
Apr-91	1 717	1 271	979	807	47415	27 291	16 907	11 868
Jun-91	327	242	187	154	2 267	1 305	808	567
Aug-91	721	534	411	339	9 657	5 558	3 443	2 417
Oct-91	2 354	1 742	1 342	1 106	84 523	48 649	30 138	21 155
Dec-91	1 599	1 183	911	752	41 592	23 939	14 830	10 410
Feb-92	698	516	398	328	9 078	5 225	3 237	2 272
Apr-92	935	692	533	440	15 554	8 952	5 546	3 893
Jun-92	589	436	336	277	6 658	3 832	2 374	1 666
Aug-92	745	551	425	350	10 245	5 897	3 653	2 564
Oct-92	399	295	227	187	3 251	1 871	1 159	814
Dec-92	468	347	267	220	4 373	2 517	1 559	1 094
Feb-93	599	443	342	282	6 871	3 955	2 450	1 720
Apr-93	575	426	328	270	6 376	3 670	2 273	1 596
Jun-93	268	198	153	126	1 572	905	561	393
Aug-93	502	371	286	236	4 958	2 854	1 768	1 241
Oct-93	547	405	312	257	5 813	3 346	2 073	1 455
Dec-93	621	460	354	292	7 335	4 222	2 616	1 836

Table 4.13: Scenarios for reduced phosphorus loading and predicted algal count in the

 Inanda impoundment as a result of eliminating detergent phosphorus.

Results of the calculation indicated that a significant reduction in algal numbers would occur as a result of reducing the soluble phosphorus loading on the Inanda impoundment.

For reduction scenarios of 26, 42 and 53 %, the corresponding algal count will reduce by 42, 64 and 75 %. The cost implications of this reduction are discussed in *Section 4.5*.

4.4 PHOSPHORUS SPECIATON

4.4.1 Species distribution between dissolved and precipitated phases.

The phosphorus distribution between dissolved and particulate phases, not taking adsorption into account are shown in **Table 4.14**. Other species details are provided in **Appendix F**.

Table 4.14: Equilibrium composition showing the mass distribution between dissolved and precipitated phases in the Inanda impoundment in December 1990, at a site close to the inflow.

% distribution between dissolved	Dominant species	% species composition
and precipitated phases		
Dissolved		
0.7%	HP04 ²⁻	72.6
	MgHPO ₄ (aq)	8.4
	MgPO ₄ -	4.5
	CaHPO ₄ (aq)	6.2
	CaPO ₄ -	3.3
	H ₂ PO ₄ -	4.8
Precipitated		
99.3%	Fluorapatite	100

Modeling runs predicted that in summer at the pH, temperature and concentrations present in the water, the bulk of the phosphorus (99,3 %) would be present in particulate form precipitating out as fluorapatite. Only a fraction of the phosphorus (0.7 %) would be present as dissolved species. The dissolved species were predicted to be largely HPO_4^{2-} species (73 %) with small amounts of calcium and magnesium complexes (22 %).

The equilibrium tendency of phosphorus in summer therefore appears to be precipitation and sedimentation of insoluble phosphates with only a small fraction of phosphate remaining in solution. The formation of soluble complexes is not a significant factor in determining the bio-availability of phosphate in the Inanda impoundment.

4.4.2 The impact of phosphate adsorption on the distribution of phosphate species.

Figure 4.4 shows that for a range of phosphate concentrations, adsorbed species are predicted to be the dominant phosphate species present in the water, except for very high

total phosphate concentrations (0.01 moles. ℓ^{-1} or 940 mg. ℓ^{-1}), which are unlikely to be reached in the Inanda impoundment.

Thus adsorption processes are predicted to successfully compete with precipitation as the major control on the distribution of phosphate species. The net effect of adsorption would be similar to precipitation, in that phosphate is effectively removed from solution and would not be available for further bio-uptake.

Figure 4.4: Phosphorus species distribution between dissolved, adsorbed and precipitated phases at varying phosphorus concentration.



4.4.3 Effect of pH and redox on phosphate desorption from an iron hydroxide surface.

The percentage of total phosphate present as an adsorbed species plotted against pH, is shown in **Figure 4.5** for a range of total phosphate concentrations.

The plots indicate that apart from high total concentrations (94 to 940 mg. ℓ^{-1}) of phosphate, which are unlikely to occur in the Inanda impoundment, the amount of phosphate present as an adsorbed phase is independent of pH, up to pH values of 9 or over.

At high pH values and for high phosphate concentrations the phosphate released from the adsorbed phase, is predicted to report to the dissolved species fraction and would thus be available for bio-uptake.

Inspection of water quality data for the impoundment indicated that pH 9 is exceeded 10 % of the time. This suggests that dissolution as a result of pH may occur for only a small percentage of the time.

With regard to redox, model runs indicated that even under extremely reducing conditions (E_H values of -200 mV) and over a range of pH values, an iron-bearing solid (hematite or magnetite) would be the stable phase and not a soluble Fe²⁺ ion or ionic complex. An increase in the partial pressure of carbon dioxide, such as might be experienced at a particle/microbe interface, would lead to an iron carbonate (siderate) becoming the dominant iron species. Effectively these modeling runs suggest that it would be extremely difficult to solubilize already precipitated ferric hydroxide, which would remain the stable solid phase over a wide variety of water conditions.



Figure 4.5 : Percent adsorbed species versus pH value for varying phosphorus concentrations.

4.5 COST-BENEFIT ANALYSIS OF DETERGENT PHOSPHORUS ELIMINATION

4.5.1 Costs of reformulating detergents

Lever Bros estimated that reformulating phosphate built detergents with zeolite A (the most popular substitute) would result in the following costs increases:

- Increase in raw material costs at R 250 per tonne of finished product.
- Plant modifications to Boksburg plant at R 60 per tonne of finished product.

This works out to a total cost of R 310 per tonne or 31 cents per kg of detergent.

The calculated cost increase to consumers in the Inanda catchment (shown in **Table 4.15**) was R 551 100 and was calculated from the per capita detergent consumption (for urban and rural areas), the total population and the cost increase of 31 cents per kg of detergent.

	<u> </u>			
Consumer	Per capita detergent	Total	Total detergent	Total Cost
	consumption	Population	consumed	increase
	kg per capita		kg	Rand
Urban	3.53	274 800	970 900	301 00
Rural	1.63	494 800	808 900	250 100
			•	
Total				551 100

Table 4.15: Cost increase to consumers in the Inanda catchment as a result of

eliminating detergent phosphorus.

4.5.2 Cost savings at a wastewater works

At Darvill WWW phosphorus is removed by a combination of biological treatment and alum dosage. De Haas [1993] indicated that no savings would be made for biological phosphorus removal as the costs remain essentially the same for any normal domestic wastewater in the range *ca*. 6 to 12 mg. ℓ^{-1} as soluble phosphorus since the same capital equipment is needed. Halving the influent phosphorus load is however likely to half the alum dose required.

The Darvill WWW is however currently being upgraded to improve biological phosphorus removal which would result in a lower alum dose being required. De Haas [1993] therefore made two projections of cost savings that would occur with and without this upgrade. The projections (**Table 4.16**) indicate that with the current wastewater treatment system reducing the influent phosphorus load by 50 % would reduce alum costs by 50 % from R 1 040 000 to R 518 000 per annum. With the upgrade in place, improved biological phosphorus would further reduce the alum dose by half. The cost saving as a result of a reduced influent phosphorus load and with the upgrade in place would therefore be R 259 000 or one quarter the current costs.

Table 4.16 : Cost estimates for Darvill Wastewater Works showing the current cost of aluminium sulphate used and the predicted costs as a result of improved biological phosphorus removal and/or reduced influent phosphorus load.

Scenario	Daily Alum Dose		Annual Cost
	mg Al.ℓ ⁻¹	kg.d ⁻¹	Rand (1993)
Current	60	3 000	1 040 000
Predicted with improved biological phosphorus			
removal OR half influent phosphorus loading	30	1 500	520 000
Predicted with improved biological phosphorus			
removal AND half influent phosphorus loading	15	750	260 000

Costs were at 1992/93 prices and based on a flow of 50 M/.d⁻¹. De Haas [1993] indicated that the cost estimates were conservative but realistic and the alum dosage of 15 mg ℓ^{-1} was the very best that could be expected.

4.5.3 Cost savings at water treatment works.

The Inanda impoundment has no water treatment history, therefore the cost increases as a result of treating eutrophic water were predicted by extrapolating data from the upstream Nagle impoundment, which occasionally had to be treated for taste and odour problems at the Durban Heights Water Works.

For the Nagle impoundment treatment problems due to algae generally occurred from January to April (end of summer to mid-autumn) of 1989, 1990, 1993, and 1994, with the 1989 and 1994 events being the most severe. During autumn of each of these years the algal distribution was dominated by the genus Anabaena. Water is drawn from two sites at the impoundment for treatment at the Durban Heights Water Works and considerable rupture of the algal cells occurs in the pipelines between the impoundment and the treatment works [Dickens, 1994]. As indicated in the Tables 4.17 to 4.19, the Anabaena count in the raw water was directly proportional to the severity of the taste and odour problem experienced, measured in kg of carbon used.

Table 4.17: Average algal count at the Nagle impoundment and activated carbon

Period	Average algal count for the Nagle impoundment (average of sites 1 & 2)	Mass activated carbon used at Durban Heights Water Works
	cells.mℓ ⁻¹	kg
Jan-Apr 1989	40 700	90 300
Jan-Apr 1990	15 900	38 000
Jan-Apr 1991	16 000	0
Jan-Apr 1992	10 800	0
Jan-Apr 1993	3 400	1 400
Jan-Apr 1994	53 700	250 000

dosed at the Durban Heights Water Works.

Table 4.18: Average Anabaena count at the Nagle impoundment and activated

carbon dosed at the Durban neights water works.			
Period	Average Anabaena count at the Nagle	Mass activated carbon used at	
	impoundment (average of sites 1 & 2)	Durban Heights Water Works	
	cells.mℓ ⁻¹	kg	
Jan-Apr 1989	26 300	90 300	
Jan-Apr 1990	4 700	38 000	
Jan-Apr 1991	955	0	
Jan-Apr 1992	750	0	
Jan-Apr 1993	1 100	1 400	
Jan-Apr 1994	39 800	250 000	

carbon dosed at the Durban Heights Water Works

Table 4.19: Maximum Anabaena count at the Nagle impoundment and activated

Period	Maximum Anabaena count at the Nagle	Mass activated carbon used at
	impoundment (average of sites 1 & 2)	Durban Heights Water Works
	cells.mℓ ⁻¹	kg
Jan-Apr 1989	147 700	90 300
Jan-Apr 1990	24 000	38 000
Jan-Apr 1991	4 600	0
Jan-Apr 1992	4 200	0
Jan-Apr 1993	4 100	1 400
Jan-Apr 1994	203 300	250 000

carbon dosed at the Durban Heights Water Works

Figure 4.6 shows that the relationship between the average *Anabaena* count in the impoundment and carbon used at the Durban Heights Water Works is generally linear.

Figure 4.6 : Relationship between the average *Anabaena* count in the Nagle impoundment and carbon used at the Durban Heights Water Works (data from **Table 4.18**).



The total algal and Anabaena counts for the Inanda impoundment are shown in Table 4.20.

Table 4.20: Total algae, average and maximum *Anabaena* count and predicted carbon mass required for the Inanda main basin near wall.

Period	Average algal	Average Anabaena	Maximum Anabaena	Predicted Mass of
	count <i>cells.mℓ</i> ⁻¹	count <i>cells.mℓ</i> ⁻¹	count <i>cells.mℓ⁻¹</i>	carbon required
				Kg
Jan-Apr 1989	74 300	7 100	45 800	34 000
Jan-Apr 1990	44 900	26 700	140 400	150 000
Jan-Apr 1991	135 000	3 700	20 000	15 000
Jan-Apr 1992	30 000	700	4 800	0
Jan-Apr 1993	4 500	200	1 500	0
Jan-Apr 1994	4 600	1 400	6 500	2 000

The results show that very high numbers of *Anabaena* were present in January to April of 1989, the year of filling, and the following two years, 1990 and 1991 which could be

classified as normal rainfall and flow years. From 1992 to 1994 the catchment experienced severe drought which significantly reduced the nutrient loading to the impoundment.

Assuming that *Anabaena* blooms would have given rise to taste and odour problems in the Inanda impoundment, then the counts in 1989, 1990, 1991 and 1994 would have been high enough to cause problems. The predicted carbon dose based on these counts show that for a normal rainfall year, about 65 000 kg carbon will be required on average per season to treat the water abstracted. At a carbon cost of R3.53 per kg this amounts to R230 000 per season in additional treatment costs. Elimination of detergent phosphorus was shown to reduce the algal count by 42 to 75 %. From the regression equation, 65 000 kg carbon is equivalent to 12 600 cells.m ℓ^{-1} . A 75 % reduction in count will result in 3 100 cells.m ℓ^{-1} , requiring 12 000 kg carbon and resulting in a cost savings of R190 000, while a 42 % reduction will result in a cost savings of R104 000.

4.5.4 The cost of reduced life of washing machines and fabric as a result of using non-phosphate builders.

The life-cycle of washing machines and the value of fabrics are expected to decrease as a result of using non-phosphate built detergents [Heynike & Wiechers, 1986]. These costs were estimated for the current study by extrapolating the estimates made by Heynike & Wiechers using annual inflation rates, as indicated in **Table 4.21**.

Year	Inflation	Loss in value		
	Rate % ¹	Washing Machines in Rands ²	Fabrics in Rands ³	
Estimates for So	outh Africa			
1983		R3.8 million	R62.5 million	
Estimates for the	e Umgeni catchm	ent		
1983		0.044 million	2.2 million	
1984	11.6	0.049 million	2.4 million	
1985	14.0	0.056 million	2.7 million	
1986	15.7	0.064 million	3.2 million	
1987	12.5	0.072 million	3.6 million	
1988	11.4	0.081 million	4.0 million	
1989	13.8	0.092 million	4.5 million	
1990	14.3	0.110 million	5.2 million	
1991	15.3	0.120 million	6.0 million	

 Table 4.21 : Loss in life of washing machines and fabric in the Umgeni catchment

1 Packer, 1993.

2 Adjusted by ratio of urban population in Umgeni catchment (303 849) to population in South Africa (26 504 191).

3 Adjusted by ratio of total population in Umgeni catchment (914 320) to population in South Africa (26 504 191).

In 1983 Heynike & Wiechers [1986] estimated the loss in value of washing machines and fabrics in *South Africa* due to detergent reformulation to be R 3.8×10^6 per annum and R 62.5×10^6 per annum, respectively. Corresponding values were estimated for the Umgeni catchment by multiplying these costs by the ratio of population in the Umgeni catchment to the population in *South Africa*. as shown in **Table 4.21**.

4.5.5 The cost-benefit of detergent reformulation

The costs and benefits of detergent reformulation are shown in **Tables 4.22** to **4.25** for the various options as described below.

A lower influent phosphorus concentration will benefit a wastewater works by reducing the amount of treatment chemicals required to maintain the effluent standard. However, for the environment and therefore water treatment works to benefit, the wastewater works would have to maintain chemical dosage and reduce the effluent phosphorus concentration. As both the environment and wastewater works cannot benefit simultaneously from detergent phosphorus elimination, these benefits were taken into account in two different calculations.

In addition, reformulation of detergents may or may not accelerate deterioration in the lifetime of fabrics and washing machines, so these scenarios were also shown separately.

Issue	Cost	Benefit
Increase to consumers as a result of eliminating detergent phosphorus.	551 100	
Predicted saving with half influent phosphorus loading and improved biological phosphorus removal at Darvill WWW.		260 000
Total	551 100	260 000
Cost-benefit ratio	2:1	

 Table 4.22: Cost-benefit analysis 1 - Cost of detergent phosphorus elimination and benefits to Darvill WWW.

 Table 4.23: Cost-benefit analysis 2 - Cost of detergent phosphorus

 elimination and water treatment benefits.

Issue	Cost	Benefit
Increase to consumers as a result of eliminating		
detergent phosphorus.	551 100	
Reduced water treatment costs.		190 000
Total	551 100	190 000
Cost-benefit ratio	3:1	

Table 4.24: Cost-benefit analysis 3 - Cost of detergent phosphoruselimination, reduction in the value of fabrics and washing machines andbenefits to Darvill WWW.

Issue	Cost	Benefit
Increase to consumers as a result of eliminating		
detergent phosphorus.	551 100	
Loss in value of washing machines.	120 000	
Loss in value of fabrics.	6 000 000	
Predicted saving with half influent phosphorus		
loading and improved biological phosphorus		260 000
removal at Darvill WWW.		
Total	6 671 100	260 000
Cost-benefit ratio	26 : 1	

 Table 4.25:
 Cost-benefit analysis 4 - Cost of detergent phosphorus

 elimination, reduction in the value of fabrics and washing machines and

 water treatment benefits.

Issue	Cost	Benefit
Increase to consumers as a result of eliminating		
detergent phosphorus.	551 100	
Loss in value of washing machines.	120 000	
Loss in value of fabrics.	6 000 000	
Reduced water treatment costs.		190 000
Total	6 671 100	190 000
Cost-benefit ratio	35 : 1	

The results of the cost-benefit analysis show that all scenarios are in favour of not eliminating detergent phosphorus. Even the worse scenario for detergents, indicates that it is more expensive to eliminate detergent phosphorus than to treat the consequences of higher phosphorus loadings.

Uncertainty exists in the actual cost of eutrophication as there are a number of hidden costs. These include influences on, recreation, the aquatic environment, agriculture and human health (extracellular products of certain algal genera e.g. *Microcystis* are known to contain toxins carcinogenic to man).

The loss in revenue to the local phosphorus industry as a result of importation of other raw materials was also not considered in the cost-benefit calculations.

4.6 SUMMARY

The rural and urban per capita detergent consumptions formed the basis for all detergent phosphorus loading calculations. These were estimated to be: **1.63** kg.(capita.annum)⁻¹ for rural areas, and **3.53** kg.(capita.annum)⁻¹ for urban areas. Rural dwellers were found to use half as much detergent as urban dwellers, which is realistic from economic considerations and life styles.

These per capita estimates were lower than that determined by Heynike & Wiechers [1986] who calculated the per capita detergent consumption for the whole country in 1983 to be 5.2 kg. The Heynike & Wiechers estimate was derived from the value of the South African detergent market and total population, while the results for the current study were obtained from surveys of washing practices undertaken in KwaZulu-Natal in both rural and urban areas. It is possible that the country-wide estimate is less applicable than the more recent survey undertaken in the study region. Alternately the discrepancy may be due to a harsher economic climate over the years leading to more sparing use of detergents by the majority of the population.

In the Umgeni catchment the population residing in rural areas, namely, 610 000, was found to be twice the urban population of 304 000. Despite this, the overall detergent phosphorus loading from rural areas was slightly lower than that from urban areas due to the lower rural per capita consumption and the factor of 16 % taken as the percentage of the rural population that washed laundry directly at a river or stream. This percentage was obtained from a survey of washing practices undertaken by Lever Bros in KwaZulu-Natal. The percentage may not be completely representative of specific settlement areas in the Umgeni catchment, but only a more detailed survey in the area of interest could improve the estimate. It is predicted that this percentage would decrease in future as greater attention becomes focused on provision of rural water supply and sanitation schemes which would reduce laundering done at rivers or streams in preference for more formal washing facilities. This would however, reroute the phosphorus via the wastewater works. In the event of this happening the load entering the aquatic environment from these areas may increase to 100 % as compared with the value of 16 % currently predicted to be discharged to river and will include a phosphorus component from human excreta. Therefore, once the informal areas are serviced the phosphorus budget for Inanda would have to be revised.

The Inanda catchment has the largest rural population and therefore the greatest rural detergent phosphorus contribution to the environment. 8.4 tonnes.annum⁻¹ detergent

phosphorus were estimated to be discharged to the Inanda catchment, compared with a range of 0.3 to 1.4 tonnes.annum⁻¹ for the 3 upstream catchments.

The Inanda catchment also has the largest urban population and therefore the greatest urban detergent phosphorus contribution to the environment. It was estimated that 9.2 tonnes.annum⁻¹ would be discharged to the Inanda catchment, compared with a range of 0.3 to 2.1 tonnes.annum⁻¹ for the 3 upstream catchments.

Detergents comprised 51 % of the phosphorus loading of urban wastewaters except for the Inanda catchment where it comprised 37 % as a result of industries in the Pietermaritzburg area contributing *ca*. 30 % to the phosphorus loading.

With the Inanda catchment having the largest phosphorus loadings from both urban and rural areas it was expected that the largest phosphorus loading on impoundments would be measured at the inflow to the Inanda impoundment. For the study period, October 1990 to September 1991, 20.9 tonnes of soluble phosphorus were measured at the Inanda impoundment inflow compared with a range of 2.8 to 3.6 tonnes for the 3 upstream impoundments.

In the absence of measured phosphorus inputs from agriculture and informal landuse (excluding detergents) and data on river losses, it was difficult to determine which of the three scenarios of catchment loading was most likely to occur. A comparison of quarterly loading data for the Inanda impoundment extracted from **Appendix H**, with quarterly data for the Darvill WWW effluent extracted from **Appendix C** (which contributed more than 90 % of the point source loading), and the loading from rural laundering (**Table 4.26**), indicated the following:

The impoundment received the bulk of its soluble phosphorus loading during the January to March season when rainfall and therefore streamflow was highest for the catchment. During this period the sum of the Darvill WWW loading and the input from rural laundering of 11.3 tonnes, practically equaled the loading on the Inanda impoundment of 11.5 tonnes.

Table 4.26 : Comparison of quarterly soluble phosphorus loading data for the Umgeni inflow to Inanda with the Darvill WWW loading and the loading from rural laundering.

	Umgeni inflow to Inanda		Darvill WWW	Rural
	Flow	Measured loading	loading	detergents
Season / Quarter	10 ⁶ m ³	tonnes	tonnes	tonnes
Oct 90 to Dec 90	70	5.0	4.5	2.1
Jan 91 to Mar 91	425	11.5	9.2	2.1
Apr 91 to Jun 91	73	1.8	2.9	2.1
Jul 91 to Sep 91	28	1.7	6.1	2.1
Total	596	19.9	22.7	8.4

During the other three seasons when river flow was lower, only a portion of the WWW and rural loading reached the impoundment. It is believed that low streamflow allows sufficient time for soluble phosphorus to be adsorbed, precipitated or utilized instream, whereas high streamflow decreases the travel time from point of discharge to the impoundment, thereby increasing the loading on the impoundment.

The above mass balance calculation therefore indicated that during the season when soluble phosphorus is most likely to reach the impoundment, all of the loading measured at the inflow to the Inanda impoundment could be accounted for by the Darvill Wastewater Works and rural laundering undertaken in the catchment. These results are in favour of scenario 1, for which it was assumed that the only sources of soluble phosphorus were wastewater effluents and detergents that entered from rural laundering carried out directly at the water course. The other two scenarios assumed that other non-point source soluble phosphorus loading (e.g. agricultural lands) contributed 30 and 50 % to the soluble phosphorus budget for the catchment.

A regression model relating soluble phosphorus loading to algal production was successfully developed for the Inanda impoundment. A comparison of observed and predicted algal count (**Figure 4.2**) indicated a very good model which although developed specifically for this project, could be used in future by Umgeni Water for predicting algal production in the Inanda impoundment.

Using the phosphorus-loading/algal-production model it was found that eliminating detergent phosphorus would significantly reduce algal numbers in the Inanda impoundment. For the most likely reduction scenario of 53 %, the algal count was predicted to reduce by 75 %.

An examination of the species distribution between dissolved and precipitated phases in the Inanda impoundment, using the MINTEQA2 equilibrium speciation model, indicated that

precipitation was the dominant process and removed more than 99% of the phosphorus from solution at equilibrium.

The phosphorus remaining in solution in dissolved form, was predominantly in the form of HPO_4^{2-} and a small percentage of calcium and magnesium complexes. The formation of soluble complexes was therefore not a significant factor in determining the bioavailability of phosphorus in the impoundment.

Phosphorus adsorption onto a ferric hydroxide surface was shown to successfully compete with precipitation as the major control on the distribution of phosphate species at the pH, temperature and concentrations present in the Inanda impoundment. The net effect of adsorption would be similar to precipitation, in that phosphate is effectively removed from solution and would thus not be available for further bio-uptake.

Phosphate desorption from an iron hydroxide surface would only make a significant contribution to the soluble phosphorus pool, when the pH exceeded 9. This is expected to occur only 10% of the time in the Inanda impoundment.

Low redox conditions did not favour resolubilization of precipitated phosphorus. Modeling results indicated that reduction of ferric to ferrous ions, which has been suggested as the mechanism for phosphorus release from the adsorbed phase, would not readily occur in the impoundment and ferric hydroxide would remain the stable phase over a wide range of water conditions.

This modeling investigation was a first attempt at examining phosphorus speciation in the Inanda impoundment using the MINTEQA2 model which considers only the thermodynamic driven equilibrium chemical composition. While equilibrium modeling is valuable for interpreting the relationships among constituents in the aquatic environment, it cannot be rigorously used for predictions, since biological processes may also affect these relationships. Using the equilibrium results predicted by MINTEQA2 together with the results of on-site monitoring however, provides greater understanding and insight into phosphorus inter-relationships in the impoundment. Algal production in the Inanda impoundment appears to be driven by the external nutrient loading and the modeling serves to support this by suggesting that phosphorus entering the impoundment if not taken up rapidly is lost from solution and is not made available at a later stage.

A review of the literature on the impact of detergent phosphorus bans on water quality suggested that both the environment and wastewater works cannot benefit simultaneously from detergent phosphorus elimination. In addition, reformulating detergents may or may

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not accelerate deterioration of washing fabrics and washing machines. These factors led to four cost-benefit scenarios of which all results were in favour of not eliminating detergent phosphorus. The best scenario for detergents, *Scenario 4*, which took into consideration the increased cost to consumers as a resulting of reformulating with a zeolite builder, loss in value of washing machines and fabrics and reduction in water treatment costs, was 35 to 1 in favour of not reformulating detergents. The worse scenario for detergents, *Scenario 1*, which took into consideration the increased cost to consumers as a resulting of reformulating with a zeolite builder, and saving at the Darvill WWW as a result of a reduced influent phosphorus loading was 2 to 1 in favour of not reformulating detergents.

A review of the literature has suggested that phosphate-free detergents have been formulated to give performance equaling that of phosphate detergents and certain reformulations would not result in extra wear and tear on fabrics and washing machines (*Chapter 2, Sections 2.3.4.3 and 2.3.7*). If this were the case for South Africa, then Scenarios 1 and 2 which considers wastewater treatment and water treatment costs, would be the more likely forecasts. The results of these scenarios show that the cost of treating the consequences of eutrophication is less expensive than reducing the phosphorus loading at wastewater works. This finding may however be specific to the Inanda catchment where significant river losses occurs between the discharge point and the impoundment for most of the year. In addition, the phosphorus loading enters the impoundment *ca.* 16 km river distance away from the point of abstraction for water treatment which further improves the quality. These estimates also do not consider the costs of environmental and recreational losses associated with eutrophication.

CHAPTER FIVE Conclusions & Recommendations

The contribution of detergent phosphorus to eutrophication and the economic and water quality consequences of eliminating detergent phosphorus were assessed in the Umgeni catchment. The results indicated that detergents made a significant contribution to the phosphorus loading on the environment. However, an investigation of the costs and benefits of eliminating detergent phosphorus indicated that the costs outweighed the benefits.

Despite the Umgeni catchment being populated by twice as many rural dwellers (610 000) as urban (304 000), the overall contribution from rural areas was slightly lower (46 %) than that from urban areas (54 %). This may be attributed to rural people using half the quantity of detergent as urban residents and only 16 % of the rural laundry detergents entering the watercourse.

Detergents comprised 51 % of the phosphorus loading of urban wastewaters except for the Inanda catchment where it comprised 37 % as a result of industries in the Pietermaritzburg area contributing *ca*. 30 % to the loading.

The phosphorus loading on the Inanda impoundment was found to be significantly greater than that on the 3 upstream impoundments. This was primarily due to the large urban and rural populations residing in the catchment area, leading to greater discharges to the aquatic environment. Three scenarios for obtaining the catchment loading showed detergents to comprise 26, 42 and 53 % of the loading on the Inanda impoundment.

A regression model relating phosphorus loading to algal production was successfully developed for the Inanda impoundment. A comparison of observed and predicted algal count indicated a very good model which although developed specifically for this project, could be used in future by Umgeni Water for predicting algal production in the Inanda impoundment.

The model was used to assess the impact of the reduced loading corresponding to detergent phosphorus elimination. Three scenarios were investigated, all of which indicated that eliminating detergent phosphorus would significantly reduce the algal count in the impoundment. For the most probable reduction scenario of 53 %, the algal count was predicted to reduce by 75 %.

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The phosphorus species distribution between dissolved, precipitated and adsorbed phases was examined in the Inanda impoundment using the MINTEQA2 equilibrium speciation model. The results indicated that only a small percentage of the phosphorus remains in dissolved form (predominantly as HPO $_4^2$ -) for possible algal uptake.

Phosphorus adsorption onto a ferric hydroxide surface was shown to successfully compete with precipitation as the major control on the distribution of phosphate species at the pH value, temperature and concentrations present in the impoundment. The net effect of adsorption or precipitation, is phosphorus removal from solution. Desorption appeared to play only a minor role in making adsorbed phosphorus available, while low redox conditions did not favour resolubilization of precipitated phosphorus.

The MINTEQA2 modeling exercise therefore indicated that the natural tendency of phosphorus in the Inanda impoundment is loss by sedimentation with a small amount being left in solution for algal uptake. This suggests that only new inputs would sustain algal blooms in the impoundment and supports the observed trend of algal production being driven by the external nutrient loading.

Four different scenarios investigating the costs and benefits of eliminating detergent phosphorus were assessed. The best scenario for detergents which took into consideration the increased cost to consumers as a resulting of reformulating with a zeolite builder, loss in value of washing machines and fabrics and reduction in water treatment costs, was 35 to 1 in favour of not reformulating detergents. The worse scenario for detergents, which took into consideration the increased cost to consumers as a result of reformulating with a zeolite builder, and savings at the Darvill WWW as a result of a reduced influent phosphorus loading, was 2 to 1 in favour of not reformulating detergents.

Overseas experiences suggest that phosphate-free detergents could be reformulated with performance equaling that of phosphate-built detergents and without increasing the wear and tear on fabrics and washing machines. If this were the case in South Africa, it would still be twice as expensive to reformulate than to reduce phosphorus at a wastewater works, and 3 times more expensive to reformulate than to treat the consequences of eutrophication at a water treatment works. All cost-benefit scenarios therefore indicate that the costs of reformulating detergents outweigh the benefits.

A comparison of water treatment and wastewater treatment costs, suggests that the cost of treating the consequences of eutrophication is less expensive than reducing the phosphorus loading at a wastewater works. This finding may however be specific to the Inanda catchment where significant river losses occur between the discharge point and the

5.2

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impoundment. In addition the long length of impoundment results in further losses and water quality improvement. Uncertainty also exists in the actual cost of eutrophication as there are a number of hidden costs. These include influences on, recreation, the aquatic environment, agriculture and human health (extracellular products of certain algal genera e.g. *Microcystis* are known to contain toxins carcinogenic to man).

A methodology has been provided for assessing the impact of eliminating detergent phosphorus on eutrophication which could be applied to other important catchments in *South Africa* or to the entire country. An example of a major economic centre which has eutrophic impoundments and to which the methodology could be applied is the highly urbanized and industrialized Gauteng area.

For the Inanda system, the cost of treating nuisance algae is cheaper than either detergent reformulation or phosphorus removal at a wastewater works. As this is likely to be a function of river distance between the discharge point and the impoundment as well as the length of the impoundment, the methodology should be applied to an impoundment where the phosphorus discharge points are closer to the impoundment and abstraction site. In such a situation fewer river losses would occur and the loading may have a greater impact on algal production and therefore water treatment costs.

The South African detergent industry currently solely formulates with a phosphorus builder and therefore uses the maximum amount of phosphorus. The cost of binary, ternary or other systems which use less phosphorus should be investigated, as they may be cheaper to produce than phosphate-free formulations and still provide some benefit to the environment.

Apart from rural laundering at a watercourse, other non-point sources such as agriculture and informal settlements may contribute to the soluble/bioavailable phosphorus loading during periods of high runoff when particulate phosphates may resolubilise. Monitoring programmes should be set up to isolate these inputs and improve quantification of their contribution to the catchment phosphorus budget.

It is difficult to put a cost on losses to users other than domestic, as a result of eutrophication. Methods of quantifying these losses should therefore be developed as they all are as important as domestic. With environmental awareness gaining momentum in *South Africa*, the detergent industry, water authorities, other institutions and the public, should continue to work together and explore avenues that would minimise the impact of products on the environment while still being acceptable to users.

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APPENDIX A Urban and Rural Population in the Umgeni Catchment

Population data for the Umgeni catchment were obtained from the Institute of Natural Resources and comprised the unverified 1991 census data for the region. The data were provided in spreadsheet format per enumerative sub-district (*ESD*) and the location of *ESD* boundaries were displayed on a map. The rural population was obtained by manually overlaying the subcatchment boundaries in the area of study onto the *ESD* boundaries, to obtain the *ESD*'s or portions of *ESD*'s that fell into each subcatchment of interest. The population per subcatchment was then estimated by summing the populations in the appropriate *ESD*'s or fractions of *ESD*'s. An example of this for the Midmar-Lions subcatchment (Code F) is shown in *Section 3.1.3* of the text. **Table A1** shows the results for the entire Umgeni catchment.

	1				
Subcatchment	Code	Subcatchment	Inflow Sites	Inflow	Total
		Population		Population	Population
Midmar					
Umgeni Petrus Stroom 2.1	Е	1 800	Umgeni inflow to Mid	13 849	16 678
Lions 1	F	10 099	Umthinzima inflow	870	
Umgeni Midmar inflow 2	G	1 950	KwaGqishi inflow	439	
Kwa Gqishi Midmar inflow 35	н	439	Nguku inflow	1 137	
Nguku Midmar inflow 34.1	I	1 137	Direct inflow	383	
Umthinzima Midmar inflow 31	к	445			
Umthinzima Midmar inflow 31	L	267			
Umthinzima Midmar inflow 31	М	59			
Umthinzima Midmar inflow 31	Ν	99			
Direct Midmar catchment	0	60			
Direct Midmar catchment	01	124			
Direct Midmar catchment	02	99			
Direct Midmar catchment	O3	99			
Albert Falls					
Karkloof1	А	6 049	Umgeni Inflow to AF	12 856	16 514
Umgeni at Howick	Р	240	Nculwane inflow	1 191	
Umgeni above Karkloof confl.	Q	5 743	Doringspruit inflow	895	
Nculwane	W	1 191	Direct inflow	1 572	
Karkloof2	х	528			
Karkloof3	Y	296			
Doringspruit	Z	895			
Direct Albert Falls catchment	AB	1 333			
Direct Albert Falls catchment	AC	48			
Albert Falls inflow	AF	190			

Table A1: Rural population in the Umgeni catchment

Subcatchment	Code	Subcatchment	Inflow Sites	Inflow	Total
		Population		Population	Population
Nagle					
Mpolweni	В	14550	Umgeni inflow to Nag	75355	82493
Mkabela	С	1857	Impetu inflow	3893	
Cramond	AD	154	Direct inflow	3244	
Below Albert Falls	AE	2050			
Above Nagle	AA				
Above Nagle	AH	3477			
Mpumalanga Impetu inflow		3893			
Mpumalanga Direct inflow		3244			
Mpumalanga above Nagle		52560			
Inanda					
Mqeku	D	4010	Umgeni Inanda inflow	443907	494786
Henley Inflow	J	3909	Mshazi inflow	18385	
Edendale	R	17564	Mtata inflow	4276	
Edendale	S	18314	Kwanyuswa inflow	2565	
Edendale	Т	31640	Imbozamo inflow	1710	
Edendale	U	33928	East Inanda inflow	1710	
Slangspruit	V	305	Kwa Ngcolosi inflow	3848	
Mswati	AG	5593	Direct inflow	18385	
Mpushini	AI	1822			
Below Darvill	AJ	2941			
Below Darvill	AK	26			
Henley inflow	AL	8119			
Mpumalanga		182641			
Ndwede		179092			
Camperdown		4883			

Table A1 continued: Rural	population in the I Impeni catchment
	population in the origen catennent

The Urban population for each subcatchment was obtained by summing the population in towns in the subcatchment. These are shown in **Table A2**.

Sub Catchment	Magisterial District	Town	Population	Total Population
Midmar	VULINDLELA	MPOPHOMENI	16 370	16 370
Albert Falls	LIONS RIVER	HILTON HOWICK	180 10 444	10 624
Nagle	NEW HANOVER	ALBERT FALLS COOL AIR	172 1 835	2 007
Inanda	CAMPERDOWN	CATO RIDGE LYNNFIELD PARK	876 324	274 848

 Table A2: Urban Population in the Umgeni catchment.

Sub Catchment	Magisterial District	Town	Population	Total			
				Population			
Inanda continued	PIETERMARITZBURG	ALBERT FALLS	239				
		ASHBURTON	755				
		ASHDOWN	6 520				
		HILTON	3 348				
		IMBALI	38 395				
		MOUNT MICHAEL	1 394				
		PLESSISLAER	1 232				
		SOBANTU	10 207				
		ATHLONE	3 236				
		BISLEY	4 539				
		BLACKRIDGE	3 143				
		BOUGHTON	1 005				
		CHASE VALLEY	3 386				
		CITY	16 614				
		CLARENDON	1 846				
		CLELAND	2 928				
		EASTWOOD	6 624				
		HAYFIELDS	5 407				
		LINCOLN MEAD	1 448				
		MASONS MILL	3 502				
		MKONDENI	115				
		MONTROSE	2 198				
		MOUNTAIN RISE	3 377				
		NAPIERVILLE	4 992				
		NORTHDALE	38 398				
		PELHAM	5 700				
		PRESTBURY	1 954				
		RAISETHORPE	19 548				
		SCOTTSVILLE	10 782				
		WEMBLEY	3 221				
		WILLOWTON	733				
		WOODLANDS	6 064				
		WORLDS VIEW	821				
	VULINDLELA	EDENDALE	59 977				

 Table A2 continued : Urban Population in the Umgeni catchment.

APPENDIX B Industrial Phosphorus Loadings

The results of the industrial phosphorus loadings discharged to the Darvill Wastewater Works are shown in **Table B1**. The industry names have been kept anonymous as they were not contacted for permission to distribute the data. The nature of the manufacturing process is indicated for the large industries.

Umgeni Water reference No	Average P conc.	Average flow	P loading		
	µg.ℓ ⁻¹	kℓ.d ⁻¹	tonnes.a ⁻¹		
1013 Brewery	13 439	471	2.31		
1014	5 300	430	0.83		
1015	3 661	386	0.52		
1016 Edible oil	47 495	372	6.44		
1017 Tannery	10 795	366	1.44		
1018	5 746	349	0.73		
1019	3 760	316	0.43		
1020 Lithographic	224 178	256	20.97		
1021	5 895	237	0.51		
1022	9 709	231	0.82		
1023 Edible oil	16 804	174	1.06		
1024 Power Cables	43 730	157	2.50		
1025 Edible oil	81 868	152	4.54		
1026	13 838	139	0.70		
1027	9 911	120	0.43		
1028	16 461	101	0.61		
1029	17 147	96	0.60		
1031	6 653	78	0.19		
1032	6 952	77	0.20		
1033	7 526	77	0.21		
1034	4 635	71	0.12		
1038	16 243	55	0.32		
1042	22 787	41	0.34		
1044	16 770	39	0.24		
1046	17 853	38	0.25		
1061	4 322	21	0.03		

Table B1: Industrial phosphorus loadings on the Darvill Wastewater Works.

Umgeni Water reference No	Average P conc. µg.ℓ ⁻¹	Average flow kℓ.d ⁻¹	P loading tonnes.a ⁻¹		
1070	9 177	15	0.05		
1071	11 756	14	0.06		
1075	9 751	12	0.04		
1077	3 785	12	0.02		
1079	1 244	10	0.00		
1083	3 636	7	0.01		
1088	3 906	6	0.01		
1091	1 663	6	0.00		
1096	2 638	5	0.00		
1101	98 321	3	0.12		
1102	170 866	3	0.19		
1111	112 105	1	0.04		
1114	50 822	1	0.01		
1115	53 209	1	0.01		
Total loading			47.9		

Table B1 continued: Industrial phosphorus loadings on the Darvill Wastewater

 Works.

Flow is the average for the period August 1991 to January 1992

Concentration is the average of fortnightly or monthly monitoring for the period June 1992 to February 1993

APPENDIX C The Darvill Wastewater Work's Phosphorus Loading

C1 Background

In past years some of the influent to the Darvill Wastewater Works passed untreated into the Umsunduze river during heavy storm flow when the works capacity was exceeded. At the works an attempt was made to reduce the overflow to river by detention in five maturation ponds with a total capacity of $100M\ell$. Overflow to the river occurred when the capacity of the detention ponds was exceeded in consecutive events. With the works being taken over by Umgeni Water, plans were drawn up for a works upgrade to prevent future discharges to river. These are currently being implemented. However, for the calculation period (October 1990 to September 1991) estimates of the phosphorus loadings from both the treated effluent and untreated overflow were required to obtain the total loading of the works on the environment. [De Haas, 1993].

C2 Estimation of overflow

The volume of overflow was not measured and had to be estimated from the discrepancy between influent and effluent flows. The influent and effluent flow volumes were compared graphically as shown in **Figures C1** and **C2** to obtain the flow volume at which significant deviation between influent and effluent flow occurred and therefore the start of overflow.



Figure C1: Darvill WWW Influent and effluent flows for October 1990 to September 1991.

Figure C1 showed that during periods of low flow the influent flow was similar to the effluent flow but during high flows exceeded the effluent flow significantly.

Appendix C

Figure C2: Sorted line plot showing point of significant deviation between influent and effluent flow for the Darvill WWW.



The cutoff flow volume at which the influent flow deviated significantly from the effluent flow was estimated to be 60 M ℓ .d⁻¹ by interpolation on the plot in **Figure C2**. i.e. flows exceeding 60 M ℓ .d⁻¹ would result in some overflow to river.

As shown in **Table C1**, the influent and effluent flow during low flow periods were not necessarily equal and it could not be assumed that the difference between influent and effluent flow equaled overflow. Therefore to quantify the overflow, the relationship between influent and effluent volumes during dry periods (i.e. flows less than 60 M ℓ .d⁻¹) was determined statistically. This relationship shown in **Equation C1** was then used to estimate the volume of treated influent during wet periods.

For influent flows exceeding 60 M ℓ .d⁻¹, the overflow volumes were calculated as the difference between measured influent volume (i.e. treated and untreated) and influent volume calculated from **Equation C1** (treated only). A sample of the results is shown in **Table C1**. Overflow occurred for 65 days during the October 1990 to September 1991 period.

C3 Calculation of phosphorus loadings

The total load discharged from the wastewater works would equal the sum of the treated and untreated overflow loadings.

Date	Influent	Mℓ.d ⁻¹	Measured	Calculated	Calculated overflow
	Measured	Calculated	effluent	overflow	allowing for 100 M ℓ
	Medsured	Calculated	Mℓ.d ⁻¹	$M\ell.d^{-1}$	detention ponds
01-Oct-90	43	41	35	0	0
02-Oct-90	44	43	38	0	0
03-Oct-90	44	41	35	0	0
04-Oct-90	43	40	33	0	0
05-Oct-90	41	41	35	0	0
06-Oct-90	39	40	34	0	0
07-Oct-90	34	42	36	0	0
17-Jan-91	54	53	54	0	0
18-Jan-91	55	53	54	0	0
19-Jan-91	50	50	50	0	0
20-Jan-91	68	53	54	16	0
21-Jan-91	88	67	78	21	0
22-Jan-91	124	61	69	63	0
23-Jan-91	208	70	84	138	138
24-Jan-91	269	69	82	200	200
25-Jan-91	198	70	83	129	129
26-Jan-91	148	71	84	78	78
27-Jan-91	169	69	81	100	100
28-Jan-91	240	69	82	171	171
29-Jan-91	193	67	79	126	126
30-Jan-91	230	69	81	161	161
31-Jan-91	160	68	80	92	92
01-Feb-91	124	68	79	56	56
02-Feb-91	101	66	76	35	35

Table C1: A sample data set showing volumes of influent, effluent and overflow,

for the Darvill Wastewater Works.

The treated effluent load was determined by combining daily effluent volumes with daily effluent SRP concentrations. The annual load discharged in this way was estimated to be 15.0 tonnes for the period October 1990 to September 1991. Monthly and annual loads are summarized in **Table C2**.

The first 100 M ℓ of overflow calculated was omitted to allow for storage in the maturation ponds. The remaining overflow volumes were combined with the corresponding *influent* SRP concentrations to determine the overflow loading. Results are summarized in **Table C2**.

Appendix C

	Т	reated Effluer	nt	Un	ow			
Month	Average	Average	Monthly	Average	Average	Monthly	Total	
	Flow	Conc.	Loading	Flow	Conc.	Loading	Loading	
	$M\ell.d^{-1}$	mg.ℓ ⁻¹	tonnes	$M\ell.d^{-1}$	mg.ℓ ⁻¹	tonnes	tonnes	
Oct-90	44	0.724	0.97	0	0	0	0.97	
Nov-90	44	1.254	1.66	0	0	0	1.66	
Dec-90	51	0.524	0.78	25	3.459	1.04	1.82	
Jan-91	57	0.785	1.30	138	3.380	1.87	3.17	
Feb-91	63	0.318	0.57	62	2.013	2.96	3.53	
Mar-91	57	0.374	0.64	18	3.779	1.83	2.46	
Apr-91	50	0.705	1.06	0	0	0	1.06	
May-91	47	0.302	0.44	0	0	0	0.44	
Jun-91	46	1.018	1.44	0	0	0	1.44	
Jul-91	46	1.414	1.97	0	0	0	1.97	
Aug-91	47	1.106	1.64	0	0	0	1.64	
Sep-91	49	1.705	2.52	0	0	0	2.52	
Annual			14.99			7.70	22.69	

Table C2: Soluble phosphorus loadings from the Darvill Wastewater Works for

 October 1990 to September 1991.

The total load discharged from Darvill Wastewater Works for October 1990 to September 1991 was therefore estimated to be 22.7 tonnes, of which 15.0 tonnes (66%) could be attributed to treated effluent and 7.7 tonnes (34%) to untreated overflow.

APPENDIX D FLUX load calculation program

FLUX was developed by the US Army Corps of Engineers, Washington DC and is an interactive program for estimating loadings passing a river or outflow (e.g. effluent) site. FLUX interprets the flow and water quality data obtained from grab or event sampling and estimates the mean or total loading over the complete flow record between two dates. The loading estimates can be used to formulate impoundment nutrient balances over annual or seasonal averaging periods appropriate for application of empirical eutrophication models. [Walker, 1987].

Since the appropriate loading calculation method depends on the concentration, flow and seasonal dynamics, FLUX provides a choice of five different calculation methods. The program provides an option to stratify the samples into groups based on flow and/or date, which in many cases increases the accuracy and reduces potential biases in loading estimates. [Walker, 1987].

Data for the major inflows to impoundments in the Umgeni catchment show a strong relationship between flow and phosphorus concentration and the method best suited to this type of variation was therefore chosen for the loading calculation. The algorithm used by this method is presented in **Equation D1**.

$$Loading = Mean(w) \left[\frac{Mean(Q)}{Mean(q)} \right]^{b+1}$$
[D1]

Where

- w measured loading = cq
- c measured sample concentration
- q measured flow during sample
- Q mean daily flow
- b slope of log (c) versus log (q) regression

APPENDIX E ACRU Streamflow Simulation

The Department of Agricultural Engineering (*DAE*), University of Natal had developed the Agricultural Catchments Research Unit (*ACRU*) model for the Umgeni catchment in the first phase of the Water Research Commission funded project, entitled, *Development of a Systems Hydrological Model to Assist with Water Quantity and Quality Management in the Mgeni Catchment* [Tarboton & Schulze, 1992]. The model uses a daily rainfall input to simulate, *inter alia*, runoff for rivers and streams. Additional climatic information such as temperature and evaporation plus information on catchment characteristics including location, soils and landuse are also required to generate the runoff.

The ACRU model was used for the present project, Detergent Phosphorus in South Africa: Impact on Eutrophication with Specific Reference to the Umgeni Catchment, to generate inflow to impoundments on the Umgeni river where streamflow gauging was absent. The DAE had sub-divided the Umgeni catchment into 123 relatively homogeneous cells and had collected data for each cell from various sources. The data had been set up by the DAE in the ACRU menu, which serves as the input to the ACRU model. Apart from the changes indicated below, this menu was used as is for the runoff generation. The ACRU model version 2, housed at the Computing Centre for Water Research (CCWR) and accessed via a dial-up modem was used for the runoff simulations.

E1 Modifications to the DAE ACRU menu

- The model was run for 24 of the 123 cells, which were selected to provide inflow volumes to impoundments on the Umgeni river. With the DAE cell divisions this could be done for the Midmar, Albert Falls and Inanda subcatchments. (Inflows to the Nagle impoundment were obtained from measurements made by Umgeni Water Operations Division). Table E1 shows the ACRU cells used.
- The model time period was set for 1988 to 1992 which provided data until the end of 1991. Although flow data were only needed for the period October 1990 to September 1991, additional years were simulated as it is recommended that the first two years of data be discarded to allow the water budget to stabilise [Schulze et al, 1989a & 1989b].
- Some of the rainfall stations set up in the *DAE* menu had been discontinued and other stations had to be chosen. The choice of rainfall station depended on its proximity to

the cell, similarity of mean annual and monthly precipitation and completeness of dataset. The selected rainfall stations are shown in **Table E1**.

- A monthly precipitation correction was applied to relate the precipitation of the rainfall station to the cell to which it was applied. The rainfall station used for the simulation was not necessarily located in the cell of interest. Correction factors are shown in Table E2 together with monthly precipitation data for the cell and rainfall station.
- At sites where stream gauges were present, the gauged flow was allowed to override the simulated flow. A comparison of simulated and observed flows was however carried out (*Section D4*), to determine the accuracy of the *ACRU* simulations.

ACRU	Cell Characteristics										
Cell Number	Cell Description	Area	Coords	(ddmm)	Rainfall						
		km²	Lat	Long	Station						
7	Umgeni above Lions	30.10	2930	3003	0239002						
8	Umgeni above Lions	39.52	2930	3007	0239002						
15	Lions above Umgeni confluence	27.65	2928	3010	0268806						
16	Umgeni Midmar inflow	5.95	2929	3010	0268806						
25	Nguku Midmar inflow	57.06	2935	3006	0239097						
26	KwaGqishi Midmar inflow	28.97	2935	3010	0239097						
27	Umthinzima Midmar inflow	15.62	2935	3012	0239483						
28	Midmar impoundment	69.73	2932	3011	0239482						
29	Umgeni above Albert Falls	21.31	2929	3012	0269388						
30	Umgeni above Albert Falls	24.26	2928	3014	0269388						
31	Umgeni above Albert Falls	8.64	2931	3014	0239482						
32	Umgeni above Albert Falls	13.93	2930	3015	0239482						
33	Umgeni above Albert Falls	10.04	2934	3015	0239483						
34	Umgeni above Albert Falls	3.15	2934	3017	0239483						
35	Umgeni above Albert Falls	14.13	2932	3016	0239482						
24	Karkloof above Umgeni confluence	48.20	2925	3017	0269532						
36	Umgeni Albert Falls inflow	52.91	2929	3017	0239483						
37	Nculwane Albert Falls inflow	64.07	2922	3021	0269532						
38	Doringspruit Albert Falls inflow	36.28	2931	3020	0239483						
39	Albert Falls impoundment	97.39	2927	3023	0269775						
101	Tributary inflow to Inanda	40.03	2944	3046	0240586						
102	Tributary inflow to Inanda	15.62	2939	3049	0240586						
103	Tributary inflow to Inanda	27.46	2940	3052	0240586						
104	Direct inflow into Inanda	57.85	2942	3049	0240586						

Table E1: ACRU cells used in the runoff simulation for the Umgeni catchment. Cellnumbers refer to the ACRU cells shown in the schematics in **Figures D1** to **D3**.

Cell Number																
and Rainfall Station	Lat	Long	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Alt	MAP
7	2930	3003	159.0	135.8	131.4	55.2	17.2	4.2	8.7	16.0	42.2	84.4	123.6	162.4	1270	1034
0239002	2932	3001	172.7	119.8	128.7	50.9	18.0	4.0	9.0	17.0	40.9	83.8	112.8	160.7	1203	998
			0.92	1.13	1.02	1.09	0.96	1.05	0.97	0.94	1.03	1.01	1.10	1.01	1.06	1.04
8	2930	3007	146.2	129.6	121.5	51.9	16.2	3.9	9.3	15.6	40.2	79.7	120.1	154.4	1168	977
0239002	2932	3001	172.7	119.8	128.7	50.9	18.0	4.0	9.0	17.0	40.9	83.8	112.8	160.7	1203	998
			0.85	1.08	0.94	1.02	0.90	0.98	1.03	0.91	0.98	0.95	1.06	0.96	0.97	0.98
15	2928	3010	144.2	125.7	111.4	53.5	16.0	5.1	7.6	17.5	43.8	82.2	118.1	148.1	1115	965
0268806	2926	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			0.90	0.95	0.90	1.07	0.97	1.05	1.12	1.04	1.11	1.03	1.03	1.01	0.74	0.99
16	2929	3010	140.1	120.4	108.2	52.3	16.1	5.2	7.3	17.5	41.9	80.0	114.9	142.6	1079	939
0268806	2926	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			0.87	0.91	0.88	1.05	0.98	1.07	1.07	1.04	1.06	1.00	1.00	0.97	0.71	0.96
24	2925	3017	158.9	136.0	117.4	58.9	17.4	5.0	7.3	19.3	50.2	95.5	129.2	158.2	1029	1070
0269532	2922	3018	178.1	154.2	132.6	62.1	16.7	7.2	9.6	20.3	63.3	107.5	142.2	174.5	1100	1195
			0.89	0.88	0.89	0.95	1.04	0.70	0.77	0.95	0.79	0.89	0.91	0.91	0.94	0.90
25	2935	3006	140.3	115.6	115.3	49.7	18.1	5.2	7.6	18.4	40.2	74.3	110.7	137.4	1342	926
0239097	2937	3004	141.0	134.1	116.2	50.6	19.9	5.0	7.9	20.9	47.7	87.4	115.2	148.0	1500	993
			1.00	0.86	0.99	0.98	0.91	1.05	0.96	0.88	0.84	0.85	0.96	0.93	0.89	0.93
26	2935	3010	129.6	110.6	108.7	45.1	16.8	4.6	6.3	16.6	36.0	70.5	108.9	127.7	1262	881
0239097	2937	3004	141.0	134.1	116.2	50.6	19.9	5.0	7.9	20.9	47.7	87.4	115.2	148.0	1500	993
			0.92	0.82	0.94	0.89	0.85	0.91	0.80	0.80	0.75	0.81	0.95	0.86	0.84	0.89
27	27	27	133.1	114.3	109.1	46.9	17.2	4.8	6.6	16.9	37.6	74.3	112.0	130.3	1253	910
0239483	2933	3017	136.7	116.6	105.5	48.1	18.3	5.1	7.3	16.4	42.2	79.3	113.8	129.6	1165	938
			0.97	0.98	1.03	0.98	0.94	0.94	0.91	1.03	0.89	0.94	0.98	1.01	1.08	0.97

 Table E2: Monthly precipitation data for cells and selected rainfall stations and calculated precipitation correction factors.

Subcatchment No.																
and Rainfall Station	Lat	Long	Jan	Feb	Mar	Apr	Мау	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Alt	MAP
28	2932	3011	127.9	109.1	103.6	46.0	16.0	4.8	6.7	16.1	35.4	71.2	107.7	128.1	1096	870
0239482	2932	3017	129.6	112.1	102.5	44.7	18.4	4.4	7.9	14.0	37.7	71.8	109.5	120.9	1134	876
			0.99	0.97	1.01	1.03	0.87	1.08	0.85	1.15	0.94	0.99	0.98	1.06	0.97	0.99
29	2929	3012	137.4	113.7	101.2	54.4	16.5	5.8	7.0	18.7	41.2	81.2	110.1	136.0	1065	916
0269388	2928	3013	149.9	109.6	98.0	67.3	18.3	7.7	5.8	25.0	49.0	95.1	109.6	144.1	1100	961
			0.92	1.04	1.03	0.81	0.90	0.75	1.21	0.75	0.84	0.85	1.00	0.94	0.97	0.95
30	2928	3014	152.3	122.8	107.1	61.0	17.7	6.0	6.7	21.4	47.9	93.4	120.6	150.9	1100	1007
0269388	2928	3013	149.9	109.6	98.0	67.3	18.3	7.7	5.8	25.0	49.0	95.1	109.6	144.1	1100	961
			1.02	1.12	1.08	0.91	0.97	0.78	1.16	0.85	0.98	0.98	1.10	1.05	1.00	1.05
31	2931	3014	122.4	107.0	93.5	47.2	15.9	5.3	8.2	15.2	33.1	70.3	102.0	118.3	1080	839
0239482	2932	3017	129.6	112.1	102.5	44.7	18.4	4.4	7.9	14.0	37.7	71.8	109.5	120.9	1134	876
			0.94	0.95	0.91	1.06	0.87	1.21	1.03	1.09	0.88	0.98	0.93	0.98	0.95	0.96
32	2930	3015	129.5	109.9	96.4	49.7	16.2	5.2	7.3	16.5	37.5	76.2	106.3	126.0	1020	876
0239482	2932	3017	129.6	112.1	102.5	44.7	18.4	4.4	7.9	14.0	37.7	71.8	109.5	120.9	1134	876
			1.00	0.98	0.94	1.11	0.88	1.18	0.92	1.18	0.99	1.06	0.97	1.04	0.90	1.00
33	2934	3015	132.1	113.1	104.0	47.4	17.2	5.0	7.0	16.6	39.0	76.0	109.6	126.9	1213	903
0239483	2933	3017	136.7	116.6	105.5	48.1	18.3	5.1	7.3	16.4	42.2	79.3	113.8	129.6	1165	938
			0.97	0.97	0.99	0.98	0.94	0.98	0.96	1.01	0.92	0.96	0.96	0.98	1.00	0.96
34	2934	3017	144.4	122.9	111.7	51.3	18.9	5.5	7.4	18.2	44.7	84.7	119.7	138.1	1189	994
0239483	2933	3017	136.7	116.6	105.5	48.1	18.3	5.1	7.3	16.4	42.2	79.3	113.8	129.6	1165	938
			1.06	1.05	1.06	1.07	1.03	1.08	1.01	1.11	1.06	1.07	1.05	1.07	1.02	1.06
35	2932	3016	126.8	109.1	197.7	46.5	16.7	4.9	7.4	15.3	36.6	72.8	105.6	121.4	1082	863
0239482	2932	3017	129.6	112.1	102.5	44.7	18.4	4.4	7.9	14.0	37.7	71.8	109.5	120.9	1134	876
			0.98	0.97	0.95	1.04	0.91	1.11	0.94	1.09	0.97	1.01	0.96	1.00	0.95	0.99

Table E2 continued: Monthly precipitation data for cells and selected rainfall stations and calculated precipitation correction factors

Subcatchment No.																
and Rainfall Station	Lat	Long	Jan	Feb	Mar	Apr	Мау	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Alt	MAP
36	2929	3017	133.1	112.9	100.0	48.9	16.6	4.6	6.6	16.2	40.2	78.4	109.4	128.3	982	900
0239483	2933	3017	136.7	116.6	105.5	48.1	18.3	5.1	7.3	16.4	42.2	79.3	113.8	129.6	1165	938
			0.97	0.97	0.95	1.02	0.91	0.90	0.91	0.99	0.95	0.99	0.96	0.99	0.84	0.96
37	2922	3021	167.7	148.4	127.3	64.7	17.2	5.9	8.7	20.2	54.0	97.7	128.4	161.8	907	1125
0269532	2922	3018	178.1	154.2	132.6	62.1	16.7	7.2	9.6	20.3	63.3	107.5	142.2	174.5	1100	1195
			0.94	0.96	0.96	1.04	1.03	0.82	0.91	1.00	0.85	0.91	0.90	0.93	0.82	0.94
38	2931	3020	142.8	119.7	107.1	51.6	17.9	5.0	6.7	17.0	42.7	82.6	113.4	131.5	966	955
0239483	2933	3017	136.7	116.6	105.5	48.1	18.3	5.1	7.3	16.4	42.2	79.3	113.8	129.6	1165	938
			1.04	1.03	1.01	1.07	0.98	0.99	0.92	1.04	1.01	1.04	1.00	1.01	0.83	1.02
39	2927	3023	135.7	115.9	102.0	52.1	15.2	5.0	6.8	16.9	41.7	75.7	102.3	123.5	709	899
0269775			140.6	118.4	103.9	51.6	14.6	5.6	7.1	18.6	43.1	77.1	103.1	125.6	680	916
			0.97	0.98	0.98	1.01	1.04	0.90	0.96	0.91	0.97	0.98	0.99	0.98	1.04	0.98
101	2944	3046	117.2	98.1	96.1	42.1	17.3	8.1	10.1	21.1	42.5	81.3	101.2	103.9	507	878
0240404	2946	3050	148	117	122.1	52.8	23.8	10.3	14.5	23.8	55.9	91.1	112.8	123.2	551	1035
			0.79	0.84	0.79	0.80	0.73	0.78	0.70	0.89	0.76	0.89	0.90	0.84	0.92	0.85
102	2939	3049	115.6	97.0	95.5	42.1	18.3	7.6	9.1	20.6	44.1	78.3	96.7	101.4	380	860
0240404	2946	3050	148	117	122.1	52.8	23.8	10.3	14.5	23.8	55.9	91.1	112.8	123.2	551	1035
			0.78	0.83	0.78	0.80	0.77	0.74	0.63	0.86	0.79	0.86	0.86	0.82	0.69	0.83
103	2940	3052	106.0	89.3	90.0	40.1	18.1	7.8	9.2	20.0	41.5	72.6	89.8	93.9	209	814
0240404	2946	3050	148	117	122.1	52.8	23.8	10.3	14.5	23.8	55.9	91.1	112.8	123.2	551	1035
			0.72	0.76	0.74	0.76	0.76	0.76	0.63	0.84	0.74	0.80	0.80	0.76	0.38	0.79
104	2942	3049	123.1	102.6	100.4	43.9	17.3	6.7	8.8	19.3	41.3	76.0	99.2	106.8	549	870
0240404	2946	3050	148	117	122.1	52.8	23.8	10.3	14.5	23.8	55.9	91.1	112.8	123.2	551	1035
			0.83	0.88	0.82	0.83	0.73	0.66	0.61	0.81	0.74	0.83	0.88	0.87	1.00	0.84

Table E2 continued: Monthly precipitation data for cells and selected rainfall stations and calculated precipitation correction factors

E2 Combination of ACRU cells needed to provide inflows to impoundments

E2.1 Midmar subcatchment

Figure E1 depicts the cells used to obtain flows into the Midmar impoundment. Cells 16, 25, 26, and 27 corresponded to the Umgeni, KwaGqishi, Nguku and Umthinzima inflows to the Midmar impoundment, respectively, while cell 28 provided the direct inflow to the Midmar impoundment.

The total Umgeni inflow to the Midmar impoundment was obtained by summing the estimated flows for cells 7, 8, 15 and 16 and adding to it the gauged flows at U2H013 (Umgeni at Petrus Stroom) and U2H007 (Lions at Weltevreden).

The *ACRU* cell 27 fell short of the Umgeni Water, water quality monitoring site by about 3.4 km². This was corrected by adjusting the area from 15.6 to 19 km² when calculating the flow from runoff data. It was assumed that the same catchment properties applied to the added area. The return flow from the Mpophomeni Wastewater Works was also added to the simulated flow for cell 27 to give the total inflow to the Midmar impoundment from the Umthinzima stream.





E2.2 Albert Falls subcatchment

Cells 36, 37, 38 and 39 corresponded to the Umgeni, Nculwane, Doringspruit and direct inflows to the Albert Falls impoundment, respectively.

The total Umgeni inflow to the Albert Falls impoundment was estimated by simulating flows starting at cell 29 on the Umgeni and 24 on the Karkloof (**Figure E2**) and adding to these the gauged outflow from the Midmar impoundment (U2H048) and the gauged flow on the Karkloof river (U2H006).

Figure E2: Schematic showing *ACRU* cells, rainfall stations and gauging sites used to simulate flow to the Albert Falls impoundment.



E2.3 Inanda subcatchment

Runoff from *ACRU* cells 101, 102, 103 and 104 enabled runoff for tributaries flowing into the Inanda impoundment to be estimated. Flow for the Umgeni into Inanda was obtained from measured outflow and a water balance for the impoundment using data from Umgeni Water Operations.

Figure E3: Schematic showing *ACRU* cells, rainfall stations and gauging sites used to simulate flow to the Inanda impoundment.



The *ACRU* cell 101 corresponded to the Mshazi inflow to the Inanda impoundment. Cells 102, 103 and 104 were area-weighted as indicated in **Table E3** to provide runoff corresponding to other inflows to the impoundment for which water quality data were available.

Table E3: Water quality monitoring sites in the Inanda subcatchment for which runoff were estimated using *ACRU* cells.

Water quality monitoring site	Area	Closest	Area factor
	km ^	ACRU cell	
Mshazi above Umgeni confluence	40.03	101	1.00
Imbozamo inflow	8.19	102	0.52
KwaNyuswa inflow	9.10	104	0.16
Mtata inflow	11.83	103	0.43
Stream draining KwaNgcolosi	6.37	104	0.11
Direct inflow (quality not monitored)	63.7	104	1.10

E3 Results

For each cell, runoff was multiplied by the appropriate area to give streamflow. Flow data were later combined with measured phosphorus concentrations to provide phosphorus loadings on impoundments (**Appendix H**). Monthly and annual flow volumes (calculated from simulated daily data) are shown in **Tables E4** to **E6**.

			Flow 10 ⁶ m ³		
Month	Umgeni	KwaGqishi	Nguku	Umthinzima	Direct
Oct-90	6.61	0.44	0.20	0.20	0.86
Nov-90	8.01	0.26	0.11	0.06	0.23
Dec-90	19.18	0.50	0.22	0.30	0.73
Jan-91	53.36	1.92	0.84	0.82	5.08
Feb-91	86.64	1.93	0.80	1.67	3.26
Mar-91	34.44	1.31	0.49	0.16	0.84
Apr-91	12.17	0.55	0.18	0.12	0.55
May-91	7.49	0.37	0.09	0.07	0.43
Jun-91	4.78	0.30	0.09	0.06	0.27
Jul-91	3.74	0.18	0.09	0.05	0.22
Aug-91	2.65	0.18	0.05	0.04	0.22
Sep-91	3.01	0.18	0.02	0.04	0.20
Annual	242.08	8.12	3.16	3.59	12.90

Table E4: Monthly and annual totals of simulated daily flow volumes for inflows to the Midmar impoundment.

Table E5: Monthly and annual totals of simulated daily flow volumes for inflows

		Flow 1	0 ⁶ m ³	
Month	Umgeni	Nculwane	Doringspruit	Direct
Oct-90	12.10	0.53	0.24	0.66
Nov-90	9.42	0.08	0.02	0.03
Dec-90	22.27	0.67	0.19	0.43
Jan-91	80.37	1.83	0.84	5.91
Feb-91	150.89	4.47	2.07	3.55
Mar-91	61.03	0.11	0.05	0.70
Apr-91	19.46	0.14	0.10	0.45
May-91	11.00	0.01	0.00	0.31
Jun-91	9.13	0.01	0.00	0.29
Jul-91	8.45	0.00	0.00	0.30
Aug-91	7.25	0.00	0.00	0.02
Sep-91	7.57	0.03	0.00	0.08
Annual	398.95	7.86	3.51	12.73

to the	Albert	Falls	impound	ment.

Table E6: Monthly and annual totals of simulated daily flow volumes for inflows to the Inanda impoundment.

			Flow 1	10 ⁶ m ³		
Month	Mshazi	Imbozamo	KwaNyuswa	Mtata	KwaNgcolosi	Direct
Oct-90	1.19	0.11	0.04	0.11	0.02	1.81
Nov-90	0.16	0.01	0.01	0.01	0.00	0.22
Dec-90	0.64	0.06	0.02	0.05	0.01	1.16
Jan-91	0.44	0.04	0.02	0.03	0.01	0.78
Feb-91	0.93	0.08	0.04	0.08	0.02	1.71
Mar-91	0.37	0.02	0.01	0.02	0.01	0.58
Apr-91	0.11	0.003	0.002	0.002	0.001	0.10
May-91	0.10	0.004	0.002	0.005	0.001	0.11
Jun-91	0.06	0.001	0.001	0.000	0.001	0.06
Jul-91	0.05	0.001	0.001	0.000	0.000	0.04
Aug-91	0.04	0.001	0.001	0.000	0.000	0.04
Sep-91	0.04	0.001	0.001	0.001	0.000	0.03
Annual	4.13	0.33	0.14	0.31	0.07	6.64

E4 Comparison of simulated and observed data

Runoff was simulated for the Lions river at Weltevreden in the Midmar subcatchment (U2H007) and compared to the gauged flow to assess the accuracy of the *ACRU* simulations. The *ACRU* cells used for the simulation shown in **Tables E7** and **E8**.

Cell Number																
and Rainfall Station	Lat	Long	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Alt	MAP
9	2926	2953	178.2	146.2	134.2	53.0	18.3	4.3	6.9	18.0	41.4	82.8	121.1	154.2	1648	1054
268806	2626	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			1.11	1.10	1.09	1.06	1.11	0.96	1.01	1.08	1.05	1.04	1.06	1.05	1.09	1.08
10	2926	2958	153.1	128.7	120.8	49.2	15.9	4.7	7.0	15.8	38.6	77.5	112.9	143.9	1494	951
268806	2926	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			0.95	0.97	0.98	0.98	0.96	0.98	1.02	0.94	0.98	0.97	0.98	0.98	0.99	0.97
11	2923	3002	152.9	135.7	119.6	49.8	16.8	5.4	7.5	16.0	40.6	80.8	118.3	148.3	1369	970
268806	2926	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			0.95	1.02	0.97	1.00	1.02	1.13	1.10	0.96	1.03	1.01	1.03	1.01	0.91	0.99
12	2926	3005	157.5	144.2	125.4	55.6	16.5	4.7	7.6	17.6	45.6	87.1	129.3	164.5	1242	1047
268806	2926	2957	160.8	132.5	123.6	50.0	16.5	4.8	6.8	16.7	39.4	79.7	114.8	146.3	1511	977
			0.98	1.09	1.01	1.11	1.00	0.98	1.12	1.06	1.16	1.09	1.13	1.12	0.82	1.07
13	2921	3006	152.6	141.7	119.3	52.2	15.2	4.5	6.7	15.4	39.8	81.3	121.1	151.7	1391	988
269111	2921	3004	159.0	160.1	125.6	52.7	13.2	4.1	6.1	16.2	34.4	81.0	125.6	159.0	1510	1013
			0.96	0.88	0.95	0.99	1.15	1.09	1.10	0.95	1.16	1.00	0.96	0.95	0.92	0.98
14	2925	3010	147.3	131.6	110.3	53.6	15.7	5.5	7.6	16.8	48.1	84.2	121.3	150.5	1190	988
269532	2922	3018	178.1	154.2	132.6	62.1	16.7	7.2	9.6	20.3	63.3	107.5	142.2	174.5	1100	1195
			0.83	0.85	0.83	0.86	0.94	0.76	0.79	0.83	0.76	0.78	0.85	0.86	1.08	0.83

 Table E7: Monthly precipitation data for cells and selected rainfall stations for cells used for verification.

ACRU	Cell Characteristics								
Cell	Cell	Area	Coords	(ddmm)	Rainfall				
Number	Description	km²	Lat	Long	Station				
7	Umgeni above Lions	30.10	2930	3003	0239002				
9	Lions river	38.96	2926	2953	0268806				
10	Lions river	112.9	2926	2958	0268806				
11	Lions river	65.13	2923	3002	0268806				
12	Lions river	55.30	2926	3005	0268806				
13	Lions river	55.22	2921	3006	0269111				
14	Lions river at Weltevreden	29.25	2925	3010	0269532				

Table E8: ACRU cells used to compare simulated and observed flows.

The simulated and observed flows were compared graphically and statistically as shown in **Table E9** and **Figure E4**. Both the graphical and statistical comparisons indicated that simulated data did not differ significantly from observed. The *ACRU* flows were therefore accepted as reliable for use in the ungauged catchments.

Statistic	Observed	Simulated			
Mean	0.270	0.311			
Variance	0.225	0.433			
Observations	365	365			
Pearson Correlation	0.	79			
Pooled Variance	0.246				
Hypothesized Mean Difference	0				
degrees of freedom	364				
t	-1.	89			
t Critical two-tail	1.	97			

Table E9: Paired two-sample t-test for means for simulated and observed flows.

Figure E4: Time-series of simulated versus observed flows for the Lions river at Weltevreden.



APPENDIX F MINTEQA2 Phosphorus Speciation Modeling

Results of the equilibrium phosphorus speciation modelling using MINTEQA2 are shown below. The input data set comprised results of a chemical analysis of a water sample taken from the Inanda impoundment in December 1990, at a site near the inflow. Results shown are for the modelling of soluble complex formation and precipitation processes.

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
330	H+1	5.01E-09	-8.30	5.05E-06
140	CO3-2	4.47E-06	-5.35	2.91E+01
150	Ca+2	2.57E-04	-3.59	1.04E+01
460	Mg+2	2.29E-04	-3.64	5.60E+00
500	Na+1	9.12E-04	-3.04	2.09E+01
410	K+1	6.17E-05	-4.21	2.40E+00
281	Fe+3	8.51E-06	-5.07	4.80E-01
180	CI-1	7.41E-04	-3.13	2.62E+01
270	F-1	7.94E-07	-6.10	1.51E-01
732	SO4-2	1.26E-04	-3.90	1.22E+01
580	PO4-3	1.35E-05	-4.87	1.28E+00
2	H2O	1.00E+00	0.00	0.00E+00

Table F1: Input data to MINTEQA2 before type modifications.

Table F2: Components as species in solution.

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
580	PO4-3	3.93E-12	0.0	-11.6	0.6	0.2	0.0

Table F3: Other phosphorus species in solution.

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
3305801	H2PO4 -	2.04E-09	0.00	-8.7	0.9	19.5	-4.5
3305802	H3PO4	1.51E-15	0.00	-14.8	1.0	21.7	0.0
4605800	MgPO4 -	1.88E-09	0.00	-8.7	0.9	6.6	3.1
4605801	MgH2PO4 +	1.28E-11	0.00	-10.9	0.9	21.1	-1.1
4605802	MgHPO4 AQ	3.53E-09	0.00	-8.5	1.0	15.2	-0.2
1505800	CaHPO4 AQ	2.60E-09	0.00	-8.6	1.0	15.1	-0.2
1505801	CaPO4 -	1.41E-09	0.00	-8.9	0.9	6.5	3.1
1505802	CaH2PO4 +	1.01E-11	0.00	-11.0	0.9	21.0	-1.1
5005800	NaHPO4 -	4.69E-11	0.00	-10.4	0.9	12.7	0.0
4105800	KHPO4 -	3.20E-12	0.00	-11.5	0.9	12.7	0.0
2815800	FeHPO4 +	5.58E-30	0.00	-29.3	0.9	17.7	-7.3
2815801	FeH2PO4 +2	6.21E-31	0.00	-30.3	0.8	25.1	0.0
3305800	HPO4 -2	3.05E-08	0.00	-7.6	0.8	12.4	-3.5

Appendix F

MINTEQA2 Speciation Modeling

ID					Ц
	INAME	CALC NOL		NEW LOGK	DH
3028100	HEMATITE	4.30E-06	-5.37	4.32	30.85
7015002	FCO3APATITE	2.80E-06	-5.55	114.00	-39.39

Table F4: Finite solids present at equilibrium.

Table F5: Percentage distribution of phosphorus components among dissolved species.

PO4-3	4.8	%	BOUND IN SPECIES #3305801	H2PO4 -
	4.5	%	BOUND IN SPECIES #4605800	MgPO4 -
	8.4	%	BOUND IN SPECIES #4605802	MgHPO4 AQ
	6.2	%	BOUND IN SPECIES #1505800	CaHPO4 AQ
	3.3	%	BOUND IN SPECIES #1505801	CaPO4 -
	72.6	%	BOUND IN SPECIES #3305800	HPO4 -2

Table F6: Equilibrated phosphorus mass distribution.

IDX	NAME	DISSO	DISSOLVED		BED	PRECIPI	TATED
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
580	PO4-3	4.20E-08	0.3	0.00E+00	0.0	1.34E-05	99.7
140	CO3-2	9.58E-04	99.7	0.00E+00	0.0	3.36E-06	0.3
150	Ca+2	2.33E-04	89.8	0.00E+00	0.0	2.66E-05	10.2
460	Mg+2	2.30E-04	99.8	0.00E+00	0.0	4.03E-07	0.2
500	Na+1	9.08E-04	99.9	0.00E+00	0.0	1.01E-06	0.1
410	K+1	6.14E-05	100.0	0.00E+00	0.0	0.00E+00	0.0
732	SO4-2	1.27E-04	100.0	0.00E+00	0.0	0.00E+00	0.0
180	CI-1	7.39E-04	100.0	0.00E+00	0.0	0.00E+00	0.0
281	Fe+3	6.17E-16	0.0	0.00E+00	0.0	8.60E-06	100.0
330	H+1	9.50E-04	100.0	0.00E+00	0.0	0.00E+00	0.0
2	H2O	3.00E-06	100.0	0.00E+00	0.0	0.00E+00	0.0
270	F-1	1.01E-06	12.7	0.00E+00	0.0	6.94E-06	87.3

Table F7: Saturation indices and stoichiometry of phosphorus containing minerals.

ID	NAME	SAT INDEX	STOICHIOMETRY				
7015003	HYDRAPATITE	-1.1	(5.000)150	(3.000)580	(1.000) 2	(-1.000)330	
7015002	FCO3APATITE	0.0	(9.496)150	(0.360)500	(0.144)460	(4.800)580	
			(1.200)140	(2.480)270			
7028100	STRENGITE	-12.3	(1.000)281	(1.000)580	(2.000) 2		

APPENDIX G Point Source Phosphorus Loadings

The results of the point source phosphorus loadings in the Umgeni catchment are shown in **Table G1**.

Catchment and	Description	Average	Average	SRP	Total
River or stream system		flow	SRP	loading	loading
		10 ³ m ³ .d ⁻¹	µg.ℓ ⁻¹	tonnes.a ⁻¹	tonnes.a ⁻¹
Midmar					
Umthinzima-Umgeni	Mpophomeni ¹	0.927	3595	1.094	1.09
Albert Falls					
Unnamed stream-Umgeni	Howick Mid Hosp	0.160	4533	0.265	
Umgeni	Howick WWW	0.447	3360	0.549	
Umgeni	Sarmcol 1	5.184	272	0.515	
umgeni	Sarmcol 2	5.184	1107	2.095	
Umgeni	Mountain Home	0.005	6080	0.011	
Umgeni	Midmar	0.222	6108	0.495	
Rietspruit-Umgeni	Cedara	0.800	316	0.092	
Bush adjacent school	Ladsworth	0.010	2579	0.009	
Unnamed stream	Hilton College	0.075	5435	0.148	
Umgeni	Golden Pond	0.007	398	0.001	4.18
Nagle					
Cramond-Umgeni	Albert Falls 2	0.029	3329	0.036	
Mhalane-Mpolweni-Umgeni	Cool Air WWW	0.391	3476	0.495	0.55
Inanda					
Mngeweni-Umgeni	Cato Ridge	1.541	829	0.466	
Umsunduzi-Umgeni	Darvill treated effluent ²	50.09	852	14.99	
Umsunduzi-Umgeni	Darvill overflow ²	20.25	1053	7.70	
Mshwati-Umsunduzi-Umgeni	Feralloys	0.008	987	0.003	
Mshwati-Umsunduzi-Umgeni	Camperdown	0.059	3896	0.083	
Umsunduzi-Umgeni	Sefontein Prison New	1.020	2761	1.028	
Mpushini-Umsunduzi-Umgeni	Lynnfield Park	0.100	3713	0.136	
Mngeweni-Umgeni	Enthembeni Hospital	0.180	7434	0.488	24.9

Table G1:	Annual	point source	phos	phorus	loadings	in	the	Umaeni	catchmen	t
	/		prico	priorus	louunigo			omgon	outormon	ι.

1 Estimated from daily flow and weekly concentration data

2 Estimated from daily flow and daily concentration data (see Appendix C)

APPENDIX H Phosphorus Loadings on Impoundments

Soluble phosphorus loadings on the Midmar, Albert Falls, Nagle and Inanda impoundments are shown in **Tables H1.1 to H1.4**. Seasonal and annual loadings are given together with the corresponding flow and concentration data.

Table	H1.1:	Seasonal	and	annual	flow	volumes,	phosphorus	concentrations	and
phosph	norus lo	adings on t	he Mi	dmar imp	bound	ment for O	ctober 1990 to	September 199	1.

Sito	Saaaan	Flow	Flow Weighted	SRP Loading
Sile	Season	10 ⁶ m ³	Concentration	tonnes
			μg.ℓ -1	
Umgeni Inflow	October-December	33.81	9.6	0.325
	January-March	174.44	13.1	2.291
	April-June	24.43	6.4	0.155
	July-September	9.40	4.5	0.418
	Annual	242.08	11.6	2.813
KwaGqishi Inflow	October-December	1.20	26.8	0.032
	January-March	5.16	18.4	0.095
	April-June	1.23	7.9	0.010
	July-September	0.53	8.0	0.004
	Annual	8.12	17.4	0.141
Nauku Inflow	October-December	0.52	13.6	0.007
	January-March	2 12	6.4	0.014
	April-June	0.36	5.3	0.002
	July-September	0.16	8.0	0.001
	Annual	3.16	7.5	0.024
Umthinzima Inflow	October-December	0.56	301.6	0.170
	January-March	2.65	125.9	0.334
	April-June	0.24	251.0	0.062
	July-September	0.13	614.8	0.082
	Annual	3.59	180.2	0.647
Direct Inflore	Ostakan Daasakan	4.04		0.010
Direct inflow	October-December	1.81	9.8	0.018
		9.19	25.4	0.233
	April-June	1.26	5.2	0.007
	July-September	0.63	3.5	0.002
	Annual	12.9	20.1	0.260
Total soluble phospho	brus loading on impound	dment	I	3.89

 Table H1.2:
 Seasonal and annual flow volumes, phosphorus concentrations and phosphorus loadings on the Albert Falls impoundment for October 1990 to September 1991.

0:4-	0	Flow	Flow Weighted	SRP Loading
Site	Season	10 ⁶ m ³	Concentration	tonnes
			μg.ℓ -1	
Umgeni Inflow	October-December	43.79	5.1	0.226
	January-March	292.29	6.6	1.917
	April-June	39.60	3.0	0.117
	July-September	23.27	4.6	0.107
	Annual	398.95	5.9	2.366
Nculwane Inflow	October-December	1.27	3.0	0.004
	January-March	6.41	4.5	0.029
	April-June	0.15	4.1	0.001
	July-September	0.03	6.8	0.000
	Annual	7.86	4.2	0.033
Doringspruit Inflow	October-December	0.45	7.2	0.003
	January-March	2.96	43.2	0.128
	April-June	0.10	5.2	0.001
	July-September	0.00	6.0	0.000
	Annual	3.51	37.5	0.132
Direct Inflow	October-December	1.12	2.1	0.002
	January-March	10.16	3.2	0.033
	April-June	1.14	2.0	0.002
	July-September	0.31	1.9	0.001
	Annual	12.73	3.0	0.038
Total soluble phospho	orus loading on impound	ment		2.569

Table H1.3: Seasonal and annual flow volumes, phosphorus concentrations and phosphorus loadings on the Nagle impoundment for October 1990 to September 1991.

Site	Season	Flow 10 ⁶ m ³	Flow Weighted Concentration	SRP Loading tonnes
Umgeni Weir above Inflow	October-December	62.62	3.9	0.243
	April-June	64.90	5.6	0.364
	July-September	50.84	8.5	0.434
	Annual	463.53	6.7	3.095
Umgeni Inflow	October-December	52.99	2.5	0.132
	January-March	45.73	6.2	0.286
	April-June	41.84	3.6	0.152
	July-September	35.74	7.7	0.276
	Annual	176.31	4.8	0.845
Total soluble phosphorus load	ling on impoundment			0.845

Appendix H

		Flow	Flow Weighted	SRP Loading
Site	Season	10^{6} m^{3}	Concentration	tonnes
			ug. ℓ -1	
Umaeni Inflow	October-December	70.42	71.1	5.005
	January-March	424.64	27.1	11.513
	April-June	72.70	24.2	1.763
	July-September	28.33	58.5	1.658
	Annual	596.09	33.4	19.938
Mshazi Inflow	October-December	1.98	21.5	0.042
	January-March	1.73	26.5	0.046
	April-June	0.28	14.3	0.004
	July-September	0.13	8.8	0.001
	Annual	4.13	22.5	0.093
Imbozamo Inflow	October-December	0.18	28.2	0.005
	January-March	0.14	23.3	0.003
	April-June	0.01	26.3	0.000
	July-September	0.00	26.0	0.000
	Annual	0.33	26.0	0.009
Kwanyuswa Inflow	October-December	0.07	31.8	0.002
rtwariyuswa mnow	January-March	0.06	27.0	0.002
	April-June	0.00	25.4	0.000
	July-September	0.00	25.3	0.000
	Annual	0.14	29.2	0.004
Mtata Inflow	October-December	0.18	13.6	0.002
	January-March	0.13	12.9	0.002
	April-June	0.01	9.9	0.000
	July-September	0.00	13.7	0.000
	Annual	0.31	13.2	0.004
KwaNgcolosi Inflow	October-December	0.03	10.3	0.000
	January-March	0.03	15.8	0.001
	April-June	0.00	18.8	0.000
	July-September	0.00	14.3	0.000
	Annual	0.07	13.3	0.001
Direct Inflow	October-December	3 20	40.6	0 130
	January-March	3.07	32.6	0.100
	April-June	0.26	12.5	0.003
	July-September	0.11	9.8	0.001
	Annual	6.64	35.2	0.234
I otal soluble phospho	orus loading on impoundr	nent		20.05

Table H1.4: Seasonal and annual flow volumes, phosphorus concentrations and phosphorus loadings on the Inanda impoundment for October 1990 to September 1991.