DETERGENT PHOSPHORUS IN SOUTH AFRICA: IMPACT ON EUTROPHICATION WITH SPECIFIC REFERENCE TO THE MGENI CATCHMENT

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EXECUTIVE SUMMARY

In 1986, Heynike & Wiechers of the Water Research Commission (WRC) assessed the contribution made by detergent phosphorus to wastewater phosphorus discharges in South Africa and its impact on eutrophication. Their study showed that detergents comprised between 35 and 50 % of the total wastewater phosphorus load and thus presented a significant source of phosphorus to the environment, but the costs associated with eliminating or banning detergent phosphorus outweighed the benefits. The authors indicated that there was lack of suitable data for the study and several assumptions had to be made. They therefore recommended that the WRC continue to keep a watching brief on the situation, while the South African detergent industry investigates and tests cost effective substitutes for phosphate builders.

Towards the latter part of 1990, Lever Brothers (Pty.) Ltd. (Lever) approached the University of Natal, Pollution Research Group (PRG) and the University of Cape Town to discuss sponsoring an investigation into the effect of substitute detergent builders on wastewater treatment. This study was given the go ahead and commenced at UCT in 1991 as a Masters research project. Following this, a meeting was held in 1991, with representatives of the WRC, Lever, the PRG and Umgeni Water where it was agreed that the Pollution Research Group in collaboration with Umgeni Water would undertake a WRC funded study which updated the 1986 Heynike & Wiechers study. The latter investigation commenced in 1992, with the principal researcher stationed at Umgeni Water in Pietermaritzburg.

The Mgeni catchment was chosen as the study area because 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. It was also an important catchment in that it constituted a major developmental region in South Africa and served the water needs of major urban centres, notably, Pietermaritzburg and Durban, and several surrounding small towns and rural areas.

The topic of detergent phosphorus and its contribution to eutrophication, i.e. nutrient enrichment, is also particularly relevant to South Africa where many impoundments have become eutrophic or are threatened by eutrophication. Walmsley & Thorton investigated the trophic status of 31 major impoundments in South Africa In 1982, and reported that 9 were eutrophic and 13 bordering on eutrophication.

The major consequence of eutrophication is prolific growth of algae or certain rooted macrophytes, which may result in severe water quality problems, including, unpleasant tastes and odours, deoxygenation and fish kills. 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. Eutrophication may be controlled by the reduction of the nutrient discharges to the environment. Phosphorus, in particular is often singled out for reduction, as it is frequently the growth-limiting nutrient for aquatic plants.

Phosphorus sources include point discharges such as domestic and industrial wastewaters and diffuse sources such as agricultural wastes and fertilizers. In detergents, phosphorus serves as a builder that works in synergy with the surfactant to perform the cleaning function. Phosphorus arising from detergent consumption is usually in the form of orthophosphate - the bio available phosphorus form, and is therefore an attractive 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 to impoundments. Should this be the case in the Mgeni catchment, elimination of detergent phosphorus could contribute significantly to improving water quality in impoundments.

Over the years following the Heynike and Wiechers [1986] study, additional data and information have become available, including more detailed water quality and land use data, as well as better data and information on the costs and implications of treating water drawn from eutrophic impoundments. In addition, the number of eutrophic impoundments appears to have increased. The Nagle impoundment on the Mgeni system, previously classified as oligotrophic by Walmsley & Thornton [1982] has since 1989 displayed recurring blooms of *Cyanophycae* (or blue-green algae), resulting in severe water treatment problems [Umgeni Water, 1994]. In the light of these developments, the contribution of detergent phosphorus to eutrophication of water bodies has been re-examined in the Mgeni catchment.

The main study objectives were to assess the contribution of detergent phosphorus to eutrophication in the Mgeni system and determine the economic and water quality consequences of eliminating detergent phosphorus plus provide a methodology that could be used for studies in other catchments.

The area of study **(Figure 1.1)** - extended from the headwaters of the Mgeni river at the foothills of the Drakensberg mountains, to the Mgeni river outflow from the Inanda impoundment and comprised 4 078 km^2 of catchment area. This catchment lies in the summer rainfall region of South Africa and receives 800 to 1 200 mm of rainfall per annum. Four major impoundments, namely, the Midmar, Albert Falls, Nagle and Inanda impoundments are fed by this catchment and 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 Mgeni system.

Land use practices in the upper subcatchments (Midmar, Albert Falls and Nagle) are 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 drains the city of Pietermaritzburg with an urban population of approximately 275 000 people (1991 Census) as well as surrounding industrial, rural and informal areas.

Various point sources of phosphates are located throughout the Mgeni 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 the most impacted in this system owing to the nature and extent of the land use practices.

Data for the study were assimilated over the period 1990 to 1994. The assessment of detergent usage was undertaken for the October 1990 to September 1991 period, using population data from the 1991 census, while the development of phosphorus-eutrophication models and assessment of the impact of detergent phosphorus elimination on water quality utilised data collected over the four year period from February 1990 to January 1994.

Various investigations were undertaken to satisfy the identified objectives, including, calculation of the phosphorus loadings arising from urban and rural detergent usages; quantification of total and detergent phosphorus loading contributions to the four major impoundments in the Mgeni catchment; development of a predictive equation for the Inanda impoundment relating phosphorus loading to algal production and using it to determine the impact of detergent phosphorus elimination on algal production; investigation of the fate of phosphorus compounds in an impoundments, using the MINTEQA2 geochemical equilibrium speciation model; and a cost-benefit assessment of detergent reformulation.

The rural and urban per capita detergent consumptions formed the basis for all detergent phosphorus loading calculations and were estimated to be 1.63 kg per capita per annum and 3.53 kg per capita per annum, respectively. The rural population therefore used less than half as much detergent as the urban population.

The rural population in the Mgeni catchment of 610 000 people, was found to be twice the urban population of 304 000 people, but the overall detergent phosphorus loading from rural areas was still slightly lower than that from urban areas. A factor of 16 % was taken as the percentage of the rural population that washed laundry directly at a river or stream, obtained from a survey of washing practices undertaken by Lever in KwaZulu-Natal.

The Inanda sub-catchment with the largest urban and rural populations had the largest detergent phosphorus contributions to the environment. The urban area in the Inanda catchment yielded 9.2 tonnes detergent phosphorus per annum, compared with 0.3 to 2.1 tonnes per annum for the 3 upstream catchments (Midmar, Nagle and Albert Falls), while rural areas yielded 8.4 tonnes per annum, compared with a range of 0.3 to 1.4 tonnes per annum for the upstream catchments.

The proportion of detergent phosphorus relative to the total phosphorus loading was 51 % from urban areas in the upper catchments but 37 % in the Inanda catchment where industries in the Pietermaritzburg area comprised approximately 30 % of the phosphorus loading.

At the dam inflow sites, for the study period October 1990 to September 1991, 20.9 tonnes of soluble phosphorus were measured at the Mgeni inflow to the Inanda impoundment compared with only 2.8 to 3.6 tonnes at the 3 upstream impoundments inflow sites.

In the absence of detailed in-stream modelling of phosphorus, three scenarios were considered for estimating the total soluble phosphorus loading from the catchment:- 1)The only sources of soluble phosphorus were wastewater effluents and detergents that entered from rural laundering undertaken directly at the water course; 2) In addition to the above loadings, non point sources (e.g. agriculture, informal settlements) contributed 20 % to the catchment soluble phosphorus loading; and 3) Non point sources contributed 50 % to the catchment soluble phosphorus loading. These showed detergents to comprise 53, 42 and 26 % of the SRP loading to the Inanda dam, respectively.

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 indicated a very good relationship, which could be used in future by Umgeni Water for predicting algal production in the 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 reduction scenario of 53 % (scenario 1), the algal count was estimated 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 little phosphorus remaining in solution 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 bio availability 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 biological 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 for less than 10% of the time in the impoundment.

Low redox conditions did not favour resolubilisation of precipitated phosphorus. Modelling 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 modelling 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. Using the equilibrium results predicted by MINTEQA2 together with the results of on-site monitoring provides improved 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 modelling results serve to support this by suggesting that phosphorus entering the impoundment, if not taken up rapidly, is lost from solution and 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 could not benefit simultaneously from detergent phosphorus elimination. In addition, reformulating detergents may or may not accelerate deterioration of washing fabrics and washing machines. These factors led to four cost-benefit analyses, the results of which were all in favour of not eliminating detergent phosphorus.

The best option for the detergent manufacturer, 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 least favourable option for the detergent manufacturer, which took into consideration: the increased cost to consumers as a resulting of reformulating with a zeolite builder, and savings at the Darvill WWW as a result of a reduced influent phosphorus loading, was still 2 to 1 in favour of not reformulating detergents.

The literature has suggested that phosphate-free detergents have been formulated to give performance equalling that of phosphate detergents and certain reformulations would not result in extra wear and tear on fabrics and washing machines. If this were the case in South Africa, then the cost-benefit analysis models 1 and 2 which only consider wastewater treatment and water treatment costs, would be the more likely forecasts. The results of these two cost-benefit analyses show that the cost of treating the consequences of eutrophication is less than reducing the phosphorus loading at wastewater works. This finding may however be specific to the Inanda catchment where significant river losses occur between the discharge points and the impoundment for most of the year. In addition, the phosphorus loading enters the impoundment approximately 16 river kilometers away from the point of abstraction for water treatment and the water treatment abstraction site, resulting in significant further improvement in water quality. The scope of this project, precluded estimates of the costs of environmental and recreational losses associated with eutrophication, which would need more rigorous economic modelling.

In summary, the results of the assessment of the detergent phosphorus contribution to eutrophication and the economic and water quality consequences of eliminating detergent phosphorus indicated that detergents made a significant contribution to the phosphorus loading on the environment, however, the costs of eliminating detergent phosphorus outweighed the benefits.

For the Inanda system, the cost of treating nuisance algae was 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 and assimilative capacity of the impoundment, the methodology should be applied to an impoundment where the phosphorus discharge points are closer to the impoundment and water treatment abstraction site. In such a situation fewer river losses would occur and the loading may have a greater impact on algal production and therefore treatment costs.

Alternately a study of the transport and fate of phosphorus in river systems may better help quantify movement of the constituent from point and non-point sources into bulk supply impoundments.

It is difficult to put a cost to losses to users other than domestic, which would arise from eutrophication. Methods of quantifying these losses should therefore be developed, as they may be critical components of the cost-benefit equation.

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 that 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 (e.g. agriculture, informal settlements) could contribute to the soluble/bio available phosphorus loading, especially during periods of high runoff when particulate phosphates may resolubilise. Monitoring programmes that improve quantification of these inputs and their contributions to the catchment phosphorus budget would provide information to decide on the more cost-effective catchment management intervention.

This project successfully met the stated objectives. The contribution of detergent phosphorus to eutrophication in the Mgeni catchment was determined by quantification of rural, industrial and domestic phosphorus loadings. In addition, the relationship between soluble phosphorus loading and algal count was determined for the Inanda impoundment. The economic and water quality consequences of eliminating detergent phosphorus was determined incorporating the results of the relationship between phosphorus loading and algal count into cost-benefit analysis procedures. The project has also provided a simple methodology that can be extrapolated to other catchments where further eutrophication control measures need to be considered.

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The Steering Committee responsible for this project, consisted of the following persons:

Dr O O Hart	Water Research Commission
Mr H F Furness	Umgeni Water
Mr R J J Egenes	University of Natal
Mr A Gialerakis	University of Natal (alternate)
Mr S H Palmer	Lever Brothers
Mr G Bradfield	Lever Brothers (alternate)

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- The Computing Centre for Water Research, for the use of the mainframe computer, access to the Agricultural Catchments Research Unit (*ACRU*) modeling software, access to hydrological and meteorological data and for software support;
- The Department of Agricultural Engineering, University of Natal for making recommendations for execution of the *ACRU* hydrological model.

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1 INTRODUCTION

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Objectives

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

Study area

The area of study **(Figure 1.1)** - extended from the headwaters of the Mgeni river at the foothills of the Drakensberg mountains, to the Mgeni river outflow from the Inanda impoundment and comprised 4 078 km^2 of catchment area. This catchment lies in the summer rainfall region of South Africa and receives 800 to 1 200 mm of rainfall per annum. Four major impoundments, namely, the Midmar, Albert Falls, Nagle and Inanda impoundments are fed by this catchment and 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 Mgeni system.

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Various point sources of phosphates are located throughout the Mgeni catchment, the largest being the Darvill Wastewater Works, in the Inanda subcatchment, serving the greater Pietermaritzburg area. Water quality in the Inanda impoundment is thus expected to be the affected the most in this system owing to the nature and extent of the land use practices.

Time Period

Data for the study were assimilated over the period 1990 to 1994. The assessment of detergent usage was undertaken for the October 1990 to September 1991 period, using population data from the 1991 census, while the development of phosphorus-eutrophication models and assessment of the impact of detergent phosphorus elimination on water quality utilised data collected over the four year period from February 1990 to January 1994.

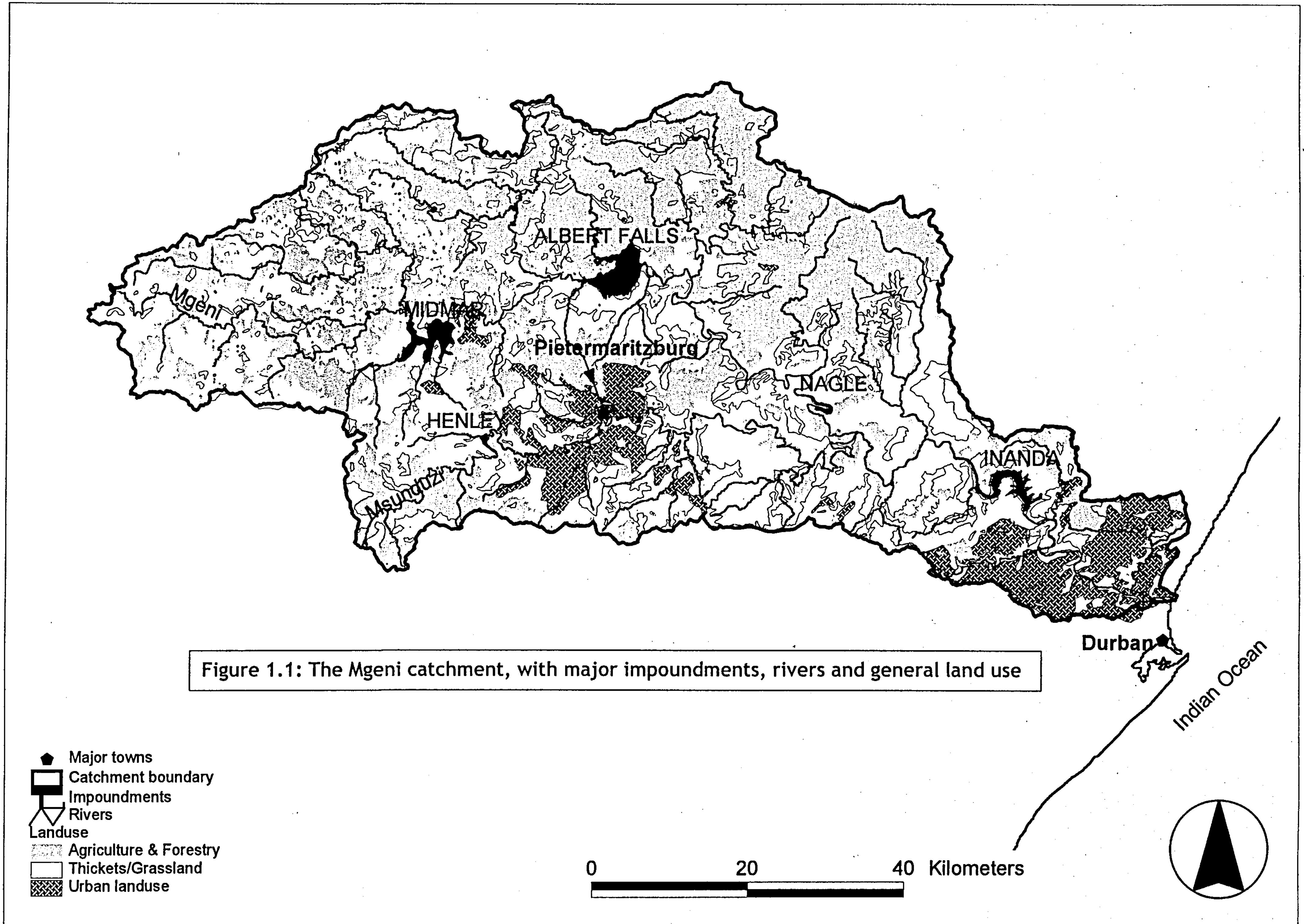


Figure 1.1: The Mgeni catchment, with major impoundments, rivers and general land use

2 LITERATURE SURVEY (Synopsis)

The literature review focused on three topics, 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 reformulation on water quality. The detailed review is contained in **Appendix 1.**

3 METHODS

The calculations undertaken to assess the contribution of detergent phosphorus to eutrophication and determine the economic and water quality consequences of eliminating detergent phosphorus, included:

3.1 The catchment phosphorus loading due to detergent usage, for urban and rural areas;

3.2 Quantification of phosphorus loadings to the four major impoundments in the Mgeni catchment and the percentage contribution by detergents;

3.3 Development of a predictive equation relating phosphorus loading to algal production in a major impoundment and using it to determine the impact of detergent phosphorus elimination;

3.4 Investigation of the fate of phosphorus compounds in an impoundment, using the MINTEQA2 geochemical equilibrium speciation model; and

3.5 A cost-benefit assessment of detergent reformulation.

4 RESULTS AND DISCUSSION

4.1 Catchment phosphorus loading due to detergent usage in urban and rural areas

- RURAL AND URBAN PER CAPITA DETERGENT CONSUMPTION

Lever Brothers (Pty.) Ltd. (*Lever Bros.*) carried out a market survey of washing practices in both rural and urban areas in KwaZulu-Natal in 1988, which provided data to estimate the per capita detergent consumption for both rural and urban areas.

The survey collected information on the mass of product dosed per wash load, the number of wash loads per day, the number of people in the household and other relevant details shown in Table 4.1.

Table 4.1: 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 grams.	104	111	128	79	70
Number in survey doing one or more washes.	124	19	4	61	1
Average mass of product per washday, in grams.	105.6			78.9	
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	Had 1 to 4 persons		27	Had 1 to 4 persons
	178	Had 5 to 8 persons		85	Had 5 to 8 persons
	92	Had 9+ persons		41	Had 9+ persons
Average number of persons per family surveyed.	6.8			6.5	

Based on the above data the per capita detergent consumption was calculated as: -
Rural per capita detergent consumption: **1.63 kg detergent/person/annum.**
Urban per capita detergent consumption: **3.53 kg detergent/person/annum.**

- PHOSPHATE CONTENT OF SOUTH AFRICAN LAUNDRY DETERGENTS

To relate detergent consumption to phosphorus consumption, the phosphorus content of detergents was calculated using data on percentage phosphate builder - tripolyphosphate (STPP) in the various products and detergent sales (shown in Table 4.2).

Table 4.2: Sodium-tripolyphosphate (STPP) content and fraction of sales of laundry detergent products in KwaZulu-Natal in 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

The average phosphorus content of detergents was calculated to be 6.5 % as P, and the annual per capita detergent phosphorus consumption was thus: -
Rural areas: **0.106 kg P /person/annum.**
Urban areas: **0.229 kg P /person/annum.**

- RURAL AND URBAN POPULATION

Population data for the Mgeni catchment were obtained from the Institute of Natural Resources and the 1991 census data for the region. The rural population was obtained by overlaying the subcatchment boundaries in the area of study onto the ESD boundaries. The data sets for the Mgeni catchment are shown in **Appendix 2** and summarised in Table 4.3.

Population data were combined with the per capita detergent phosphorus consumption to give the detergent phosphorus loadings for urban and rural areas shown in **Table 4.3.** The fractions discharged to the watercourse were calculated as shown in the next section on 'pathway of detergent phosphorus to the environment'.

Table 4.3: Rural and urban population and detergent loading per subcatchment (tonnes/annum)

Subcatchment	Population		Detergent P Loading			
			Rural Load		Urban Load	
	Rural	Urban	Total	Discharge to Watercourse (Table 4.4)	Urban	Discharge to Watercourse (Table 4.5)
Midmar	16 678	16 370	1.8	0.28	3.8	0.56
Albert Falls	16 514	10 624	1.7	0.28	2.4	2.1
Nagle	82 493	2 007	8.7	1.4	0.5	0.28
Inanda	494 786	274 848	52.4	8.4	63.1	9.2

- PATHWAY OF DETERGENT PHOSPHORUS TO THE ENVIRONMENT

Rural and urban wastewaters have separate pathways to the environment. Urban wastes are treated and discharged via wastewater works, while a portion of rural wastewaters enter the watercourse directly and others never get there.

Rural detergent load

Data on washing practices in rural areas were obtained from a survey undertaken by *Lever Bros* in KwaZulu-Natal **(Table 4.4)**. The survey indicated that 16 % of the rural population washed laundry directly at a watercourse. This was therefore taken as the percentage load discharged to the water environment. Revised rural detergent loadings are shown in **Table 4.3**.

Table 4.4: Washing practices in rural areas [Lever Brothers (Pty.) Ltd., 1993]

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

Urban detergent load

The major sources of _soluble phosphorus_ in wastewater influents were detergents, urine and industrial discharges - shown in **Table 4.5.**

The phosphorus loading from urine was obtained using population data and the per capita phosphorus content of urine obtained from the literature (600 mg/person/day or 0.219 kg/person/annum [Machlin, 1973]). The industrial phosphorus loading was quantified using data from the Umgeni Water routine trade effluent monitoring programme **(Appendix 3)**.

The percentage detergent phosphorus calculated for the influent was applied to the effluent loadings to estimate the detergent phosphorus loading on the environment via wastewater works. Details of point source loadings are shown in **Table 4.6.**

Table 4.5: Urban wastewater _influent and effluent_ SRP phosphorus loadings due to detergents, urine and industrial discharges (1990/1991). (Load in tonnes per annum).

Subcatchment	Urban Population (Table 4.3)	Urban detergents (Table 4.3)	Urine	Industry	Total WWW Influent	% detergent P	Total WWW Effluent (Table 4.6)	Urban detergent P to environment
Midmar	16 370	3.8	3.6	0	7.3	51	1.1	0.56
Albert Falls	10 624	2.4	2.3	0	4.8	51	4.2	2.1
Nagle	2 007	0.5	0.4	0	0.9	51	0.55	0.28
Inanda	274 848	63.1	60.2	47.9	171.1	37	24.9	9.2

Point source (wastewater) loadings
Information and water quality data were obtained from the Umgeni Water routine monitoring programme.

For the Darvill Wastewater Works (the largest point source in the catchment area), 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 (See **Appendix 4**).

Catchment and point sources	SRP load Tonnes/a
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

4.2 Phosphorus loadings to impoundments and percentage due to detergents

The phosphorus loadings to the four impoundments in the Mgeni system were quantified by combining inflow volumes and phosphorus concentrations using the Flux Model developed by Walker [1987] Flow data were acquired from the Department of Water Affairs and Forestry, or calculated using the ACRU hydrological model. (**Appendices 5 and 6** have details of ACRU modelling and Flux model, respectively).

Details of flow and loading are shown in Table 4.7.

Results show that the SRP loading to Inanda dam is highly significant.

- PERCENTAGE DETERGENT PHOSPHORUS IN THE SRP LOADING TO THE DAM.

The total catchment (urban & rural) detergent phosphorus loading is shown in Table 4.8 for each of the four impoundments.

To provide estimates of the contribution of detergent phosphorus to SRP loads at dam inflows, three scenarios were considered to take into account other sources of SRP. The three models are shown in Tables 4.9 to 4.11.

As an example, for the Inanda dam, detergents comprise 53 %, 42 % and 26% of the bio available phosphorus load to the dam for scenarios 1, 2 and 3 respectively.

Table 4.7: Phosphorus loadings at river inflows to the four major impoundments in the Mgeni system.

Site	Flow $10^6.m^3$	Loadings Tonnes/annum
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: Total detergent phosphorus loading, arising from urban and rural laundering.

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

Table 4.9: Proportion of dam SRP load due to detergents. **Scenario 1**: Two catchment sources of SRP, namely, wastewater point source effluents (which included urban detergents) and rural detergents (non-point source) would contribute to the dam inflow load.

Subcatchment	Two Sources of catchment SRP			Total Detergents	%
	Point (Table 4.3)	Rural detergent (Table 4.3)	**Total**	(Table 4.8)	**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 4.10: Proportion of dam SRP load due to detergents. **Scenario 2:** Three catchment sources of SRP, namely, wastewater point source effluents, rural detergents, & a further 20 % SRP from other non-point sources (e.g. agriculture, informal settlement) would contribute to the dam inflow load.

Subcatchment	Three Sources of catchment SRP				Total Detergents	%
	Point (Table 4.3)	Rural detergent (Table 4.3)	20% non-point	**Total**	(Table 4.8)	**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

Table 4.11: Proportion of dam SRP load due to detergents. **Scenario 2:** Three catchment sources of SRP, namely, wastewater point source effluents, rural detergents, & a further 50 % SRP from other non-point sources (e.g. agriculture, informal settlement) would contribute to the dam inflow load.

Subcatchment	Three Sources of catchment SRP				Total Detergents	%
	Point (Table 4.3)	Rural detergent (Table 4.3)	50% non-point	**Total**	(Table 4.8)	**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

4.3 Relationship between soluble phosphorus loading and algal count

Analysis of seasonal variations in algal genera and chlorophyll *a* measurements, indicated that chlorophyll *a* was not appropriate to use in developing the relationship, as different genera had different chlorophyll *a* concentrations. Thus, the total algal count in the impoundment was preferentially modelled with the soluble phosphorus loading to 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 *data* over an eight week period (i.e. two consecutive months). Four years of data were used (weekly measurements) and the SRP loading was shifted forward by one month to compensate for an observed lag between P loading and algal growth. (This may be attributed to the 16 km distance between the P loading, which was measured at the river inflow to the dam, and the algal count, which was measured at the water works abstraction near the dam wall.

A good correlation (r = 0.79) existed between algal count and SRP loading but was significantly improved (r = 0.91) by deleting a single outlier.

Soluble phosphorus-loading/algal growth equation for predicting the algal count in the Inanda main basin.

$$\text{Log (Algal Count)} = 1.83 \text{ Log (SRP loading)} - 1.26 \qquad ...4.1$$

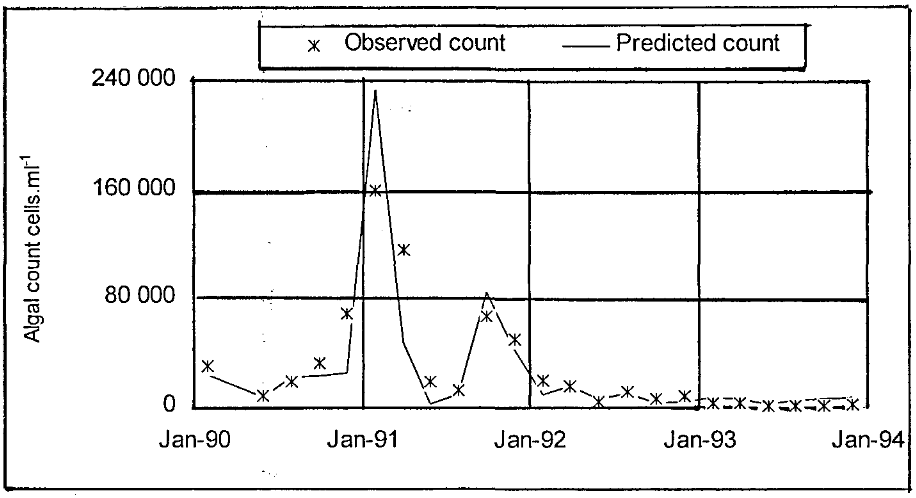
$$\text{or} \quad \textbf{Algal Count} = \textbf{0.055 SRP Loading}^{\mathbf{1.83}} \qquad ...4.2$$

Where *SRP Loading* = *average SRP loading at the river inflow to the impoundment over two consecutive months, in kilograms per month*

Algal Count = *Predicted average count one month after the SRP loading*

A plot of observed and predicted algal count is shown in **Figure 4.1**.

Figure 4.1: Plot of observed and predicted algal count for the Inanda main basin.



- IMPACT OF DETERGENT PHOSPHORUS ELIMINATION ON ALGAL GROWTH

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 to algal growth, the measured loading on the impoundment was sequentially reduced by these percentages and the resulting algal count predicted using the equation developed.

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 %.

4.4 Phosphorus speciation

Investigation of phosphorus speciation using the MINTEQA2 model was an added exercise undertaken to assess the fate of phosphorus compounds 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. (See Literature review - **Appendix 1** - for more information).

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 modelling 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 modelling was accomplished by investigating soluble complex formation and precipitation to determine their relative contributions to the phosphorus speciation, then assessing the effect of adsorption processes on the species distribution using the MINTEQA2 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. 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.

Amorphous iron oxide surfaces were assumed to be present at a solids concentration of 3.422 g/ℓ and with an amorphous iron concentration of 0.721 mg/g. 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. 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 (**Appendix 1**).

Desorption could not be modelled directly with the Diffuse Layer Model and the MINTEQA2 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 modelling.

Initial MINTEQA2 runs indicated that the water was over saturated 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 modelling 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 total carbonate concentration was calculated from an alkalinity value, taking account of the carbonate speciation. Total phosphorus includes soluble orthophosphate and particulate phosphate.

- SPECIES DISTRIBUTION BETWEEN DISSOLVED AND PRECIPITATED PHASES

Modelling 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 %). (Detail in Appendix 7).

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 bioavailability of phosphate in the Inanda impoundment.

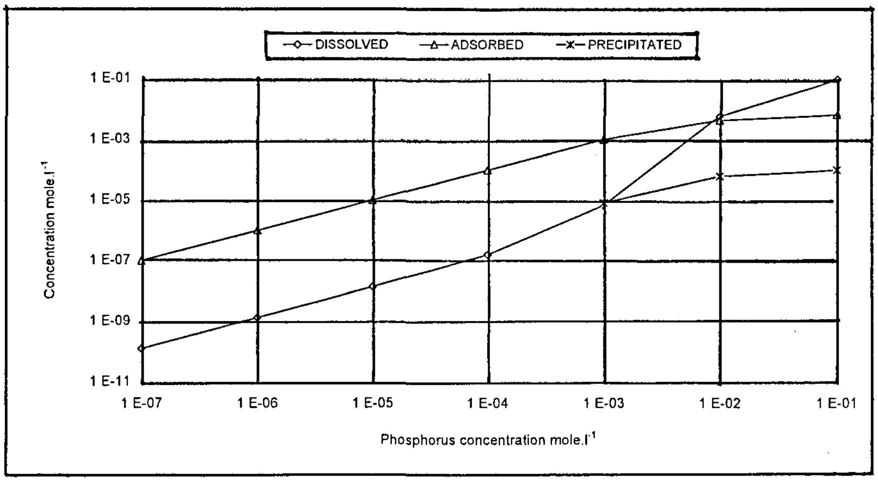
Table 4.11: Equilibrium composition showing the mass distribution between dissolved and precipitated phases in the Inanda impoundment in December 1990, at a site close to the Mgeni river inflow.

% Distribution between dissolved and precipitated phases	Dominant species	% Species composition
Dissolved 0.7%	HPO_4^{2-} $MgHPO_4$ (aq) $MgPO_4^-$ $CaHPO_4$ (aq) $CaPO_4^-$ $H_2PO_4^-$	72.6 8.4 4.5 6.2 3.3 4.8
Precipitated		
99.3%	Fluorapatite	100

- THE IMPACT OF PHOSPHATE ADSORPTION ON THE DISTRIBUTION OF PHOSPHATE SPECIES

Figure 4.2 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 or 940 mg/ℓ), 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 4.2: Phosphorus species distribution between dissolved, adsorbed and precipitated phases at varying phosphorus concentration.

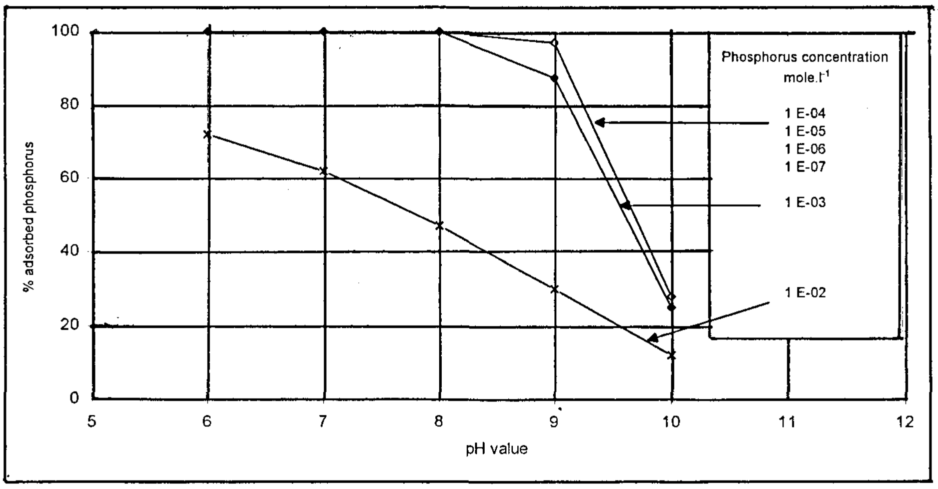


- pH AND REDOX ON PHOSPHATE DESORPTION FROM AN IRON HYDROXIDE SURFACE

Apart from high total concentrations (94 to 940 mg/ℓ) 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. 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. (Figure 4.3).

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 Fe^{2+} ion or ionic complex. Effectively these modelling 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 4.3: Percent adsorbed species versus pH value for varying phosphorus concentrations.



4.5 Cost-benefit analysis of detergent phosphorus elimination

- 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 Mgeni catchment using the per capita detergent consumption values (kg per capita) and the total population in the catchment.

Lever Bros estimated that reformulating phosphate built detergents with zeolite A (the most popular substitute) would result in 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 was R 551 100 and was calculated from the per capita detergent consumption (for urban and rural areas).

- COST SAVINGS AT WASTEWATER WORKS

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

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 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 at the time of the study was 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 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.

- 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 had no water treatment history with regard to costs at the time of the study. Water treatment costs were therefore predicted for the Inanda system 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.

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 R 230 000 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 was equivalent to 12 600 cells/mℓ. A 75 % reduction in count will result in 3 100 cells/mℓ requiring 12 000 kg carbon and resulting in a cost savings of R 190 000. A 42 % reduction will similarly result in a cost savings of R 104 000.

- THE COST OF REDUCED LIFE OF WASHING MACHINES AND FABRIC

Heynike & Wiechers [1986] reported that the lifetime 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 lifetime of washing machines and fabrics occurs when detergents are incorrectly formulated. Nevertheless these costs were estimated for a scenario in the current study by extrapolating the estimates made by Heynike & Wiechers.

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 x 10^6 per annum and R 62.5 x 10^6 per annum, respectively. After taking into account inflation, the corresponding values for the Mgeni catchment were estimated by multiplying these costs by the ratio of population in the Mgeni catchment to the population in South Africa.

- THE COST-BENEFIT OF DETERGENT REFORMULATION

A summary of the four cost-benefit scenarios are presented in Tables 4.13.

Table 4.13: Cost-benefit analysis (Cost in R/annum)

	Scenario 1		Scenario 2		Scenario 3		Scenario 4	
Cost Area	Cost	Benefit	Cost	Benefit	Cost	Benefit	Cost	Benefit
Increase to consumers as a result of eliminating detergent P	551 100		551 100		551 100		551 100	
Predicted Darvill WWW saving with half influent P loading and improved biological P removal.		260 000				260 000		
Reduced water treatment costs.				190 000				190 000
Loss in value of washing machines.					120 000		120 000	
Loss in value of fabrics.					6 000 000		6 000 000	
Totals	551 100	260 000	551 100	190 000	6 671 100	260 000	6 671 100	190 000
Cost-benefit ratio		**2:1**		**3:1**		**26:1**		**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).

However, 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 Discussion

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/person/annum for rural areas, and **3.53** kg/person/annum for urban areas. Rural dwellers were found to use half the quantity of detergent of urban dwellers.

The Inanda catchment has the largest rural population and therefore the greatest rural detergent phosphorus contribution to the environment. 8.4 tonnes/annum detergent phosphorus were estimated to be discharged to the Inanda catchment, compared with a range of 0.3 to 1.4 tonnes/annum 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 would be discharged to the Inanda catchment, compared with a range of 0.3 to 2.1 tonnes/annum 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 approximately 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 dam. 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.

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 indicated a very good model which although developed specifically for this project, could be used by Umgeni Water for predicting algal production in the Inanda impoundment on an operational basis, due to the lag effect between the phosphorus loading and the algal bloom manifestation.

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 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. Modelling 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 modelling 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 modelling is valuable for interpreting the relationships among constituents in the aquatic environment, consideration needs to be given to the fact that 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 modelling 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 could not benefit simultaneously from detergent phosphorus elimination. In addition, reformulating detergents may or may 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 had suggested that phosphate-free detergents have been formulated to give performance equalling that of phosphate detergents and certain reformulations would not result in extra wear and tear on fabrics and washing machines. 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 however still show that the cost of treating the consequences of eutrophication is cheaper than reducing the phosphorus loading at wastewater works. This finding may however be specific to the Inanda catchment where significant river losses occur 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, which would need more rigorous economic modelling.

5 CONCLUSIONS AND RECOMMENDATIONS

The contribution of detergent phosphorus to eutrophication and the economic and water quality consequences of eliminating detergent phosphorus were assessed in the Mgeni 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.

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 reduction scenario of 53 %, the algal count was predicted to reduce by 75 %.

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 that 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 equalling 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 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 (extra cellular 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 that 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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M Pillay, 1995. *Phosphorus-Loading/Algal-Production Regression Model for the Inanda Impoundment*. Presented at the Natural Resources Modelling conference in 1995, at UNP.

M Pillay, 1994. *Impact of Detergent Phosphorus on Eutrophication in South Africa with Specific Reference to the Mgeni catchment*. MScEng Thesis, Department of Chemical Engineering University of Natal.

M Pillay, Kerr, C, Buckley, CA and HD Furness, 1993. *Phosphorus Speciation in the Inanda Impoundment*. Presented at the Hydrological Symposium 1993, UNP.

M Pillay, Hudson, H, Furness, HD & CA Buckley, 1993. Detergent Phosphorus in South Africa: Impact on Eutrophication with Specific Reference to the Mgeni catchment. Presented at WISA 1993.

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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 that 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 Assessment	Life cycle assessment is a new and developing discipline that evaluates the environmental performance of products and processes on a *cradle to grave* basis.
Macrophyte	Large aquatic plants, macroscopic in size.
Non-point or Diffuse Source	Refers to the discharge of pollutants from distributed or dispersed sources, which enter the receiving water body *via* surface or subsurface flow and also atmospheric depositions.
Oligotrophic	A term applied to a water body that 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.

Appendix 1: Literature Survey

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.

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 $P_3O_{10}^{5-}$ used in detergents, 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].

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, dissolved organic compounds and 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.

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.
- Adsorption on surfaces and precipitation to form low solubility compounds. 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 by chemical and biological action to orthophosphates.

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 A1.1**

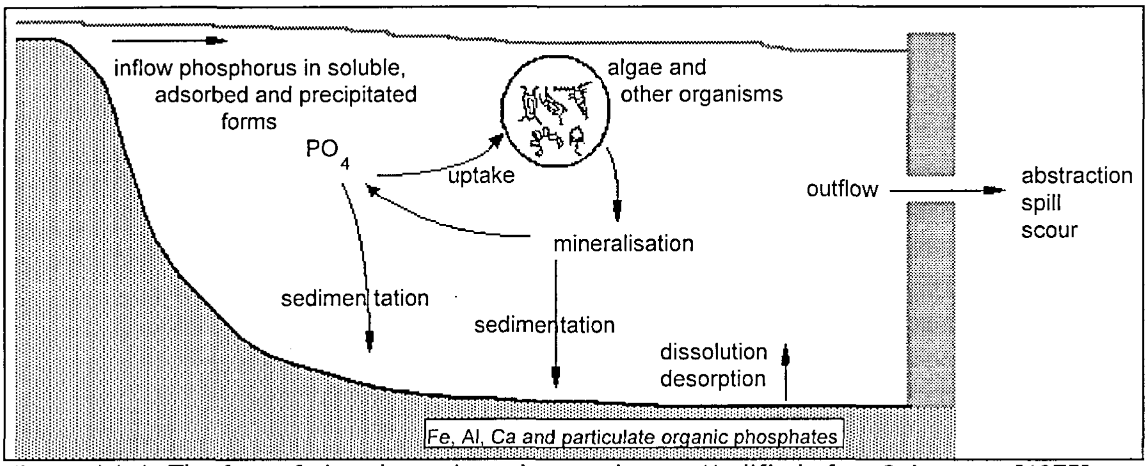


Figure A1.1: The fate of phosphorus in an impoundment. Modified after Golterman [1975], cited in Dallas & Day [1993].

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].

Precipitation, adsorption and sedimentation

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].

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 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.

Redox process, 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.

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, 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 may become significant once the sediments are saturated with phosphate.

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 would dominate over the formation of soluble complexes.

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, while a limiting effect occurred at phosphorus concentration below 0.09 mg/ℓ Mackenthun [1973].

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].

During mineralisation, orthophosphate is liberated from organic compounds by the enzymes and organic acids produced by micro-organisms [Ryding, 1985]. 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.

Eutrophication

Definition

"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]

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 that 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 that 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.

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) than needed for growth, while elements such as nitrogen and phosphorus are present in much smaller concentrations (microgram/ℓ) 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].

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].

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. 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.

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 (**Appendix 8**). 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 that *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.

Phosphorus removal at WWW
Phosphorus may be removed from WWWs by both chemical and biological processes. Biological phosphorus removal is widely used in South Africa and may be supplemented by chemical processes. Large wastewater works such as the Darvill WWW in the Mgeni catchment, employ the activated sludge process whereby phosphorus is stripped by micro-organisms. Phosphorus removal may also be achieved by using artificial reed-beds. Chemical phosphorus removal is achieved by addition of salts of iron or aluminium (usually iron or aluminium sulphate) that readily forms 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, 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].

History of Detergent Legislation and Formulation

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 (**Figure A1.2**). [Austin, 1984; United Nations, 1992].

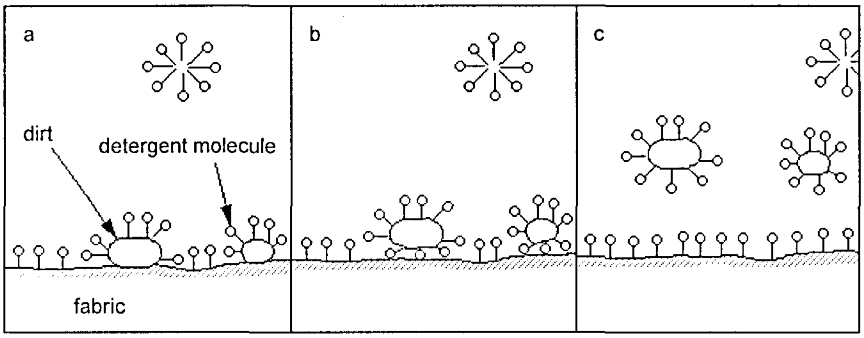


Figure A1.2: Illustration of the mechanism by which detergents remove dirt particles from the surface of fabrics. Modified after Berth, et al., [1987].

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 (Alkyl benzene sulphonate and alkyl sulphates), or non-ionic (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 that 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 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].

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 anti redeposition agents, bleach stabilizers, enzymes, fabric-whitening agents, foam controllers, corrosion inhibitors, perfumes and colourants [Austin, 1984 ; United Nations, 1992].

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]. 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. 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.

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.

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].

History of laundry detergent formulation
Morgenthaler [1987] reported that *STPP* was the preeminent detergent builder since the introduction of built detergent formulations in the 1940's. 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 multi-component 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 the above builders are summarised below.

Sodium tripolyphosphate

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;

Phosphate rock is the primary source of raw material for phosphorus [Jones, 1973].

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. *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.

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].

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 removes Ca ions in water by ion exchange. 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 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.

Sodium silicate

Sodium silicate is used in laundry detergent formulation to provide alkaline buffering and for corrosion control [Morgenthaler, 1987]. Silicate has no effect on water softening or redeposition, but is a source of alkalinity in the wash water.

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

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]. Sodium carbonate softens the wash water by precipitation of hardness ions. 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]. To produce free-flowing powders, carbonates have to be used together with silicates [United Nations, 1992].

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.

Carboxylic acids

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. They are manufactured by homopolymerization of acrylic acid but may be modified as desired by copolymerization of acrylic acid and maleic anhydride.

Soaps

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

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].

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].

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.

Recommendations for improving the environmental performance of phosphate 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.

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.

Impact of detergent phosphorus bans and reformulation on water quality

Detergent phosphates are banned or reduced in order to lower the phosphorus loading to impoundments. Various studies have shown that a reduction in the external phosphorus loading to impoundments could lead to a decrease in algal production in the impoundment. For example, Edmondson reported that Lake Washington, 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 hyper-eutrophic 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.

Appendix 2: Urban and Rural Population in the Mgeni Catchment

Population data for the Mgeni catchment were obtained from the Institute of Natural Resources and comprised the 1991 census data for the region. The rural population was obtained by overlaying the subcatchment boundaries in the area of study and the *ESD* boundaries. **Table A2.1** shows the results for the entire Mgeni catchment. The codes refer to the subcatchments displayed in **Figure A2.1**.

Table A2.1: Rural population in the Mgeni catchment

Subcatchment	Code	Subcatchment Population	Inflow Sites	Inflow Population	Total Population
Midmar					
Mgeni Petrus Stroom 2.1	E	1 800	Mgeni inflow to Midmar	13 849	16 678
Lions 1	F	10 099	Umthinzima inflow	870	
Mgeni Midmar inflow 2	G	1 950	KwaGqishi inflow	439	
Kwa Gqishi Midmar inflow 35	H	439	Nguku inflow	1 137	
Nguku Midmar inflow 34.1	I	1 137	Direct inflow	383	
Umthinzima Midmar inflow 31	K	445			
Umthinzima Midmar inflow 31	L	267			
Umthinzima Midmar inflow 31	M	59			
Umthinzima Midmar inflow 31	N	99			
Direct Midmar catchment	O	60			
Direct Midmar catchment	O1	124			
Direct Midmar catchment	O2	99			
Direct Midmar catchment	O3	99			
Albert Falls					
Karkloof1	A	6 049	Mgeni Inflow to AF	12 856	16 514
Mgeni at Howick	P	240	Nculwane inflow	1 191	
Mgeni above Karkloof confl.	Q	5 743	Doringspruit inflow	895	
Nculwane	W	1 191	Direct inflow	1 572	
Karkloof2	X	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			
Nagle					
Mpolweni	B	14550	Mgeni inflow to Nag	75355	82493
Mkabela	C	1857	Impetu inflow	3893	
Cramond	AD	154	Direct inflow	3244	
Below Albert Falls Above Nagle	AE AA	2050			
Above Nagle	AH	3477			
Mpumalanga Impetu inflow		3893			
Mpumalanga Direct inflow		3244			
Mpumalanga above Nagle		52560			
Inanda					
Mqeku	D	4010	Mgeni Inanda inflow	443907	494786
Henley Inflow	J	3909	Mshazi inflow	18385	
Edendale	R	17564	Mtata inflow	4276	
Edendale	S	18314	Kwanyuswa inflow	2565	
Edendale	T	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			

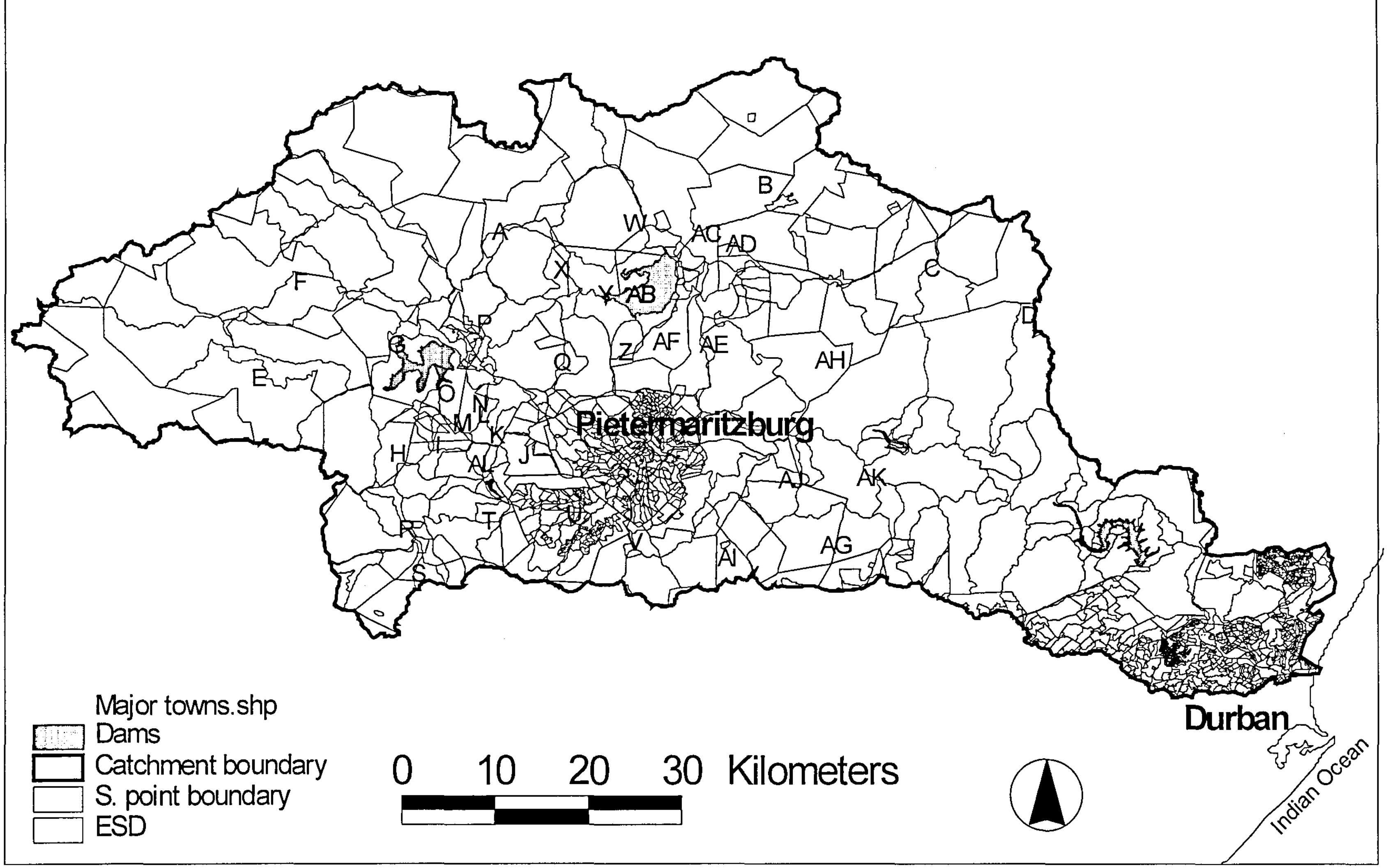
Subcatchment	Code	Subcatchment Population	Inflow Sites	Inflow Population	Total Population
Mpumalanga		182641			
Ndwede		179092			
Camperdown		4883			

The Urban population for each subcatchment was obtained by summing the population in towns in the subcatchment. These are shown in **Table A2.2**.

Table A2.2: Urban Population in the Mgeni catchment.

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

Figure A2.1: Mgeni Catchment ESD Boundaries and Codes



Appendix 3: Industrial Phosphorus Load

The results of the industrial phosphorus loadings discharged to the Darvill Wastewater Works are shown in **Table A3.1**. 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.

Table A3.1: Industrial phosphorus loading to the Darvill Wastewater Works.

Umgeni Water Reference.		Average P Conc. µg/ℓ	Average Flow kℓ/d	P loading Tonnes/annum
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
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**

Notes:
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 4: Darvill Wastewater Works Phosphorus Load

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 100Mℓ. Overflow to the river occurred when the capacity of the detention ponds was exceeded in consecutive rainfall 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 were 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].

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 A4.1** and A4.2 to obtain the flow volume at which significant deviation between influent and effluent flow occurred and therefore the start of overflow.

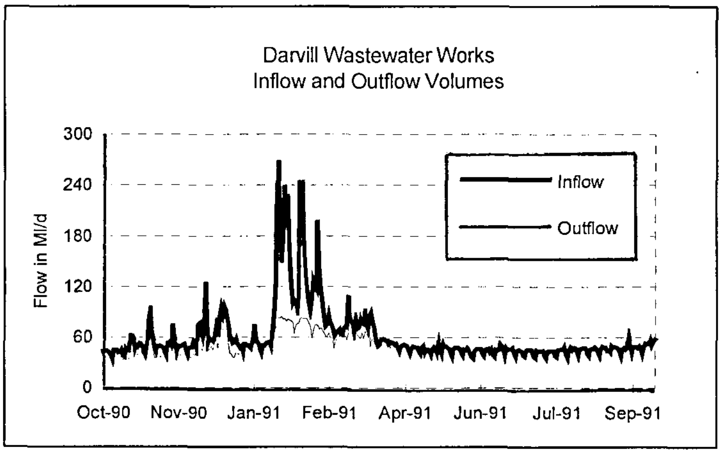


Figure A4.1: Darvill WWW Influent and effluent flows for October 1990 to September 1991.

Figure A4.1 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.

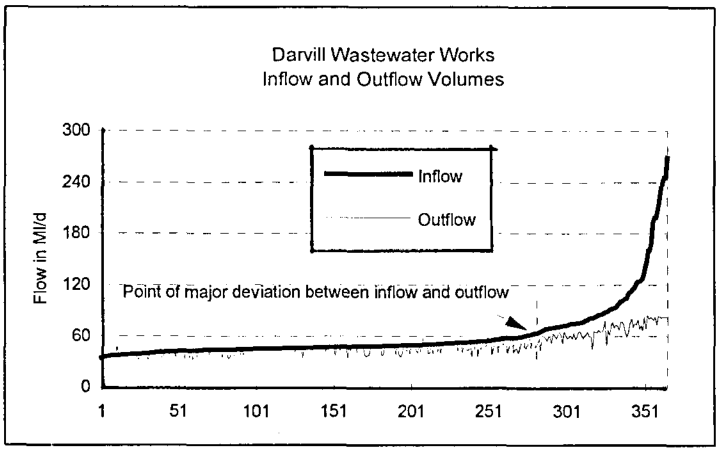


Figure A4.2: Sorted line plot showing point of significant deviation between influent and effluent flow for the Darvill WWW.

The cutoff flow volume at which the influent flow deviated significantly from the effluent flow was estimated to be 60 Mℓ/d by interpolation on the plot in **Figure A4.2.** i.e. flows exceeding 60 Mℓ/d would result in some overflow to river. This corresponds to the works design capacity.

As shown in **Table A4.1**, 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 Mℓ/d) was determined statistically. This relationship (shown in **Equation A4.1**) was then used to estimate the volume of treated influent during wet periods.

Influent = 0.6 Effluent + 20.2 (r = 0.64) .... [A4.1]

For influent flows exceeding 60 Mℓ/d, the overflow volumes were calculated as the difference between measured influent volume (i.e. treated and untreated) and influent volume calculated from **Equation A4.1** (treated only) . A sample of the results is shown in **Table A4.1.** Overflow occurred for 65 days during the October 1990 to September 1991 period.

Table A4.1: A sample data set showing volumes of influent, effluent and overflow, for the Darvill Wastewater Works.

Date	Influent Measured Mℓ/d	Influent Calculated Mℓ/d	Effluent Measured Mℓ/d	Overflow Calculated Mℓ/d	Calculated Overflow allowing for 100 Mℓ 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

Calculation of phosphorus loadings

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

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 tonnes for the period October 1990 to September 1991. Monthly and annual loads are summarized in **Table A4.2.**

The first 100 Mℓ 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 A4.2.**

Table A4.2: Soluble phosphorus loadings from the Darvill Wastewater Works for October 1990 to September 1991.

Month	Treated Effluent			Untreated Overflow			Total Loading tonnes
	Average Flow Mℓ/d	Average Conc. mg/ℓ	Monthly Loading tonnes	Average Flow Mℓ/d	Average Conc. mg/ℓ	Monthly Loading 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**

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 tonnes (66%) could be attributed to treated effluent and 7.7 tonnes (34%) to untreated overflow.

Appendix 5: ACRU Streamflow Simulation

The Department of Agricultural Engineering (*DAE*), University of Natal had developed the Agricultural Catchments Research Unit (*ACRU*) model for the Mgeni 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 Mgeni Catchment*, to generate inflow to impoundments on the Mgeni river where streamflow gauging was absent. The *DAE* had sub-divided the Mgeni 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.

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 Mgeni 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 A5.1** 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 A5.1.**

- 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 A5.2** 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 A5.4*), to determine the accuracy of the *ACRU* simulations.

Table A5.1: *ACRU* cells used in the runoff simulation for the Mgeni catchment. Cell numbers refer to the *ACRU* cells shown in the schematics in **Figures A5.1** to **A5.3.**

ACRU Cell Number	Cell Description	Area km²	Coords (ddmm		Rainfall Station
			Lat	Long	
7	Mgeni above Lions	30.10	2930	3003	0239002
8	Mgeni above Lions	39.52	2930	3007	0239002

ACRU Cell Number	Cell Description	Area km²	Coords (ddmm		Rainfall Station
			Lat	Long	
15	Lions above Mgeni confluence	27.65	2928	3010	0268806
16	Mgeni 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	Mgeni above Albert Falls	21.31	2929	3012	0269388
30	Mgeni above Albert Falls	24.26	2928	3014	0269388
31	Mgeni above Albert Falls	8.64	2931	3014	0239482
32	Mgeni above Albert Falls	13.93	2930	3015	0239482
33	Mgeni above Albert Falls	10.04	2934	3015	0239483
34	Mgeni above Albert Falls	3.15	2934	3017	0239483
35	Mgeni above Albert Falls	14.13	2932	3016	0239482
24	Karkloof above Mgeni confluence	48.20	2925	3017	0269532
36	Mgeni 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 A5.2: Monthly precipitation data for cells and selected rainfall station and calculated precipitation correction factors.

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
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

Cell Number and Rainfall Station	Lat	Long	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Alt	MAP
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
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

Combination of *ACRU* cells needed to provide inflows to impoundments

Midmar subcatchment

Figure A5.1 depicts the cells used to obtain flows into the Midmar impoundment. Cells 16, 25, 26, and 27 corresponded to the Mgeni, KwaGqishi, Nguku and Umthinzima inflows to the Midmar impoundment, respectively, while cell 28 provided the direct inflow to the Midmar impoundment.

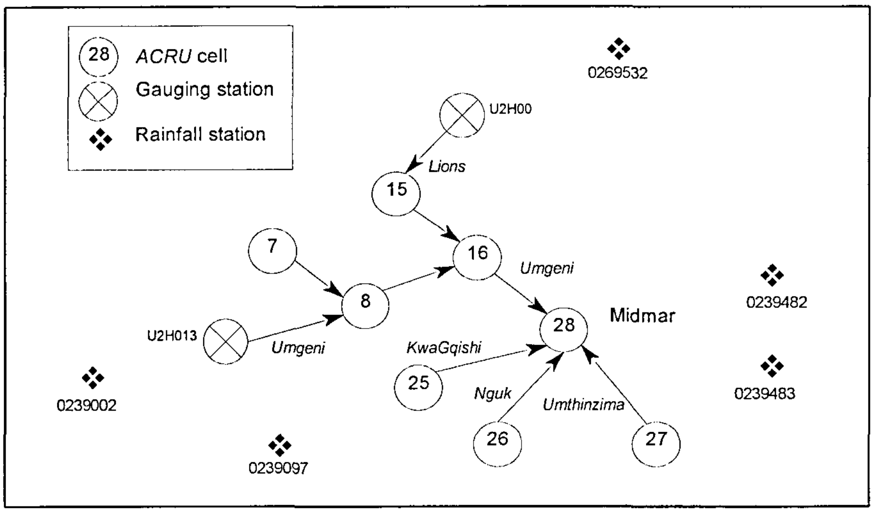


Figure A5.1: Schematic showing *ACRU* cells, rainfall stations and gauging sites used to simulate flow to the Midmar impoundment.

The total Mgeni 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 (Mgeni 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.

Albert Falls subcatchment

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

The total Mgeni inflow to the Albert Falls impoundment was estimated by simulating flows starting at cell 29 on the Mgeni and 24 on the Karkloof (**Figure A5.2**) and adding to these the gauged outflow from the Midmar impoundment (U2H048) and the gauged flow on the Karkloof river (U2H006).

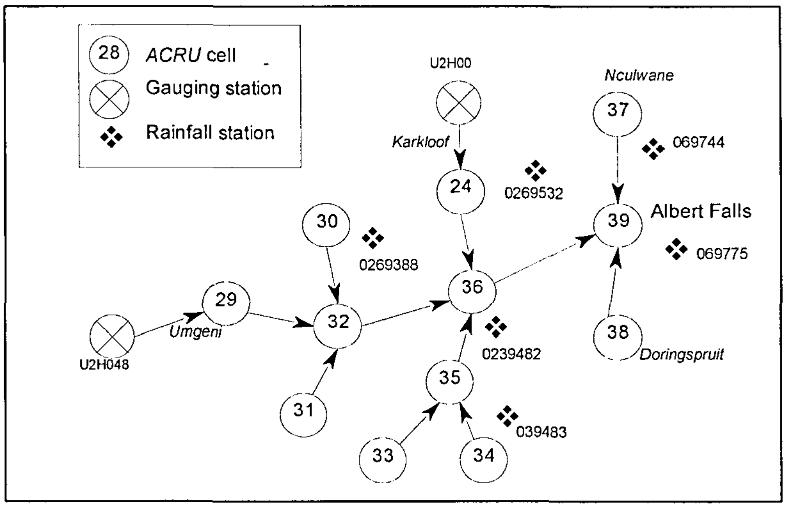


Figure A5.2: Schematic showing *ACRU* cells, rainfall stations and gauging sites used to simulate flow to the Albert Falls impoundment.

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 Mgeni into Inanda was obtained from measured outflow and a water balance for the impoundment using data obtained from Umgeni Water Operations.

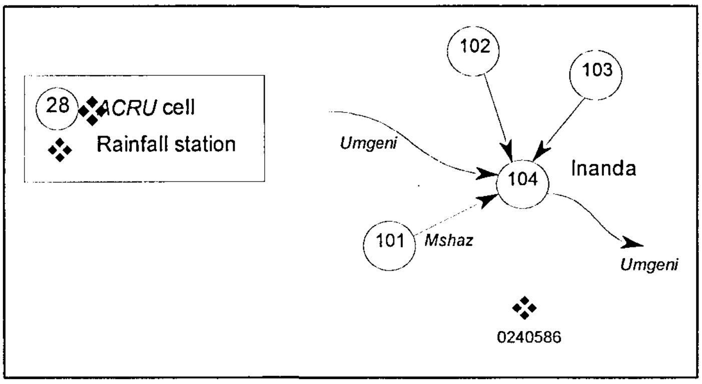


Figure A5.3: Schematic showing *ACRU* cells, rainfall stations and gauging sites used to simulate flow to the Inanda impoundment.

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 A5.3** to provide runoff corresponding to other inflows to the impoundment for which water quality were available.

Table A5.3: Water quality monitoring sites in the Inanda subcatchment for which runoff were estimated using *ACRU* cells.

Water quality monitoring site	Area km^2	Closest *ACRU* cell	Area factor
Mshazi above Mgeni 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

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 to impoundments. Monthly and annual flow volumes (calculated from simulated daily data) are shown in **Tables A5.4 to A5.6.**

Table A5.4: Monthly and annual totals of simulated daily flow volumes for inflows to the Midmar impoundment.

Month	Flow 10^6 m^3				
	Mgeni	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 A5.5: Monthly and annual totals of simulated daily flow volumes for inflows to the Albert Falls impoundment.

Month	Flow 10^6 m^3			
	Mgeni	Nculwane	Doringspruit	Direct Inflow
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

Table A5.6: Monthly and annual totals of simulated daily flow volumes for inflows to the Inanda impoundment.

Month	Flow 106 m3					
	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

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 are shown in Table A5.7.

Table A5.7: *ACRU* cells used to compare simulated and observed flows.

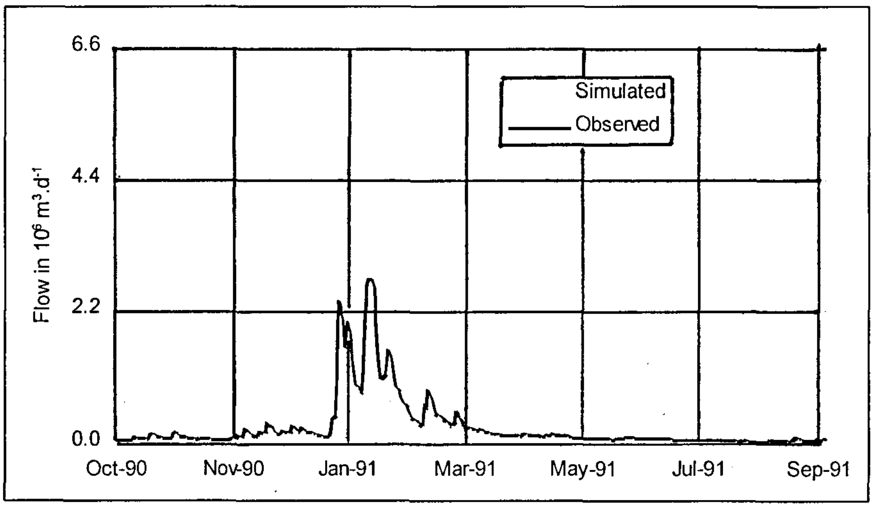
ACRU Cell Number	Cell Characteristics				
	Cell Description	Area km²	Coords (ddmm)		Rainfall Station
			Lat	Long	
7	Mgeni above Lions	30.10	2930	3003	0239002
9	Lions river	38.96	2926	2953	0268806
10	Lions river	112.9	2926	2958	0268806
11	Lions river	65.13	2923	3002	0268806
12	Lions river	55.30	2926	3005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

The simulated and observed flows were compared graphically and statistically as shown in **Table A5.9** and **Figure A5.4.** Both the graphical and statistical comparisons indicated that simulated data did not differ significantly from observed data . The *ACRU* flows were therefore accepted as reliable for use in the ungauged catchments.

Table A5.9: Paired two-sample t-test for means for simulated and observed flows.

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	

Figure A5.4: *Time-series of simulated versus observed flows for the Lions river at* Weltevreden.



Appendix 6: FLUX Load Calculation Programme

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. [Walker, 1987]. The loading estimates can be used to formulate impoundment nutrient balances over annual or seasonal averaging periods appropriate for application of empirical eutrophication models.

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 Mgeni 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 algorithim used by this method is presented in **Equation A6.1.**

$$Loading = Mean(w)\left[\frac{Mean(Q)}{Mean(q)}\right]^{b+1} \qquad \text{.............................. [A6.1]}$$

Where:-

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

Appendix 7: MINTEQA2 Phosphorus Speciation Modelling

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.

Table A7.1 : Input data to MINTEQA2 before type modifications.

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	Cl-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 7.2 : 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 A7.3 : 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**

Table A7.4 : Finite solids present at equilibrium.

ID	NAME	CALC MOL	LOG MOL	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 A7.5 : 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 A7.6 : Equilibrated phosphorus mass distribution.

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		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	Cl-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 A7.7 : 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 8: History of Detegent Phosphorus Bans

Table A8.1 : List of countries which impose detergent phosphorus restrictions or bans.

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]
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