# Collection and Evaluation of Runoff Water Quality from a Disused Feedlot in KwaZulu-Natal

**DE Simpson** 

Report to the Water Research Commission by the Division of Water, Environment and Forestry Technology CSIR

WRC Report No 498/1/98

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# COLLECTION AND EVALUATION OF RUNOFF WATER QUALITY FROM A DISUSED FEEDLOT IN KWAZULU-NATAL

D E SIMPSON

# REPORT TO THE WATER RESEARCH COMMISSION

# BY THE

# DIVISION OF WATER, ENVIRONMENT AND FORESTRY TECHNOLOGY, CSIR

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# UMGENI WATER

WRC Report No. 498/1/98

ISBN 1 86845 498 3

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# EXECUTIVE SUMMARY

# Background and aims

This project was carried out as a follow-on to a project that had been carried out on two catchments at the Cedara Agricultural College, two catchments in the vicinity of the University of Zululand and two catchments at the Ntabamhlope research farm close to Estcourt. One of the Ntabamhlope catchments, a small 0.08 km<sup>2</sup> catchment that had been used for a number of years as a wintering feedlot for cattle showed up with some extremely high phosphorus, nitrogen and COD concentrations during stormflow runoff. Concentrations up to 10 mg// soluble phosphorus, 30 mg// nitrate and 500 mg// COD had been found. No indication of these extremely high concentrations, which are close to levels commonly found in domestic sewage, was given by the analysis of earlier baseflow samples. Clearly, these results showed that runoff from this type of land-use had a very high potential to pollute receiving waters. The data set, however, was limited as only one wet season had been sampled. This follow-on project was therefore motivated by a need to continue the monitoring for a further wet season in order to build up the data set and confirm the earlier findings. The overall objective was to characterise runoff water quality from a disused feedlot and quantify its pollution potential to receiving waters. Specific aims were to:

- Determine mean runoff water quality for different flow regimes, and pollutant export coefficients, (kg/ha/a).
- · Determine flow-water quality relationships that may be used in models.
- Determine temporal trends in baseflow and stormflow water quality to quantify the residual effect of pollutants stored on the catchment.
- Investigate relationships between the water quality variables for predictive use.
- Make recommendations for use of the data collected in application to water quality models.

# Experimental approach and procedure

The project was carried out with the close collaboration of staff of the University of Natal who were collecting rainfall and flow data from a number of weirs at the Ntabamhlope research farm. An automatic sampling and data recording system was devised to collect samples on a continuous basis so that representative samples of both baseflow and stormflow could be obtained. The system involved use of a pocket sized computer which was programmed to receive weir level readings at set time intervals, convert them into flow rates by use of a look-up table and then operate a water sampler on the basis of a volume of flow interval, that is to initiate repetitive sampling when a set volume of flow (user set) had passed over the weir. In this manner samples representative of the corresponding volumes of flow were obtained to enable accurate calculation of volume weighted mean concentrations for the variables analysed and calculation of loads of pollutants. This novel approach to data collection eliminated the inaccuracy problems associated with using grab sample data to estimate mean concentrations and loads since grab samples are just snapshots of water quality at the time of sampling, which can be highly variable.

Monitoring began in late 1990 and ended in early 1993, a period encompassing three summer and two winter seasons. During this time, apart from the regular taking of baseflow samples, a total of twelve runoff events were sampled, mostly throughout their hydrographs to give comprehensive quality data during changing flow. Both small and large events were sampled. The data set was divided up into subsets of low flow (baseflow) and high flow (stormflow) data for calculation of mean water quality to characterise the different flow regimes and to further calculate the loads of pollutants delivered during low and high flow. Altogether, 66 baseflow and 179 stormflow samples were taken for this purpose.

## Results and achievement of objectives

There was a considerable difference between the low and high flow water quality means. Suspended solids, soluble phosphorus, ammonia and total Kjeldahl nitrogen concentrations for high flow compared to low flow were 38, 37, 5 and 6 times greater respectively. Nitrate concentrations and conductivity levels were closer together, indicating that the sources for these constituents were not as highly mobilised as the other constituents during high flow. These high flow concentrations were of the same order of magnitude as those found in raw sewage, particularly at the 75<sup>th</sup> percentile results.

To calculate an annual mean runoff water quality for this particular landuse, the daily runoff, as recorded and disaggragated into base and quick flow volumes was employed. The total baseflow for the sampling period, was approximately double that of the quick flow (stormflow) volume. It was assumed that the mean low and high flow analyses represented the base and quick flow volumes respectively to calculate a volume weighted overall mean water quality. The results are shown below. Concentrations of the nutrients are very high compared to normal rural river water quality.

Variable	Mean	Variable	Mean
SS, mg//	225	NO3, µg//	4 138
Turbidity, NTU	41.1	NH3, μg/ℓ	244
COND, mS/m	37.3	KNF, μg/ℓ	2 177
TPF, μg/ℓ	879	KNU, μg/ℓ	4 607
TPU, µg/ℓ	1 626		

## Weighted mean analysis for runoff for study period

To calculate loads of pollutants washed off the catchment and areal export coefficients, the mean analyses were used together with the annual mean runoff volume from the catchment during the study years. The mean annual pollutant export coefficients are shown below.

## Mean annual areal pollutant export coefficients for study period

Variable	Export, kg/ha/a	Variable	Export, kg/ha/a
SS	301	NO3	5.53
TDS	333	NH3	0.33
TPF	1.18	KNF	2.91
TPU	2.18	KNU	6.16

These export coefficients, together with the mean water quality may be used as approximations for similar landuse catchments, where measurements have not been made. An example would be estimating the runoff water quality and loads from a large catchment where such a landuse was present in smaller sub-catchments. These results satisfy achievement of the first objective of the study.

When export of the variables was calculated for the different flow regimes, it was found that more than 90% of the annual suspended solids, soluble and total phosphorus loads and slightly lesser percentages for ammonia and Kjeldahl nitrogen were contributed during high flows. Contrarily, greater loads of TDS and nitrate were contributed during low flows. It is not surprising that greater suspended solids and associated variable loads were derived from high flows, no doubt due to erosion from the catchment, but the much greater loads of soluble phosphorus and ammonia from high flows is surprising. This indicates that stores of soluble phosphorus and ammonia were available on the catchment surfaces and were subsequently dissolved and washed out during rainfall.

Examination of graphs showing variable concentrations plotted with changing flow rates indicated both good and poor relationships for some variables during events, but there was no doubt that all variables were affected by changing flow. Suspended solids, particulate phosphorus and particulate nitrogen showed fairly direct relationships to flow, that is rising and falling in unison with flow, whereas the soluble constituents, total dissolved salts (as given by conductivity), phosphorus, nitrate, ammonia and Kjeldahl nitrogen showed delayed responses, sometimes peaking well after the flow peaks, which meant that good statistical relationships with flow for these variables would be difficult to derive. Using linear regression analysis, equations relating the dependence of suspended solids, particulate phosphorus and particulate nitrogen to flow during stormflow were developed. The R<sup>2</sup> values for individual events ranged up to 0.93, but when the data for all events were combined the values were lower, that is 0.50 for suspended solids, 0.54 for particulate phosphorus and 0.57 for particulate nitrogen. Using selected event data due to the high variability of results between events, similar regression relationships were developed for soluble phosphorus, nitrate and soluble Kjeldahl nitrogen. These equations could be used to estimate constituent concentrations in stormflow from similar landuse catchments, which satisfies the second objective.

Since the catchment studied was in disuse as a wintering feedlot for cattle during the study period, the data were subjected to trend analysis to estimate the residual effect of washoff/leaching of pollutants from catchment surfaces. For the baseflow data set, the sharpest declines in concentrations from the start to the end of monitoring were for soluble phosphorus and nitrate at 83% and 98% respectively and it was concluded that it would take 4 to 5 years from the cessation of the particular landuse practice before runoff water quality returned to more normal levels. Similarly, for the stormflow data, the change in soluble phosphorus and nitrate concentrations were estimated to be 98% and 87% respectively by the exponential formulae used and in this case a 3 year period was predicted before runoff would be rehabilitated. Trends for the solids associated constituents were not as clear, but still showed downward trends in concentrations. This satisfies the third project objective.

Correlation analysis was carried out between the water quality variables to determine the strength of relationships which, if strong, would indicate their being derived from similar sources. Further, one could be predicted from another which could be used to save on analyses and applied in models. For baseflow, the only strong correlations (>0.7) were found between suspended solids and particulate phosphorus and between soluble phosphorus and soluble Kjeldahl nitrogen, although only slightly less strong correlations were shown with particulate nitrogen. Nitrate appeared to be completely independent of the other variables. For the high flow data set, as for baseflow, correlations between suspended solids and particulate nitrogen and between soluble phosphorus and soluble Kjeldahl nitrogen were good with coefficients of 0.94 and 0.82. No other particularly strong relationships were evident. When correlation analysis was carried out for data within individual events, there were many more high coefficients shown, some even as high as 0.99. This shows appreciable inconsistency in variable relationships between events, which is the reason for the low coefficients for the data set as a whole. Another factor probably contributing to the low coefficients would be the temporal trends of diminishing concentrations in the runoff over time both at low and high flow which was discussed above. This satisfies the fourth project objective.

To place the poor runoff water quality of this particular landuse into perspective, a comparison was made with water quality and loads calculated for other rural catchments that had been monitored in a similar manner. Landuses in these five catchments included smallholdings, forestry, subsistence farming and just indigenous catchment vegetation. The nutrient concentrations for the disused feedlot catchment were very much higher than those for any of the other landuse catchments, in fact more than an order of magnitude for some constituents. This was particularly true for soluble and total phosphorus concentrations which is usually the limiting nutrient for algal growth and common promoter of eutrophication in impounded waters. As a rough estimate, the runoff would need to be diluted at least 100 times in receiving waters in order to lower the phosphorus concentration to more normal and acceptable levels and not be a threat to water quality. The export coefficients calculated naturally also showed very much higher values and may be seen in the figure below for soluble and total phosphorus are expressed as fractions of those calculated for the disused feedlot, ie: as a factor of 1 for the feedlot. They range from 5 to 50 times lower than the disused feedlot (V7H010).



## Soluble and total phosphorus export coefficients as fractions of disused feedlot coefficients (this study)

Runoff from such landuse practices should be treated to prevent pollution. A common method advocated is to collect and divert runoff to holding ponds where settlement and biological processes can take place to reduce nutrient concentrations, while overflow could be prevented by irrigation of pastures. Diversion of runoff onto vegetative strips or into wetlands is also advocated where uptake of nutrients can take place to improve water quality.

#### Recommendations for further research

This study has emphasised the fact that a seemingly innocuous and fairly common landuse practice, that is concentrating cattle on a piece of landuse to feed them can result in highly polluted runoff, particularly for the algal promoting nutrients, phosphorus and nitrogen. This fact would not have been discovered unless automatic monitoring equipment had been installed to sample continuously. It is therefore essential that for future research on the effect of landuse upon runoff water quality that automatic monitoring systems be installed. The database on the different landuse effects on water quality needs to be expanded using these techniques so that when planning for or managing a catchment, informed decisions can be taken in the knowledge of accurate information on mean baseflow and stormflow runoff water quality and export coefficients of pollutants, as only then can the effect on receiving water quality be gauged. With such reliable landuse information, it will be relatively easy to predict runoff water quality and pollutant loads for a new catchment either holistically or for sub-catchments, if required. Predictions, however, will only be as good as the quality of the input data.

The investigation showed that there were strong, linear regression relationships between the solids associated pollutants and flow rate, but that for the soluble constituents such direct relationships were not as clear. Rather, in these cases there appeared to be a delayed rise in concentrations after the peak flow had been reached. This is a challenge to the modelling fraternity to build in algorithms to replicate such behaviour, that is leaching of nutrients from surface deposits, but not in a direct relationship to flow rate. The kinetics of solubility rates would have to be considered. However, the data that have been collected in this study can be used as calibration data for existing models, or for the development and testing of model algorithms for prediction of runoff concentrations. Models need not, however, be deterministically based such as the HSPF simulation model, but could be simpler and export coefficient based, which would intuitively be more reliable.

## Appendices

The analytical results together with flow rates at the time of sampling are given in Appendices B and C and will also be made available of the CCWR database. To obtain the detailed flow rates for the study period the CCWR database may be accessed for weir V7H010. The dates and times of sampling can then be matched up with the analytical records to show complete hydrographs.

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## LIST OF ABBREVIATIONS

- COND -Conductivity, expressed as mS/m.
- KNF Kjeldahl Nitrogen Filtered, the total concentration of ammonia and soluble organic nitrogen, excluding nitrate nitrogen, expressed as μg/ℓ N.
- KNU Kjeldahl Nitrogen Unfiltered, the total concentration of ammonia and total organic nitrogen, excluding nitrate nitrogen, expressed as μg// N.
- NH3 Ammonia nitrogen, expressed as µg// N.
- NO3 Nitrate Nitrogen, expressed as µg/ℓ N.
- PN Particulate Nitrogen, nitrogen attached to suspended material, the difference between KNU and KNF, expressed as µg/ℓ N.
- PP Particulate Phosphorus, phosphorus attached to suspended material, the difference between TPU and TPF, expressed as μg/ℓ P.
- SN Sample number
- SS Suspended Solids, expressed as mg//.
- TDS Total Dissolved Salts, calculated from Conductivity, mg/\ell = mS/m x 6.67.
- TPF Total Phosphorus Filtered, total soluble phosphorus, expressed as µg//.
- TPU Total Phosphorus Unfiltered, total phosphorus, expressed as µg/ℓ.
- TURB Turbidity, expressed as NTU.

# ACKNOWLEDGEMENTS

There was no Steering Committee formed to guide this project, as it was essentially an extension for one year of an existing project, which had just finished, to continue collecting data on runoff from the Ntabamhlope catchment. The project completed was entitled "Quantification of the effects of land-use on runoff water quality in selected catchments in Natal", and published as WRC Report 237/1/91. The WRC is gratefully thanked for their support of the one year extension.

The data collection was conducted while the Author was in the employment of CSIR, but due to a staff rationalisation programme being conducted at the time, the Author was retrenched before evaluation of the data could take place. The data has since been evaluated in private time and with the help of the facilities kindly provided by Umgeni Water, where the Author is currently employed. This has unfortunately led to an appreciable time delay between the end of data collection and production of this report. Umgeni Water is gratefully acknowledged for the facilities provided.

The following persons are gratefully thanked for their help in the conduct of the project:

Mr J J Pretorius of the Department of Agricultural Engineering, University of Natal, for the collection of samples and exchange of the data loggers from the Ntabamhlope catchment. Without this assistance the project would not have been possible.

The inter-campus transport system of the University of Natal for transporting the sample bottles and data loggers between the Pietermaritzburg and Durban campuses.

The Department of Agricultural Engineering, University of Natal, for the loan of an Isco water sampler.

Mr J Smithers of the Department of Agricultural Engineering, and the CCWR of the University of Natal, for the supply of flow and rainfall data for the catchment.

Mr V Stone and Mr B Bailey as consultants (formally CSIR) for construction of the data capture system and control of the sampler.

Mr M Muller and Mrs G Dor of Analytical Services, CSIR Durban (formally), for the analysis of samples.

# 1. INTRODUCTION

# 1.1 Background

As part of a Water Research Commission sponsored project entitled "Quantification of the effects of land-use on runoff water quality in selected catchments in Natal", two small catchments at the Ntabamhlope research farm near Estcourt were investigated for a period of one year. Previously, two catchments at the Cedara Agricultural College near Pietermanitzburg had been monitored for runoff water quality for two years. The purpose of the research was to characterise runoff water quality from different land-uses and to provide such water quality data to aid in the development and calibration of a water quality section to be added on to the existing distributed ACRU water quantity simulation model. This model was being developed as part of another Water Research Commission sponsored project being conducted by the Agricultural Engineering Department of the University of Natal in Pietermanitzburg. A report on results for the Cedara catchments, the limited data for the Ntabamhlope catchments and data for two Zululand catchments was produced at the time (Simpson 1991).

The preliminary results obtained for one of the Ntabamhlope catchments being monitored, V7H010, which had in the past been used as a wintering feedlot for cattle showed unexpectedly high concentrations of the nutrients, nitrogen and phosphorus during stormflow runoff. Concentrations up to 10 mg// soluble phosphorus, 30 mg// nitrate and 500 mg// COD had been found. No indication of these extremely high concentrations, which are close to levels commonly found in domestic sewage, was given by the analysis of earlier baseflow samples that had been taken. Clearly, these results showed that runoff from this type of land-use had a very high potential to pollute receiving waters. The data set, however, was limited as only one wet season had been sampled and therefore a proposal was submitted to continue the monitoring for a further wet season in order to build up the data set and confirm the earlier findings. This proposal was approved by the Water Research Commission and samples were collected during 1992 and 1993 covering the summer rainfall seasons. The project was carried out with the close collaboration of staff of the University of Natal who were collecting rainfall and flow data from a number of weirs at the Ntabamhlope research farm.

# 1.2 Objectives

The overall objective was to characterise runoff water quality from a disused feedlot and quantify its pollution potential to receiving waters. Specific aims were to:

- Determine mean runoff water quality for different flow regimes, and pollutant export coefficients, (kg/ha/a).
- Determine flow-water quality relationships that may be used in models.
- Determine temporal trends in baseflow and stormflow water quality to quantify the residual effect of pollutants stored on the catchment.
- Investigate relationships between the water quality variables for predictive use.
- Make recommendations for use of the data collected in application to water quality models.

## 1.3 Approach followed

The approach followed was to collect water samples automatically and continuously on a volume of flow basis to obtain samples representative of both baseflow and stormflow which would allow calculation of mean water quality, export coefficients and examination of possibly useful flow-water quality relationships. The methodology used is described in section 3.1.

# 2. CATCHMENT DESCRIPTION

As shown in Figure 1, the Ntabamhlope catchments are situated just south of Estcourt in KwaZulu-Natal. The historical background is that between 1962 and 1967 more than 20 weirs were constructed by the Department of Water Affairs to measure runoff from catchments of varying sizes in the Ntabamhlope/De Hoek area. The general purpose was to assess the importance of wetlands for water supply, flood control and the effect of changes in land-use upon flow regimes (Schmidt and Schulze, 1989). Their report states that the soils of the region are highly leached, non-structured and have a low erosion potential. For further information, the reader is referred to the above report. The catchment monitored as part of the present study is only 0.08 km<sup>2</sup> in area with a south aspect and an average slope of 10%, which is reasonably steep. There are a few trees present and the area is mainly covered by grass. At the upper end of the catchment, which is more or less on the level, feed troughs were laid out where cattle had previously been fed during the winter months for a number of years. At the time when the research was conducted, however, this practice had largely stopped as the farm was to be sold by the Department of Agriculture. Consequently, the catchment is described as a disused feedlot and was not at all like a normal feedlot where cattle are kept in pens and therefore at a high density. Rather, in this case the cattle could roam freely about the area and feed from the troughs. This is a situation that could be present on many farms in the country that have cattle herds and therefore may be a fairly common landuse, albeit limited to small areas. Examination of the catchment showed that no piles of manure were present, but rather the odd cow pat was distributed about, mainly in the upper section where the feed troughs were placed. Hence, the importance in investigating runoff water quality from this particular type of landuse which to all appearances appeared to be innocuous from a pollution point of view. A most unfortunate fact, however, is that there are no records of the numbers of cattle that were kept and wintered in this catchment, or for what periods, and therefore such data cannot be linked to runoff water quality and pollutant loads. A fact that must be borne in mind when reviewing the water quality data is that cattle were not present at all during the study period and therefore the data gathered really reflects a residual effect of this landuse.



#### Figure 1: Location of the Ntabamhlope research catchment

## 3. DATA COLLECTION

#### 3.1 Field equipment

The existing monitoring equipment at the weir, belonging to and being serviced by the Department of Agricultural Engineering, University of Natal, consisted of a clockwork driven Ott chart recorder connected to a float housed in a conventional stilling well. For this project, to automatically measure and record flow electronically in order to control a water sampler to sample under a volume of flow interval programme, it was necessary to either install a separate means of level measurement for flow or to connect up to the existing equipment. The latter course was chosen as being most practical and expedient. The method of control briefly described here was employed at the Cedara catchments and for a fuller explanation the reader is referred to that report (Simpson, 1991).

It was decided to translate the movement of the float driven shaft of the Ott recorder into an electrical signal as a measure of depth of flow. This was achieved by mounting a 10 turn potentiometer in line with the shaft of the Ott and connecting the two together with a flexible coupling. Then by applying a fixed voltage to the potentiometer, a variable voltage could be obtained from the third pin of the potentiometer which was proportional to the position of the shaft of the Ott, ie: the number of turns from zero height. This voltage was fed into a Sharp PC1500A pocket computer via a purpose made interface. The analogue signal was then converted into a digital one, and a purpose written programme within the computer performed functions such as conversion of depth of flow into flow rate, accumulation of flow volume since the last reading, storage of recorded data within the RAM of the computer and operation of a water sampler when required to do so, depending upon user input parameters. As

an example, if the flow interval for sampling was set at 100 m<sup>3</sup> then a sample would be initiated every time after the passage of that volume of flow over the weir. In this way samples could be analysed individually, or combined for analysis as being fully representative of the corresponding volumes of flow.

The equipment was housed in the existing brick kiosk alongside the weir, which was a V-notch multiple crest weir. The distance from the kiosk to the V-notch was about 20 m. As it was necessary to draw sample from fast flowing water in order to obtain representative samples, the 6 mm ID plastic sample line used was led right up to the V-notch. Care was taken to ensure that the sample line had a continuous fall from the sampler to the intake point so as to minimise contamination between samples. A purpose made plastic strainer was attached to the end of the tubing to prevent complete blockage of the intake. For protection, the sample tubing was housed in plastic conduit.

An Isco pump sampler with a capacity of 28 x 500 ml bottles was used. The velocity in the sample line was measured at about 0,5 m/s which was sufficient to draw up and prevent settlement of fine particles (200 microns) in the line, but the sampler was not able to draw up coarse material (> 1 000 microns) such as bedload passing through the weir. This should be borne in mind when considering suspended solids concentrations given in this report.

As a routine the installation was serviced on a weekly basis, when the data logger was exchanged for another one and any samples taken collected for analysis. Rechargeable batteries were also replaced on a routine basis. At the laboratory, the data logger was connected to a PC and the data downloaded to a file. Information recorded was date, time and flow rate as well as sample number when one had been taken. In order to limit the amount of data recorded, data records were only taken when there was a significant change in flow rate or when a sample was initiated. The default, however, was a record taken on the hour every hour in order to check correct operation of the equipment.

# 3.2 Sample analysis

All analyses were conducted using established methods and auto-analytical techniques in the CSIR laboratory in Durban. Suspended solids was determined by filtering samples through 0,45 µm membrane filters. Other methods came from the Environmental Monitoring and Support Laboratory, Cincinnati, 1979; Standard Methods for the Examination of Water and Wastes, 1980.

# 4. RESULTS

# 4.1 Rainfall and runoff amounts

The monitoring of runoff water quality from the catchment commenced in October 1990 and was terminated in April 1993. Since the catchment is small, meaningful runoff only really occurred during the summer rainfall season and in the winter months there was little, or at times no flow at all. The flows recorded by the Department of Agricultural Engineering and expressed as daily flows are shown for the study years in Figure 2. Also shown in the graphs and indicated by arrows are hydrographs or runoff events that were sampled throughout their duration and the individual sampled analysed. As may be seen, most of the high flow events were sampled, twelve in all, to give a good representation of changes in water quality at high flow. Sampling of low or baseflow to characterise this water quality was continuous throughout the study period, but is not shown in the graphs. As may be observed from Figure 2, the majority of the events sampled occurred in 1991, due clearly to much higher runoff in that than in the other years. The annual rainfall, runoff volumes and runoff coefficients are given in Table 1.

Year	Rainfall, mm	Runoff, m <sup>3</sup>	Runoff Coefficient
1990	682	9373	0.17
1991	1010	19870	0.25
1992	816	5808	0.09
1993	961	7748	0.01

#### Table 1: Rainfall, runoff volumes and runoff coefficients for the catchment



Figure 2: Daily runoff volumes from catchment, sampling period and runoff events sampled

Rainfall over the four years was quite variable, and consequently runoff as well. Runoff from rainfall coefficients ranged from 0.09 to 0.25 (9 - 25% of rainfall). This high variability would naturally have had a significant effect on the amounts of accumulated pollutants washed off from the catchment each year and therefore if annual export coefficients were to be calculated from the data they would also be highly variable. Consequently, it has been decided that an average annual export coefficient for the study period (given later in the report) should be calculated as it would be more representative of the catchment than individual values. The average annual rainfall was 867 mm which includes dry and wet years.

# 4.2 Runoff sampling strategy

The sampling philosophy employed was that the Isco sampler was activated to take a sample on a fixed volume of flow basis. The system worked as follows: After determination of flow from the water level reading within the datalogger programme, the volume of flow that had passed since the previous reading was calculated and accumulated in a register. This volume was then compared with a pre-set volume in the programme, and if equalling or exceeding it, then a signal was sent to the sampler to take a sample. The sample number, time, date and flow were then recorded by the logger and the accumulating register re-set by subtracting the two volumes for the cycle to begin again. In this manner each sample taken represented a fixed volume of flow so that, when required, samples could be combined to give samples representative of flow periods or events, and consequently also loads of pollutants when calculated. The sample interval was changed throughout the monitoring period depending upon the baseflow at the time, the main objective being to ensure that the sampling interval (volume) was sufficient to enable sampling throughout runoff events.

# 4.3 Mean water quality during base and high flow periods

A mean water quality calculated arithmetically from the entire data set, taken as being representative of runoff quality from the catchment would not have been a meaningful result, firstly as it would have been biased by either low or high flow results, depending upon the respective numbers taken, and secondly since runoff volumes representing the samples would not have been taken into account in the calculation. Rather, in order to account for the different flow regimes, the sample result data set was divided up into low flow and high flow data sub-sets. This was done intuitively by screening the data with due regard being paid to flow rate at the time of sampling and the measured suspended solids concentration, which is a good indicator of flow regime. As a result, the two data sets consisted of 66 base flow and 179 high flow samples. Naturally, the high flow samples came from the 12 storm runoff events that were sampled during the study period, as indicated in Figure 2. The mean results are given in Tables 1 and 2, together with 25<sup>th</sup>, 50<sup>th</sup> and 75<sup>th</sup> data set percentile values to show the spread of the results.

Variable	Mean	25 <sup>th</sup> Percentile	50 <sup>e</sup> Percentile	75 <sup>th</sup> Percentile	
SS, mg//	17	6	13		
Turbidity, NTU	6.8	2.6	4.0	7.6	
COND, mS/m	37	30	34	43	
TPF, μg/ℓ	68	25	44	87	
TPU, μg/ℓ	173	77	146	214	
NO3, μg/ℓ	3 430	129	2 416	4 971	
NH3, μg/ℓ	111	18	49	84	
KNF, μg//	1 006	684	879	1 166	
KNU, μg/ℓ	1 822	898	1 278	1 748	

# Table 2: Mean low flow water quality concentrations and data set percentiles

Variable	Mean	25 Percentile	50 Percentile	75 Percentile	
SS, mg/ℓ	641	88	290	1019	
Turbidity, NTU	110	16	53	130	
COND, mS/m	38	16	34	45	
TPF, µg/ℓ	2 506	121	796	4 586	
TPU, μg/ℓ	4 542	1 110	2 684	7 353	
NO3, μg/ℓ	5 557	1 198	2 549	6 203	
NH3, μg/ℓ	512	53	198	689	
KNF, μg/ℓ	4 525	1 590	3 656	6 793	
KNU, μg/ℓ	10 189	4 636	8 918	14 506	

Table 3: Mean high flow water quality concentrations and data set percentiles

As may be noted there is a considerable difference between the low and high flow water quality means. Suspended solids, soluble phosphorus, ammonia and total Kjeldahl nitrogen concentrations for high flow compared to low flow are 38, 37, 5 and 6 times greater respectively. Nitrate concentrations and conductivity levels are closer together, indicating that the sources for these constituents are not as highly mobilised as the other constituents during high flow. These high flow concentrations are of the same order of magnitude as those found in raw sewage, particularly the 75<sup>th</sup> percentile results.

A point to note here is that routine grab sampling, as often practised on a weekly or monthly basis in monitoring programmes, would mostly sample base flow and therefore would not yield representative results for characterisation of mean runoff water quality, or for the calculation of pollutant loads. To obtain more meaningful and representative results, automatic sampling as carried out here is essential to characterise the low and high flow runoff water quality from a catchment.

## 4.4 Weighted mean water quality, pollutant loads and export coefficients

To calculate an annual mean runoff water quality for this particular landuse, the daily runoff as recorded and disaggragated into base and quick flow volumes by the Department of Agricultural Engineering, University of Natal was employed. The total base flow for the sampling period, October 1990 to March 1993, was 20 142 m<sup>3</sup> and the quick flow approximately half as much at 10 047 m<sup>3</sup>. It was then assumed that the mean low and high flow analyses calculated and shown in the tables above represented these base and quick flow volumes respectively, in order to calculate a volume weighted mean water quality. The results are shown in Table 4. Concentrations of the nutrients are very high compared to normal rural river water which will be discussed in a later section.

To calculate loads of pollutants washed off the catchment and areal export coefficients, the above mean analyses were used together with the annual mean runoff volume from the catchment during the study years, which amounted to 10 700 m<sup>3</sup>/a. Table 5 shows these loads. The export coefficients together with the mean water quality may be used as approximations for similar landuse catchments, where measurements have not been made. An example would be estimating the runoff water quality and loads from a large catchment where such a landuse was present in smaller sub-catchments; then together with the estimated runoff quality from the other sub-catchments with known landuses and runoff quality, the final water quality at the outlet of the large catchment could be predicted by proportioning the results. Ideally, typical runoff water quality from different landuses should be available, but this is seldom the case.

#### Table 4: Weighted mean analysis for runoff for study period

Variable	Mean		
SS, mg//	225		
Turbidity, NTU	41.1		
COND, mS/m	37.3		
TPF, μg/ℓ	879		
TPU, μg/ℓ	1 627		
NO3, μg/ℓ	4 138		
NH3, μg/ℓ	244		
KNF, µg/ℓ	2 177		
KNU, μg/ℓ	4 607		

Table 5: Mean annual pollutant washoff loads and areal export coefficients

Variable	Export, kg/a	Export, kg/ha/a
SS	2 404	301
TDS	2 664	333
TPF	9.4	1.18
TPU	17.4	2.18
NO3	44.3	5.53
NH3	2.62	0.33
KNF	23.3	2.91
KNU	49.3	6.16

Note: TDS was calculated from conductivity, ie: COND x 6.67 = TDS mg//

The respective loads that were contributed during low and high flow periods can be calculated if the mean analyses given in Tables 2 and 3 are converted into loads using the respective total low and high flow volumes given above. This is of interest to know during which flow regimes the majority of the different variable loads were delivered. They are shown for the different variables expressed as percentages of the total loads in Figure 3.

While more than 90% of the annual suspended solids, soluble and total phosphorus loads and slightly lesser percentages for ammonia and Kjeldahl nitrogen were contributed during high flows, the reverse but not to the same degree, was the case for TDS (calculated from conductivity) and nitrate where greater loads were contributed during low flows. It is not surprising that greater suspended solids and associated variable loads such as total phosphorus and total Kjeldahl nitrogen were derived from high flows, no doubt due to erosion from the catchment, but the much greater loads of soluble phosphorus and ammonia from high flows is surprising. This indicates that stores of soluble phosphorus and ammonia were available on the catchment surfaces and were subsequently mobilised during rainfall. These results reiterate the fact that only sampling water courses during base or low flow periods will not give representative results for runoff water quality or load calculations.



# Figure 3: Percentages of loads contributed by low and high flow regimes

# 4.5 Variation in water quality during runoff events

As stated earlier, a total of 12 storm events were sampled mostly throughout the rising and falling limbs of the hydrographs with the objectives of following runoff water quality changes, investigating flow-quality relationships and relationships between constituents themselves. If good relationships could be developed, they would be of great assistance in calibrating and testing water quality models as well as saving on analyses by being able to predict constituent concentrations from one another. Further, the flow-quality relationships could be used to simulate and calculate runoff loads from similar landuse catchments.

One of the best ways to investigate such relationships is to see flow plotted with the particular variable as a time series graph. This has been done for all 12 events for each variable measured in the samples. The core variables analysed were suspended solids, conductivity, soluble and total phosphorus (particulate phosphorus calculated from the difference), nitrate, ammonia, soluble and total Kjeldahl nitrogen (particulate nitrogen calculated from the difference). For some events all variables were analysed, but for other ones variables such as nitrate, ammonia and Kjeldahl nitrogen were omitted from analysis for various reasons. Also, in the interests of conserving on analysis, on arrival at the laboratory, the hydrograph was scanned and certain samples combined, usually in cases where the flow rate had stabilised and was not changing greatly. The graphs plotted with each variable and corresponding flow rate are shown in Figures 4 to 26. It should be borne in mind here that the x-axes of the graphs showing sample number are not linear time scales, but rather the sample numbers represent equal volumes of flow in the hydrographs and where samples have been combined the scale has effectively been shrunk. The visual relationships are what is important to see.

Figure 4 show the results for Event 1 on 31/10/90. The flow rate during this event rose sharply from almost zero to a peak of 0.045 m<sup>3</sup>/s at sample number 7 before falling back to the baseflow at sample number 12. All variable concentrations changed appreciably during the event showing the following patterns:

- Suspended solids concentrations followed the hydrograph very closely, rising and falling in unison.
- Conductivity rose with flow but in a delayed manner, peaking well after the flow peak and falling very
  gradually showing a slow recession.
- Soluble phosphorus concentrations followed the hydrograph closely in the beginning, but fell slowly well
  after the peak.
- Particulate phosphorus showed a similar pattern to soluble phosphorus, falling slowly after the peak flow.
- Nitrate and soluble Kjeldahl nitrogen concentrations had similar patterns, rising with flow, but peaking well
  after the peak flow and then falling slowly, not too differently from conductivity.
- Particulate nitrogen concentrations showed almost exactly the same response as suspended solids.

The inference is that suspended solids and particulate nitrogen were mobilised immediately with increased runoff and reacted in congruence with flow, while soluble and particulate phosphorus, nitrate and soluble Kjeldahl nitrogen were mobilised in a delayed manner by flow and maintained high concentrations well after the flow peak. Conductivity, as a measure of dissolved salts, behaved in a similar manner but with the recession being even more delayed.

It would take too long to describe all the events in the above manner and draw conclusions, so the behaviour for the variables for the events in relation to flow have been categorised into three general descriptions, as follows:

- The variable follows the flow peak closely on the rising and falling limbs, sometimes preceding the rise in flow.
- The variable is affected by flow and rises behind flow and peaks later, showing a delayed response and sometimes has a slow recession.
- 3. The variable either has no apparent, or a poor, or an inverse relationship to flow.

Table 6 shows these three generic type relationships, categorised subjectively. The reader may examine the graphs for events 2 to 12 in Appendix A for confirmation or disagreement with this assessment.

Event No.	SS	COND	TPF	PP	NO3	NH3	KNF	PN
1	1	2	2	2	2	-	2	1
2	1	2	2	3	2	2	2	2
3	1	2	2	1	-	-	-	-
4	1	3	1	3	1	3	1	1
5	1	2	1	1	3	1	1	1
6	1	3	1	1	3	-	-	-
7	1	2	2	1	2	2	2	1
8	1	2	2	1	2	1	1	1
9	1	2	2	2	2	2	2	2
10	1	3	2	1	3	1	2	1
11	1	2	1	1	2	2	1	3
12	3	3	2	3	2	3	-	

# Table 6: Behaviour of variable patterns in relation to flow

Note: No analysis conducted on the variable is denoted by -.

For suspended solids, all but one event shows a close relationship to flow which may be expected. For conductivity, the most common behaviour is a delayed response to flow with a slow recession or in some cases an inverse relationship is indicated. For soluble phosphorus, the majority behaviour is the delayed response, but for the other cases a more direct relationship with flow is shown. Particulate phosphorus on the other hand shows more direct than delayed relationships to flow. The delayed response is the most common behaviour for nitrate while for ammonia both delayed and direct responses to flow are indicated. Soluble Kjeldahl nitrogen shows almost equal delayed and direct responses to flow while particulate nitrogen has mostly direct responses. Altogether, there are few results that show no apparent relationship to flow, or in other words that flow has had an effect on the variable concentration.

To summarise, suspended solids, particulate phosphorus and particulate nitrogen showed fairly direct relationships to flow, whereas the soluble constituents, dissolved salts (as given by conductivity), phosphorus, nitrate, ammonia and Kjeldahl nitrogen indicated delayed responses, sometimes peaking well after the flow peaks, which means that good statistical relationships with flow for these variables will be difficult to derive.



Figure 4: Event 1 - Variation in suspended solids, conductivity, soluble, and particulate phosphorus, quality with flow



Figure 5: Event 1 - Variation in nitrate, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow

#### 4.6 Flow - constituent concentration correlations

The strength of a variable relationship with flow may be easily seen through correlation analysis, the results of which are given in Table 7.

Event No.	SS	COND	TPF	PP	NO3	NH3	KNF	PN	Peak Flow m <sup>3</sup> /s
1	0.92	0.28	0.62	0.72	0.26	-		0.93	0.05
2	0.87	0.10	0.38	0.23	0.26	0.38	0.29	-0.10	0.02
3	0.87	0.16	0.55	0.67	-	-	-	-	0.04
4	0.79	0.66	0.86	0.25	0.73	0.38	0.69	0.78	0.23
5	0.98	0.30	0.70	0.75	0.39	0.67	0.76	0.95	0.22
6	0.92	-0.19	0.60	0.61	-0.21	-	-	-	0.16
7	0.89	-0.92	0.05	0.82	-0.81	0.32	-0.43	0.81	0.14
8	0.88	055	-0.25	0.80	-0.37	0.41	0.23	0.82	0.15
9	0.71	-0.61	-0.13	0.30	-0.49	-0.45	-0.01	0.51	0.06
10	0.87	-0.53	0.61	0.85	-0.34	0.91	0.25	0.85	0.20
11	0.19	-0.16	0.80	0.14	0.29	0.15	0.79	-0.16	0.01
12	-0.06	-0.71	-0.24	0.04	-0.36	-0.05	-	-	0.27
No. > 0.7	10+	2-	2+	5+	1+, 1-	1+	2+	6+	

Table 7: Correlation analysis between variable concentrations during event runoff and flow

The correlation coefficients marked in bold are those ones that are above 0.7, which may be regarded as being highly significant with a good prospect of deriving a fairly strong empirical relationship through regression analysis. The total numbers with coefficients greater than 0.7 together with either being positive or negative are given in the last row of the table. It is immediately apparent that only suspended solids and to a lesser degree particulate phosphorus and particulate nitrogen have highly significant relationships for a number of events. The other variables show one or two significant correlations for events, mostly with positive signs, but one event has a positive and negative sign for nitrate, which is confusing. The peak flow rates reached in the events are also shown to see if they could possibly have had an influence on the correlations. For the last two events, 11 and 12, which show very poor correlations for suspended solids, particulate phosphorus and particulate nitrogen the one peak flow rate is low and the other high, thus not providing any flow peak reason for the poor correlation. The event with the most number of significant correlations, event 7, had a peak flow of 0.14 m<sup>3</sup>/s, which being at about the middle of the range of peak flow rates does not shed any light on the reason for the higher number of good variable correlations for the event.

## 4.7 Flow - constituent concentration regression relationships

Linear regression analysis was carried out on those variables that displayed reasonable numbers of significant correlations with flow for the events. The purpose is to establish relationships that can be used in models for the prediction of runoff water quality with changing flow for similar landuse catchments.

# 4.7.1 Suspended solids

As shown in Table 7, ten of the twelve events had significant correlation coefficients. Regression analysis of suspended solids as the dependent variable and flow as the independent one was carried out on each event to give the results presented in Table 8. The R<sup>2</sup> values which explain the variance range from 0.62 to 0.96, showing very strong relationships for some events. On the other hand, there is considerable inconsistency between the values of x-coefficients given, which range from a low of 1 893 for Event 6 to 37 667 for Event 1. The constants for the equations are all different but their variation is much lower. Of note here is that the two events with the highest x-coefficients are those that both occurred at the beginning of the wet summer seasons or hydrological cycles, namely Event 1 on 31/10/90 and Event 7 on 21/10/91. The implication here is that materials that had built up on the catchment surface during the dry winter months were washed off by the first significant summer runoff resulting in very high concentrations of suspended solids. Subsequent runoff from storms in the wet season resulted in lower concentrations of suspended solids and lower x-coefficients as the loose material had been removed and suspended material then came from natural erosion processes. This shows typical examples of

first flush effects. The high variability of these x-coefficients makes the derivation of a generally applicable equation with reasonable reliability for use in models difficult. To obtain a general equation and include as much data as possible, the results for the two events at either extreme of the x-coefficients, Events 1 and 6, were excluded and data for the remainder used for regression analysis. As shown in Table 8, the R<sup>2</sup> value fell to 0.50 and the x-coefficient to a mid order range value of 6 916. This is not a particularly strong relationship, but does represent an average response from the catchment. The observed suspended solids concentrations and those predicted from the above regression equation are shown in Figure 6 for the events used to derive the relationship. It may be seen that there is both under and over prediction of suspended solids concentrations.

Event	R <sup>2</sup>	x-coefficient	Constant	n	Start date	
1	1 0.85		175	12	31/10/90	
2	0.75	4 960	73	8	5/12/90	
3	0.76	2 245	14	14	19/1/91	
4	0.62	2 397	9	15	24/1/91	
5	0.96	7 710	-34	18	31/1/91	
6	0.85	1 893	-4	13	6/2/91	
7	0.79	16 981	-60	16	21/10/91	
8	0.78	8 829	94	18	9/11/91	
9	9 0.93		-12	15	14/11/91	
10	0.76	11 575	-222	17	1/1/92	
2,3,4,5,7, 8,9,10	0.50	6 916	60	120		

Table 8: Linear regression results for suspended solids on flow for events

Figure 6: Observed and predicted suspended solids concentrations for runoff events



## 4.7.2 Particulate phosphorus

A similar exercise was performed to derive a relationship for the dependence of particulate phosphorus on flow rate. The events with correlation coefficients above 0.6 were selected, and as above regression analyses performed on each. The results are given in Table 9.

Event	R <sup>2</sup>	x-coefficient	Constant	n	Start date
1	0.50	123 641	1 771	12	31/10/90
3	0.45	13 119	114	14	19/1/91
5	0.56	20 223	820	18	31/1/91
6	0.37	4 626	290	13	6/2/91
7	0.67	56 466	-46	16	21/10/91
8	0.62	19 184	504	18	9/11/91
10	0.73	28 080	-483	17	1/1/92
3,5,7,8,10	0.54	27 464	280	83	-

Table 9: Linear regression results for particulate phosphorus on flow for events

For the same reasons given for suspended solids, events 1 and 6 with the highest and lowest x-coefficients were excluded from the data set in order to derive an average relationship between particulate phosphorus and flow. The resulting equation has an R<sup>2</sup> value of 0.54, which is actually higher than that obtained for the regression of suspended solids on flow. A time series plot of the observed concentrations and those predicted from the regression equation is shown in Figure 7. For some of the peaks the observed and predicted concentrations are quite close, the exception being the large event of 21/10/91 where the observed concentration was far higher showing a first flush effect.



Figure 7: Observed and predicted particulate phosphorus concentrations for runoff events

# 4.7.3 Particulate nitrogen

Similarly, individual regression analysis was carried out for the events which had shown significant correlations with flow, a total of six out of the twelve. The results are shown in Table 10. The R<sup>2</sup> values range from 0.61 to 0.90 which is good, but as may be seen the x-coefficients have an extremely wide range, 19 005 to 346 924. When all data were included in a regression analysis, the resultant R<sup>2</sup> was a mere 0.29, which is very poor. Consequently, as done above, the events with the highest and lowest x-coefficients were excluded and the resulting R<sup>2</sup> value greatly improved to an acceptable 0.57. The plot of observed and predicted concentrations for particulate nitrogen are shown in Figure 8. Apart from the one event in October 1991, the agreement between the observed and predicted data is considered to be quite good.

Event	R <sup>2</sup>	X-coefficient	Constant	n	Start date
1	0.87	346 924	2 460	12	31/10/90
4	0.61	19 005	539	15	24/1/91
5	0.90	69 146	-652	18	31/1/91
7	0.66	150 958	-83	16	21/10/91
8	0.67	65 703	1 156	18	9/11/91
10	0.72	89 056	-1 337	17	1/1/92
5,7,8,10	0.57	79 270	605	69	-

Table 10: Linear regression results for particulate nitrogen on flow for events





The method used to arrive at the above regression equations for the prediction of suspended solids and particulate phosphorus and particulate nitrogen concentrations may well be criticised on the basis that the results for some events were selectively excluded in the regressions since they obviously did not fit. However in defence, it should be borne in mind that there are causes for these seemingly spurious results beyond the control of the data collection methodology used. For instance the samples were drawn from water flowing over the weir V-notch from the weir basin, where it is quite possible that some settlement of suspended material entering the basin could have taken place, just as re-suspension could also have taken place. Occurrence of these physical processes would confound obtaining good variable-flow relationships. Ideally, sampling should have taken place at the inlet to the basin to obtain more direct relationships, and this was attempted but was not successful. Nevertheless, it is considered that a fairly good representation of the results has been obtained in the development of the relationships. For suspended solids 68% of all possible results were used, for particulate phosphorus 47% and for particulate nitrogen 53%.

# 4.7.4 Soluble phosphorus

The event soluble phosphorus correlation coefficients with flow rate given in Table 7 show that only two events had high R<sup>2</sup> coefficients, with other ones varying between 0.6 and 0.7 while three actually had negative coefficients. Clearly, with this data a good relationship could not be expected to be developed. To view an overall picture of the change in soluble phosphorus concentrations with flow, the data are plotted as a time series in Figure 9.



Figure 9: Variation in soluble phosphorus concentration with flow for all events

Some perspective may be seen here and it is immediately apparent that at the beginning of the study there were some extremely high soluble phosphorus concentrations in relation to the flow peaks, which changed to the reverse relationship towards the end of the study. This behaviour would indicate flushing out of the store of phosphorus from the catchment with time since there was no replenishment of the supply from the cattle. To show this effect more clearly, the weighted mean concentration for each event was calculated, that is sample concentrations weighted by the corresponding flow at the time of sampling, and the results are plotted with flow in Figure 10.



Figure 10: Weighted mean event soluble phosphorus concentrations and flow

For events 1 to 6, the means fluctuate at high levels, but then show a dramatic fall in concentrations for events 7 to 12. Event 6 was the last one of the 1990/91 summer rainfall season and event 7 the first of the 1991/92 season, which seems to support the catchment flushing statement made above. In order to derive some predictive capability for this type of landuse, the concentration and flow data for the first 6 events were lumped together and regression analysis carried out. The R<sup>2</sup> value was 0.48, the x-coefficient 31 134 and the intercept 2 910 from 80 results. A plot of observed and concentrations predicted from this equation is shown in Figure 11.



Figure 11: Observed and predicted soluble phosphorus concentrations for events 1 to 6

For the first 3 events the predicted concentrations are appreciably lower than the observed peaks and represent more or less average concentrations, but for the next 3 events the agreement is relatively good. Although not as good a relationship as was obtained for suspended solids, particulate phosphorus and nitrogen, the equation can be of use in models as an initial estimator of runoff concentrations.

# 4.7.5 Nitrate and soluble Kjeldahl nitrogen

Similarly to soluble phosphorus, both nitrate and soluble Kjeldahl nitrogen concentrations also showed mostly poor correlations coefficients with flow in Table 7, thus giving little chance of establishing good predictive relationships. To gain an overall picture of concentration changes during events in the study period, plots with flow are shown for nitrate and soluble Kjeldahl nitrogen in Figures 12 and 13.







Figure 13: Variation in soluble Kjeldahl nitrogen concentrations with flow for events measured

The delayed peak in concentration for both constituents relative to flow is clearly evident for some events and hence the poor correlations found. There is also a clear indication of much higher concentrations at the beginning than at the end of the study period. This can be more easily seen in Figures 14 and 15 where the event mean concentrations are plotted with flow.





The highest concentrations for nitrate were for events 1 and 7 which were both at the beginning of the summer wet seasons, October 1990 and October 1991 respectively. The inference is that a first flush effect occurred for nitrate, but this was not the case for soluble Kjeldahl nitrogen where the mean concentration for event 7 was quite low. All that is evident from these graphs is that the event mean concentrations are not directly related to the flow peaks and therefore reasonable relationships cannot be developed. A further conclusion is that the concentrations show a diminishing trend through the study period. This will be further explored in the next section.



Figure 15: Weighted mean event soluble Kjeldahl nitrogen concentrations and flow

# 4.8 Temporal trends in base and high flow water quality

It is natural to expect that runoff water quality from a catchment that has been polluted by a particular landuse practice, as in this case the feeding of cattle, will not be constant through time. An indication of the length of time from the cessation of such activities that it would take for runoff concentrations of the nutrients to return to normal concentrations could be useful. Towards this end the low flow and high flow data have been analysed for trends.

# 4.8.1 Base flow runoff water quality trends

The analytical data for samples considered to represent base or low flow runoff totalled 66 samples between 27/10/90 and 19/3/93, a total of 29 months. The results for soluble phosphorus, nitrate, soluble Kjeldahl nitrogen and particulate phosphorus and particulate nitrogen were subjected to trend analysis. The exponential in preference to the linear formula option was selected as it is considered more representative of the manner in which the nutrient concentrations would fall, that is reducing at a diminishing rather than at a fixed rate. The method uses the least squares method to derive the best fit line through the data points. Table 11 shows the formulas derived and predicted initial and final concentrations for the study period, while Figure 16 shows graphs of the data and trend lines extended beyond the data points for approximately a further year.

## Table 11: Base flow trend analysis formulae, predicted initial and final concentrations for the study period

	Formula	Formula Concentration, µg/			
Variable	Exp. to base 'e'	Initial	Final	% Change	
TPF	(4.75-0.027*T)	113	19	83	
NO3	(8.99-0.061*T)	7604	142	98	
KNF	(6.95-0.0055*T)	1035	726	30	
PP	(4.35-0.0057*T)	77	53	31	
PN	(5.69-0.004*T)	295	227	23	

Note: T = time series number





#### Figure 16 (continued): Base flow analytical data and trend lines



The graphs have been plotted on logarithmic axes and consequently straight trend lines are given for the exponential function. Although the above data show some high fluctuations with rapid concentration changes and there are also missing values for some of the variables, the trend analysis clearly shows decreasing concentrations for all variables. The sharpest declines are predicted for soluble phosphorus and nitrate with percentage losses of 83 and 98% respectively. For soluble Kjeldahl nitrogen and particulate phosphorus and nitrogen, the slopes of the trend lines are far flatter with percentage losses of between 23 and 31%. Extension of the trend line for soluble phosphorus shows that it would take at least a further year beyond the end of the monitoring for the concentration to fall below 10  $\mu$ g/ $\ell$ , which is still a significant concentration that would promote eutrophication of impoundments. If it is assumed that the wintering of cattle on this catchment ceased during 1990, then it can be concluded that it would take approximately 4 to 5 years from then before the base flow runoff water quality returned to more normal and acceptable levels.

# 4.8.2 High flow runoff water quality trends

To investigate trends in runoff water quality at high flows, the weighted mean concentrations for the events were used. Individual sample concentrations during events would not have been of any use since they rose and fell with flow. Graphs shown earlier clearly showed that both large and small events were more or less evenly distributed throughout the study period and therefore should not have affected any trend analysis by providing bias in either direction. Consequently, the use of weighted event means for this analysis is considered valid. As was done for the low flow analysis, the exponential formula option was selected for the same reason. The twelve events were monitored over a 17 month period and were simply ordered from one to twelve for the analysis. Table 12 gives the results of the analysis and Figure 17 shows the event mean concentrations plotted with the derived trend lines.

# Table 12: High flow trend analysis formulae, predicted initial and final concentrations for the study period

	Formula	Concentra	ation, µg/ℓ	
Variable	Exp. to base 'e'	Initial	Final	% Change
TPF	(9.64-0.35*T)	10771	221	98
NO3	(9.57-0.18*T)	11902	1569	87
KNF	(9.57-0.19*T)	11854	1466	77
PP	(8.07-0.078*T)	2971	1256	58
PN	(8.85-0.013*T)	6861	5945	13

Note: T = time series number



Figure 17: High flow event mean concentrations and trend lines



## Figure 17 (continued): High flow event mean concentrations and trend lines

For all variables the trend is distinctly downwards for concentrations, which may be expected. In order of predicted washout rates, soluble phosphorus is highest at 98% loss from the first to the last event while nitrate is just lower at 87%. The lowest rate is for particulate nitrogen at only 13%. The graphs show the trends quite strongly, particularly for the soluble variables. The data for particulate phosphorus and nitrogen is far more scattered and not as clear. What these graphs show is that over a period of 17 months, the mean concentrations for the high flow events decreased significantly, more so for the soluble nutrient forms than for the insoluble forms. By applying the equations for a further 8 periods, which would be approximately equivalent to a year from the cessation of monitoring, the predicted nutrient concentrations may be seen from the graphs. For soluble phosphorus, nitrate and soluble Kjeldahl nitrogen, the concentrations would have decreased to far lower levels, but the concentrations for particulate phosphorus and nitrogen would still be high, indicating polluted runoff. In other words, it would take about 3 years after the cessation of the particular landuse practice before runoff water was less polluted and partially rehabilitated.

# 4.9 Correlation between water quality variables

The advantage of establishing the strength of relationships between water quality variables is that if one variable can be confidently predicted from another, then sample analysis for a long term monitoring project could be significantly reduced by leaving out the analysis of certain variables. Good relationships can also be used in models for the same purpose. Further, if there is a good correlation between two variables, it implies that they probably originate from the same contaminant source or area. Accordingly, the data was examined, but separately for the low flow and high flow data sets so that any influence or variability caused by the flow rate regime would be removed.

# 4.9.1 Base flow water quality variable correlations

The correlation coefficients are given in Table 13. Those of 0.7 and above are marked in bold as they are considered to be highly significant.

	SS	PP	PN	TPF	NO3
PP	0.75				
PN	0.65	0.67			
TPF	0.16	0.02	0.38		
NO3	-0.15	-0.19	-0.31	0.29	
KNF	0.21	0.20	0.50	0.70	0.39

Only the correlations between suspended solids and particulate phosphorus and between soluble phosphorus and soluble Kjeldahl nitrogen fall into this highly significant category. Other less significant correlations are shown for particulate nitrogen with suspended solids and particulate phosphorus. The correlations between the solids associated variables is to be expected. The good correlation between soluble phosphorus and soluble Kjeldahl nitrogen, which includes ammonia indicates that they come from the same source, no doubt leaching from cattle droppings. Nitrate on the other hand does not show any significant correlation with any variable which implies some independence of the nitrate source from the other soluble nutrients. The conclusion is that particulate phosphorus and nitrogen could be estimated from suspended solids and soluble phosphorus estimated from soluble Kjeldahl nitrogen or vice versa.

# 4.9.2 High flow water quality variable correlations

The correlation coefficients determined for the high flow data set are given in Table 14. Surprisingly, there are only two highly significant relationships shown, namely between suspended solids and particulate nitrogen and between soluble phosphorus and soluble Kjeldahl nitrogen. This is similar to the finding for the base flow data set, but in this case since the nutrients originate from the catchment surface by washoff and solubilisation of deposits, thus having similar sources, higher correlation coefficients were expected. A reason no doubt is due to the pollutants washing off at different times during the hydrographs, as can be seen in Figures 4 to 26. As a consequence, correlation analysis was performed on the individual events to investigate this apparent anomaly. Results for all correlations are given in Table 15.

ALL EVENTS	SS	PP	PN	TPF	NO3
PP	0.50				
PN	0.94	0.57			
TPF	-0.03	0.12	0.05		
NO3	-0.04	0.13	0.13	0.12	
KNF	0.12	0.23	0.11	0.82	0.35

## Table 14: Correlation analysis between water quality variables during high flow

EVENT 1	SS	PP	PN	TPF	NO3
PP	0.90				
PN	0.98	0.86			
TPF	0.84	0.87	0.80		
NO3	0.56	0.74	0.52	0.88	
KNF	0.73	0.86	0.65	0.93	0.93
EVENT 2	SS	PP	PN	TPF	NO3
PP	0.16				
PN	0.22	-0.15			
TPF	0.56	-0.39	0.80		
NO3	0.53	-0.33	0.80	0.90	
KNF	0.54	-0.38	0.85	0.98	0.96
EVENT 3	SS	PP	PN	TPF	NO3
PP	0.90				
TPF	0.54	0.61			
EVENT 4	SS	PP	PN	TPF	NO3
PP	0.61				
PN	0.89	0.56			
TPF	0.48	-0.08	0.56		
NO3	0.21	-0.13	0.27	0.79	
KNF	0.58	0.52	0.55	0.69	0.51

## Table 15: Correlation analysis between water quality variables for individual events

EVENT 5	SS	PP	PN	TPF	NO3
PP	0.72				
PN	0.96	0.75			
TPF	0.79	0.50	0.73		
NO3	0.40	0.11	0.33	0.28	
KNF	0.80	0.56	0.71	0.94	0.36
EVENT 6	SS	PP	PN	TPF	NO3
PP	0.77				
TPF	0.70	0.41			
NO3	0.00	0.42		-0.28	
EVENT 7	SS	PP	PN	TPF	NO3
PP	0.99				
PN	0.99	1.00			
TPF	0.31	0.38	0.37		
NO3	-0.74	-0.68	-0.68	0.21	
KNF	-0.25	-0.17	-0.17	0.72	0.70
EVENT 8	SS	PP	PN	TPF	NO3
PP	0.97				
PN	0.98	0.96			
TPF	-0.25	-0.20	-0.31		
NO3	-0.38	-0.37	-0.38	0.52	
KNF	0.37	0.40	0.37	0.47	0.20
EVENT 9	SS	PP	PN	TPF	NO3
PP	0.81				
PN	0.88	0.93			
TPF	0.56	0.79	0.85		
NO3	-0.26	0.23	0.17	0.51	
KNF	0.26	0.57	0.65	0.92	0.73
EVENT 10	SS	PP	PN	TPF	NO3
PP	0.99				
PN	0.99	0.99			
TPF	0.20	0.21	0.21		
NO3	-0.50	-0.52	-0.50	0.04	
KNF	-0.12	-0.11	-0.09	0.71	0.04
EVENT 11	SS	PP	PN	TPF	NO3
PP	0.96				
PN	0.63	0.66			
TPF	-0.10	-0.15	-0.37		
NO3	-0.59	-0.72	-0.39	0.55	
KNF	-0.20	-0.29	-0.48	0.94	0.58
EVENT 12	SS	PP	PN	TPF	NO3
PP	0.99				
TPF	-0.60	-0.66			
NO3	-0.48	-0.51		0.79	

Table 15 (continued): Correlation analysis between water quality variables for individual events

As before, coefficients of 0.7 and above are marked in bold as being highly significant. In contrast to the few good relationships shown for the base and high flow data sets, there are many more high coefficients shown for individual events, some even as high as 0.99 to 1. These good correlations are shown between the solids related variables, suspended solids, particulate phosphorus and particulate nitrogen. For the soluble nutrients, phosphorus and Kjeldahl nitrogen show seven highly significant relationships out of a possible nine. Event 1 has the highest number of significant correlation coefficients between the variables, in fact twelve out of a possible maximum of fifteen. On the other hand, events 4 and 11 only have two significant coefficients each out of the maximum of twelve. This shows appreciable inconsistency in variable relationships between events, which is the reason for the low coefficients for the data set as a whole. Another factor possibly contributing to the low coefficients could be the temporal trends of diminishing concentrations in the runoff both at low and high flow which was shown earlier.

# 5. DISCUSSION

## 5.1 Comparison with runoff from other rural catchments

To place the poor water quality of runoff from this particular landuse, which could in loose terms be described as a disused feedlot, into perspective, a comparison is made with the water quality and loads calculated for other rural catchments where similar measurements have been made. As mentioned earlier, two catchments at Cedara Agricultural college and two in Zululand were reported on in WRC Report 237/91. The initial results for this catchment were also reported, which are now updated. The results for a small grassland catchment at Ntabamhlope which was monitored at the same time as a control are included.

The two Cedara catchments were mostly under timber, the main differences being that one also contained some smallholdings where farming activities were carried out, while the other only had timber plantations. Another major difference was that the timber only landuse catchment had a much higher average slope and therefore a greater erosion potential. The Zululand catchments which are close to the University of Zululand are very similar in size with similar topographical features, but they had a major landuse difference. The one was part of a nature reserve with no human habitation while the other was open to subsistence farming, typical of the rural African living style with some cattle and edible crops. Some commercial sugarcane growing also took place in this catchment. Details of the catchments including the one under study are given in Table 16 for comparison.

	Cedara		Zululand, Ntuze		Ntabamhlope	
Catchment	U2H016	U2H018	W1H016	W1H031	V1H028	V7H010
Area, km <sup>2</sup>	5.25	1.31	3.23	3.19	0.41	0.08
Average slope, %	16.4	29.2	22.0	20.0	13.0	10.0
Forestry, %	56.8	77.2	13.0	28.0	0	0
Scrub & veldt, %	31.8	22.8	84.0	72.0	100	0
Smallholdings, %	11.4	0	0	0	0	0
Subsistence Farming, %	0	0	3.0	0	0	0
Feedlot (disused), %	0	0	0	0	0	100

## Table 16: Catchment physical characteristics

The mean runoff water quality for each catchment and the calculated export coefficients are given in Tables 17 and 18 for comparison where the results for this study are marked in bold. Since the samples for the Zululand catchments mainly consisted of flow event samples, the results are biased in favour of high values and are not truly representative, but they nevertheless still serve a purpose for comparison with the results for the current study. As may be seen, the nutrient concentrations for the disused feedlot catchment are very much higher than those for any of the other landuse catchments, in fact more than an order of magnitude for some constituents. This is particularly true for soluble and total phosphorus concentrations which is usually the limiting nutrient for algal growth and eutrophication in impounded waters. The calculated export coefficients show the same pattern. To show more clearly the great difference in phosphorus export coefficients, the coefficients for the other catchments are given as fractions of those calculated for the disused feedlot in Figure 18.
It is clear that runoff from a catchment such as the one studied, a disused feedlot, which is a common practice carried out in many farming communities with cattle, could have a significant impact on receiving streams and rivers by increasing the nutrient concentrations and promoting eutrophication. As a rough estimate, the runoff would need to be diluted at least 100 times in receiving waters in order to lower the phosphorus concentration to more normal and acceptable levels and not be a threat to water quality.

Runoff from such landuse practices should be treated to prevent pollution. A common method advocated is to collect and divert runoff to holding ponds where settlement and biological processes can take place to reduce nutrient concentrations, while overflow could be prevented by irrigation of pastures. Diversion of runoff onto vegetative strips or into wetlands is also advocated where uptake of nutrients can take place to improve water quality.

	Cec	lara	Zululan	d, Ntuzi	Ntabamhlope		
Catchment	U2H016	U2H018	W1H016	W1H031	V1H028	V7H010	
SS, mg/ℓ	29	35	120	85	150	225	
TPF, µg/ℓ	21	16	17	10	39	879	
TPU, µg/ℓ	49	48	107	89	68	1627	
NO3, µg/ℓ	333	521	256	110	77	4138	
KNF, µg/ℓ	266	231	392	416	469	2177	
KNU, μg/ℓ	434	430	1253	1355	720	4607	

Table 17: Comparison of mean runoff water quality between catchments

#### Table 18: Comparison of export coefficients between catchments, kg/ha/a

	Ceo	iara	Zululan	d, Ntuzi	Ntabamhlope		
Catchment	U2H016	U2H018	W1H016	W1H031	V1H028	V7H010	
SS	35	82	481	428	303	301	
TPF	0.025	0.037	0.07	0.05	0.08	1.18	
TPU	0.058	0.112	0.43	0.45	0.14	2.18	
NO3	0.40	1.22	1.03	0.55	0.16	5.53	
KNF	0.32	0.54	1.57	2.09	0.95	2.91	
KNU	0.52	1.01	5.03	6.82	1.46	6.16	

#### Figure 18: Soluble and total phosphorus export coefficients as fractions of disused feedlot (this study) coefficients



### 6. RECOMMENDATIONS FOR FURTHER RESEARCH

This study has emphasised the fact that a seemingly innocuous and fairly common landuse practice, that is concentrating cattle on a piece of landuse to feed them can result in highly polluted runoff, particularly for the algal promoting nutrients, phosphorus and nitrogen. This fact would not have been discovered unless automatic monitoring equipment had been installed to sample continuously. It is therefore essential that for future research on the effect of landuse upon runoff water quality that automatic monitoring systems be installed. The database on the different landuse effects on water quality needs to be expanded using these techniques so that when planning for or managing a catchment, informed decisions can be taken in the knowledge of accurate information on mean baseflow and stormflow runoff water quality and export coefficients of pollutants, as only then can the effect on receiving water quality be gauged. With such reliable landuse information, it will be relatively easy to predict runoff water quality and pollutant loads for a new catchment either holistically or for sub-catchments, if required. Predictions, however, will only be as good as the quality of the input data.

The investigation showed that there were strong, linear regression relationships between the solids associated pollutants and flow rate, but that for the soluble constituents such direct relationships were not as clear. Rather, in these cases there appeared to be a delayed rise in concentrations after the peak flow had been reached. This is a challenge to the modelling fraternity to build in algorithms to replicate such behaviour, ie: leaching of nutrients from surface deposits, but not in a direct relationship to flow rate. The kinetics of solubility rates would have to be considered. However, the data that have been collected in this study can be used as calibration data for existing models or for the development and testing of model algorithms for prediction of runoff concentrations. Models need not, however, be deterministically based such as the HSPF simulation model, but could be simpler and export coefficient based, which would intuitively be more reliable.

### SUMMARY AND CONCLUSIONS

- The runoff water quality during stormflow had very much higher pollutant concentrations than during baseflow. For suspended solids, soluble phosphorus, ammonia and total Kjeldahl nitrogen, concentrations were 38, 37, 5 and 6 times greater respectively. The exception was conductivity, which as a measure of dissolved salt concentrations had similar means for both flow regimes. The 75<sup>th</sup> percentile concentrations of the nutrients, nitrogen and phosphorus, during high flow were of the same order of magnitude as that found in domestic sewage.
- 2. Calculation of loads of pollutants delivered during both flow regimes showed that more than 90% of the annual suspended solids, soluble and total phosphorus loads and slightly lesser percentages, about 70%, of ammonia and Kjeldahl nitrogen were contributed during high flows. Conversely, approximately 55% of the nitrate and 65% of the total dissolved salts load, calculated from conductivity, were delivered during baseflow. The annual baseflow volume was approximately double that of the high flow volume during the study period.
- To obtain meaningful results for mean water quality and export coefficients of pollutants from a catchment, it is essential to sample runoff continuously throughout baseflow and particularly during high flow events when surface runoff occurs, preferably on a volume of runoff than on a fixed time basis.
- 4. Correlation analysis between flow rate during runoff events and the different variable concentrations showed that suspended solids and the particulate forms of phosphorus and nitrogen had fairly direct relationships to flow, rising and falling concentrations in unison with flow. For the soluble constituents, dissolved salts, phosphorus, nitrate, ammonia and Kjeldahl nitrogen, delayed responses to flow sometimes peaking well after the flow peaks were found. The cause may in part be due to the time taken for rainfall to leach nitrogen and phosphorus from solids present on the catchment surfaces.
- 5. To derive relationships that may be used in models, regression analysis of variable concentrations during runoff events on flow was investigated. The strength of the relationships as given by the R<sup>2</sup> values, the variance explained by the regression equations, was high for most events for suspended solids and to a lesser extent for particulate phosphorus and particulate nitrogen, but the R<sup>2</sup> values were significantly lower when the data for all events were combined. The reason was due to rather different x-coefficients and constants being obtained for individual event equations, indicating changing conditions with time on the catchment. Nevertheless, after elimination of some data that intuitively did not fit, most of the data were used to derive regression equations for the prediction of suspended solids and particulate phosphorus and

nitrogen concentrations from flow rate for general use for this particular landuse activity. A relationship for prediction of soluble phosphorus from flow was derived by using the first six events only, as the remaining events showed a sudden dramatic fall in concentration levels. This was also evident for nitrate and soluble Kjeldahl nitrogen.

- 6. Trend analysis was carried out on the low flow and high flow data sets as it was evident from graphing the data that soluble nutrient concentrations were falling with time, due no doubt to washout of the store of nutrients from the catchment which were not being replenished. For baseflow, the trend equations fitted showed that concentrations of nitrate and soluble phosphorus had decreased by 98% and 83% respectively from the beginning to the end of the monitoring period, but that the decreases for soluble Kjeldahl nitrogen and particulate phosphorus and nitrogen were significantly less at from 23% to 31%. Prediction by extension of the trend lines indicated that it would take at least 4 to 5 years from the cessation of the landuse activity (cattle feeding) before baseflow runoff water quality returned to more normal concentrations. A similar analysis with the high flow data using event mean concentrations showed that soluble phosphorus, nitrate and soluble Kjeldahl nitrogen concentrations had fallen 98%, 87% and 77% respectively, while particulate phosphorus and nitrogen the runoff water was less polluting and partially rehabilitated. These data clearly illustrate the relatively long term effect that such a landuse may have on runoff water quality.
- 7. Correlation analysis between water quality variables for the low flow data set showed that only two were highly significant, namely between suspended solids and particulate phosphorus and between soluble phosphorus and soluble Kjeldahl nitrogen. Lower coefficients were obtained between suspended solids and particulate nitrogen and between the two particulate nutrient forms. For the high flow data set, two high coefficients were also only obtained, in this case between suspended solids and particulate nitrogen and between soluble phosphorus and soluble Kjeldahl nitrogen. Correlation analysis between the variables for individual events showed that high coefficients were far more numerous and generally higher, but also that there was inconsistency between events. The conclusion is that variable concentrations may be predicted from one another for particular runoff events, but not for all variables in the data set, where only the ones indicated above could be predicted with any confidence.
- 8. Comparison of the mean runoff water quality and export coefficients found for this landuse with those found for rural, forestry and subsistence farming landuse catchments that had been investigated in a similar manner, showed that the nitrogen and phosphorus concentrations for the study catchment were far higher than any of the other ones, in fact an order of magnitude higher for some variables. Similarly, the export coefficients were also far higher, as an example the soluble phosphorus export coefficient was 15 times greater than the highest for the other landuses. Runoff from this type of landuse can be highly polluting to receiving waters and will promote eutrophication in impoundments. It would need to be diluted at least 100 times to reduce the pollution potential. Clearly, such runoff needs to be contained and treated by various means such as the use of holding ponds, irrigation or diversion onto vegetative strips or wetlands in order to mop up and stabilise nutrients.

### 8. REFERENCES

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APPENDIX A

VARIATION IN WATER QUALITY VARIABLES WITH FLOW FOR EVENT NUMBERS 2 TO 12



Event 2 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow







Event 3 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 4 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 4 - Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 5 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 5 - Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 6 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow







Event 7 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow







Event 8 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 8 - Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 9 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 9- Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 10 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 10- Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 11 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 11- Variation in nitrate, ammonia, soluble Kjeldahl nitrogen and particulate nitrogen quality with flow



Event 12 - Variation in suspended solids, conductivity, soluble and particulate phosphorus quality with flow



Event 12- Variation in nitrate and ammonia quality with flow

# APPENDIX B

# LOW FLOW WATER QUALITY DATA

Units for variables: COND - mS/m TURB - NTU SS - mg/\ell TPF, PP, TPU, NO3, NH3, KNF, KNU, PN - µg/ℓ

DATE	SS	TURB	COND	TPF	TPU	PP	NO3	NH3	KNF	KNU	PN
01027	16	12	39.3	44	172	128			681	1249	568
01029	11	11	43	49	188	139			811	1349	538
01031	21	18	44	60	196	136			753	1306	553
01205	52	28	32.4	113	543	430		71	1195	2936	1741
01213	28	4.3	32.5	94	224	130	1726		820	1788	968
01217	25	2.4	31.2	59	192	133	1538		801	1469	668
10116	10	6.2	32	78	180	102					
10119	30	9	34.7	53	230	177					
10119	70	20	32	216	584	368					
10120	16	6.8	27.2	222	261	39					
10120	10	6.5	28.1	147	219	72					
10121	11	4.5	26.2	109	125	16					
10122	9	4	28.7	60	93	33					
10124	13	4.6	31.1	90	137	47	2241	50	952	1128	176
10125	22	5	30.9	103	171	68	2297	41	1124	1558	434
10201	28	15	21.8	423	446	23	2360	73	2399	4751	2352
11015	13	3.7	26.9	64			70	1627		566	566
11017	4	1.5	31.9	114	171	57	5214	224	842	1071	229
11020	8	3	31.3	143	214	71	5214	166	1481	1684	203
11021	4	2.2	63.5	243	329	86	26772	201	2806	2959	153
11021	4	1.8	51.4	143	186	43	16627	241	2041	2066	25
11029	13	1.7	34.2	29	86	57	3153	67	879	1101	222
11109	19	2.3	37.6	37	100	63	2013	14	736	947	211
11114	16	4.2	33.6	122	189	67	3580	19	1283	1489	206
11115	13	3.2	30.8	75	77	2	3287	12	938	1211	273
11115	53	8.7	27.4	87	306	219	2741	12	878	1634	756
11116	8	4	29.2	128	167	39	2741	44	1084	1211	127
11116	13	3.9	30.3	131	158	27	2692	44	950	1029	79
11117	8	2.9	32.6	36	96	60	3133	59	678	705	27
11118	4	2.2	27.3	17	51	34	2472	128	714	754	40
11119	5	2	31.9	22	67	45	3108	69	630	692	62
11122	6	1.5	36.7	27	69	42	5005	67	509	564	55
11202	9	3	38.1	29	77	48					
11205	16	3.5	37.1	42	77	35					
11208	8	2.6	38.4	26	64	38			-	-	
20102	7	3.7	26.5	77	170	93	3735	9	1211	1479	268
20104	10	1.7	29.1	39	67	28	3979	19	716	898	182
20106	7	1.5	33.8	27	54	27	4936	6	602	710	108
20120	17		46.6	63	141	78	5189		621	878	257
20304	29	33	47.8	81	312	231	5454	587	2964	4980	2016
20304	33	27	47.4	44	324	280	5535	18	1518	2585	1067
20305	52	22	47.4	25	374	349	8031	15	972		
20416	19	4.5	51.4	20	32	12	9094	15	397	427	30
20513	22	1.2	46.1	9	29	20	9530	187	756	897	141
20517	2	0.8	51.9	7	13	6	7821	43	462	474	12

## APPENDIX B (CONTINUED)

PN	KNU	KNF	NH3	NO3	PP	TPU	TPF	COND	TURB	SS	DATE
147	542	395	69	8337	5	22	17	52		1	920604
166	461	295	24	7603	12	14	2	51.6		2	920616
646	1333	687	18	2296	58	68	10	50.6		6	920806
967	1384	417	38	9	101	110	9	59.3		15	920903
1977	3422	1445	16	7	640	677	37	35.7	6.2	71	921119
148	1216	1068	9	493	109	162	53	36.2	4	18	921127
945	2483	1538	68	212	148	226	78	29.7	15	28	930129
612	1888	1276	53	75	84	162	78	26	3	22	930130
700	1836	1136	11	18	174	252	78	29.3	1	14	930201
			12	22	157	188	31	37.9	4.1	20	930206
			47	90	81	125	44	27.8	12	4	930208
			41	47	53	94	41	29	7.6	4	930208
			45	96	54	86	32	34.4	5.3	2	930208
			53	290	49	71	22	37.9	3.5	2	930209
			12	141	64	94	30	33.5	4.4	2	930209
			107	130			25	37.6	3	2	930209
			57	127	92	107	15	38.6	2.5	2	930210
294	1060	766	84	1781	26	45	19	40.8	2.6	12	930225
687	1707	1020	272	1766	134	151	17	38.8	18	76	930227
455	1580	1125	156	3558	89	134	45	49	9	30	930307
235	1115	880	222	3610	1	26	25	49.4	4.5	7	930319

### APPENDIX C

### RUNOFF EVENT WATER QUALITY DATA FOR INDIVIDUAL SAMPLES

Units for variables: COND - mS/m TURB - NTU

SS - mg// TPF, PP, TPU, NO3, NH3, KNF, KNU, PN + µg//

VENT	DATE	TIME	SN	FLOW	55	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	PN
1	901031	14.4	5	3E-04	21	18	44	60	136	196	11		753	1306	553
	901101	14.01	6	0.008	98	26	37.4	55	273	328	519		767	1672	905
	901101	14.14	7	0.044	1645	160	67.2	3916	6264	10180	16333		7299	24645	17346
	901101	14.21	8	0.038	1733	160	81.6	5711	5710	11421	24552		9308	25248	15940
-	901101	14.32	9	0.029	1303	170	88.3	4747	7064	11811	27086		9760	22234	12474
	901101	14.51	10	0.009	1040	170	91.2	4228	7037	11265	28742		10162	19822	9660
	901101	16.19	11	0.002	633	150	89.3	4586	4789	9375	28463	-	9409	14498	5089
	901102	3.27	12	4E-04	285	135	78.7	2916	1912	4828	25927	-	7148	10815	3667
	901102	19.35	13	3E-04	106	55	68.2	2875	483	3358	18347	-	5691	7700	2009
	901103	15.29	14\15	3E-04	120	53	70.1	1623	2661	4284	18714	-	5540	8102	2562
	901104	23.15	16117	4E-04	50	28	57.6	1021	717	1738	11777	-	1059	5691	4622
	901106	7.2	18119	4E-04	37	25	56.6	791	524	1315	9167		4499	4988	489
-	DATE	TIME	SN	FLOW	SS	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	PN
2		19.33	1	0.002	52	28	32.4	113	430	543	79	71	1195	2936	1741
£	901205	20.49	2	0.009	126	27	67.7	2963	30750	33713	6097	298	6552	9104	2552
	901205	21.13	3	0.016	150	16	104.1	6574	916	7490	12149	643	12354	14761	2407
	901205	21.13	4	0.015	154	13	117.6	7735	1550	9285	11587	713	13479	16381	2902
				0.015	134							808			2849
	901205	21.54	5			12	128.6	9398	968	10366	13294		15373	18222	
	901205	22.29	6	0.008	100	11	136.2	9182	1309	10491	11932	769	15230	18798	3568
	901205	23.33	7	0.002	110	11	139.6	7693	1237	8930	12685	700	14667	17768	3101
	901206	1.58	8	0.002	88	10	133.7	6213	926	7139	14593	617	13479	16748	3269
	DATE	TIME	SN	FLOW	55	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	PN
3		15.57	3	0.008	30	9	34.7	53	177	230					
	910119	17.25	4	0.013	70	20	32	216	368	584					
	910119	18.07	5	0.04	133	17	41.7	3374	948	4322					
	910119	18.32	6	0.042	67	8	32	2663	183	2846					
	910119	19.02	7	0.024	71	5	50.4	5401	645	6046					
	910119	19.39	8	0.026	73	2.5	67.9	6972	381	7353					
	910119	20.31	9	0.015	50	2.7	67.9	5376	484	5860					_
	910119	21.4	10	0.013	43	2	66.9	5284	334	5618					
	910119	23.54	11\12	0.008	36	3.6	68.9	2712	331	3043					
	910120	4.31	13\14	0.007	33	7	57.2	1300	272	1572					
	910120	12.32	15\17	0.003	16	6.8	27.2	222	39	261					
	910120	23.1	18\20	0.003	10	6.5	28.1	147	72	219					
	910121	18.34	21\24	0.003	11	4.5	26.2	109	16	125					
	910122	20.32	25\28	0.002	9	4	28.7	60	33	93					
	DATE	TIME	SN	FLOW	55	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	PN
4	910124	18.57	1\3	0.002	13	4.6	31.1	90	47	137	2241	50	952	1128	176
	910125	13.12	4/6	0.003	22	5	30.9	103	68	171	2297	41	1124	1558	434
	910126	1.36	7	0.058	284	4.8	47.4	1253	5898	7151	2995	55	8070	9997	1927
	910128	1.46	8	0.147	708	8.1	41.7	5974	3811	9785	2387	73	7026	12728	5702
	910128	1.52	9	0.185	703	7.9	42	7916	3809	11725	2518	50	6745	12005	5260
-	910126	1.57	10	0.228	680	34	43.5	9857	2221	12078	3749	46	7428	12406	4978
	910126	2.01	11	0.223	533	33	43.2	9712	3281	12993	4482	105	7428	14093	6665
	910126	2.06	12	0.228	433	35	42.5	10367	1541	11908	4887	64	7347	10800	3453
_	910126	2.1	13	0.217	393	38	42.3	10294	1643	11937	5654	78	6946	10078	3132
		2.15	14\15	0.18	338	3.9	43.9	10890	815	11705	4836	46	6793	10230	3437
	910126						45.4	10890	941	11831	4546	128	6793	9620	2627
-	910126		16\17	0.151	290	371					1.00				
_	910126	2.26	16\17	0.151	290	37	the second se			10380	3869	82	6729	9010	2281
	910126 910126	2.26	18\19	0.142	200	28	43.8	9234	1146	10380	3869	82	6729	9010	2281
	910126	2.26	the second se			_	the second se			10380 9559 6972	3869 3669 3000	82 50 46	6729 6793 7444	9010 8849 7942	2281 2056 498

# APPENDIX C (CONTINUED)

EVENT	DATE	TIME	SN	FLOW	55	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	PN
5	910131	14.12	1	0.109	454	90	19.9	845	2377	3222	1644	139	6222	7805	1583
	910131	14.2	2	0.18	1238	100	28.9	5863	6179	12042	1387	471	8484	21267	12783
	910131	14.25	3	0.217	1540	100	34.3	8292	6391	14683	504	2114	10068	26471	16403
	910131	14.3	4	0.217	1755	115	34.3	7764	6285	14049	507	2334	9276	24434	15158
	910131 910131	14.34	6	0.217	1583	125	34.6	7870	4541 3348	12411 11429	16135 6150	2323	10407 10068	25000	14593
	910131	14.45	7	0.156	1310	135	34.6	7606	3376	10982	12846	2141	9502	19444	9942
	910131	14.52	8	0.147	1038	145	34.6	7236	2764	10000	10583	2384	10068	17593	7525
	910131	14.59	9	0.113	1018	150	33.8	7606	2126	9732	831	2106	8937	16358	7421
	910131	15.08	10	0.106	765	170	33.8	6761	1810	8571	734	2164	9163	14506	5343
	910131	15.19	11	0.085	615	150	36.4	7658	3503	11161	916	2350	8937	15432	6495
	910131	15.34	12	0.061	555	150	35.4	7342	962	8304	1341	1998	8824	12654	3830
	910131	15.55	13	0.044	348	110	35.4	6496	1361	7857	1380	1651	8824	11420	2596
	910131	16.25		0.026	138	65	26.2	2852	3718	6570	2360	58	5401	5769	368
	910131	18.05	16\18	0.016	123	50	33.8	3856	4209	8065	2254	39	7253	7353	100
	910131	20.09		0.018	60	26	30	2641	190	2831	1911	31	5401	6335	934
	910131	23.28		0.015	50	26	33.3	2060	192	2252	2306	69	4865	6109	1244
	910201	4.31	25-28	0.008	28	15	21.8 COND	423 TPF	23 pp	446	2360	73 NH3	2399 KNF	4751 KNU	2352 PN
6	910206	22.49	SN 115	0.106	240	TURB 19	34.4	4873	1643	6516	NO3 3873	NP13	P.NP	nniu	PN
	910206	4.44	_	0.024	240	15	34.4	4146	78	4224	2089				
	910207	21.1	11\14	0.008	47	8.1	42.6	3679	393	4072	2593				
	910208	17.37	15	0.056	71	4.5	37.2	5365	470	5835	1194				
	910208	18.31	16	0.04	109	17	45.4	9096	645	9741	1331				
	910208	20.04	17	0.027	69	15	40.2	6275	596	6871	1443				
	910208	20.4	18	0.151	246	20	37.2	9074	648	9722	1195				
	910208	20.57	19	0.156	366	56	33	8397	1207	9604	1252				
	910208	21.13	20	0.142	271	57	32.6	8769	804	9573	1459				
	910208	21.32	21	0.109	157	45	26	5341	525	5866	1255				
	910208	21.58	22	0.079	65	23	19.3	2181	435	2616	803				
	910208	22.42	23/24	0.04	55	22	22.3	2626	393	3019	1380				
	910209	1.28		0.024	41	16	26.2	1740	374	2114	2323	B/847	W MIE	KNU	PN
7	911021	16.08	SN 7/0	FLOW 0.002	55	1.8	COND 51.4	143	43	186	NO3 16627	241	2041	2066	25
	911022	23.12	10	0.137	1596	45	20.1	286	4143	4429	6482	669	1403	14286	12883
	911022	23.17	11	0.137	1780	87	15.1	357	5214	5571	4509	689	1276	14541	13265
	911022	23.22	12	0.106	1036	51	15.4	571	3429	4000	14091	785	2423	10204	7781
	911022	23.28		0.113	3108	160	24.3	1571	12000	13571	8595	1078	2806	34949	32143
	911022	23.34	14	0.129	2600	180	28.9	1786	9330	11116	13105	1058	4847	30570	25723
	911022	23.4	15	0.113	1724	180	34.1	2143	6027	8170	16064	1262	4974	20207	15233
	911022	23.46	16	0.085	1808	190	31.3	2000	6705	8705	12682	1221	3699	21762	18063
	911022	23.56		0.061	1272	180	33.4	2000	4429	6429	14091	1099	3699	16062	12363
	911023	0.1		0.038	552	84	39.7	1929	2357	4286	18741	875	4592	10104	5512
	911023	0.35	19	0.017	388	53	44.8	2000	1482	3482	32550	1424	4847	8031	3184
	911023	1.18	20	0.015	44	12	56	1571	36	1607	31564	936	4974	5959	985
	911023	_	21/22	0.008	4	7.9	51.8	929	42	971	21418 31705	663 895	4714 4592	4858 4793	201
	911023 911023		23/24 25/26	0.015	4		51.4	_	16	1038	20009	523	4592	4016	508
	911023		27/27	0.008	3	2.7	64.4	786	18	804	24377	349	3890	4469	579
	DATE	TIME	SN		55	TURB	COND		pp	TPU	NO3	NH3	KNF	KNU	PN
8		5.15	_	4E-04	19	2.3	37.6		63	100	2013	14	736	947	211
	911109	19.42		0.088	1303	77	21.6	80	3320	3400	2082	6	1511	12315	10804
	911109	19.5	3	0.082	1314	70	18.3	106	3394	3500	1412	2977	6042	17857	11815
	911109	20.02	4	0.034	813	61	14.4	106	2544	2650	1451	1908	5385	12192	6807
	911109	21.25		0.003	194	27	19.3		1277	1410	2127	514	2233	4926	2693
	911110	1.35		0.002	47	8.9	24.8		323	350	572	540	1773	3017	1244
	911111	20.5		3E-04	23	3.4	28.8		173	200	474	32	985	1478	493
	911111	21.48		0.106	764	52	15.9		1747	1800	1595	543	2758	9360	6602
	911111	21.53		0.147	1108	83	10.6		2297	2350	1373	1408	4335	12129	7794
	911111	21.58		0.109	1028	93	9.4		2694	2800	1399	580	2102 2627	10468	8366 4393
	911111 911111	22.04		0.082	360	59	42.3		1787	2000	2549	776	2998	4926	4393
	911111	22.1/		0.04	330	59	61.8		1027	1800	3856	336	4203	4920	1928
	911111	22.39		0.024	222	59	_	-	803	2000	2510	672	4532	6096	1564
	911112		16/17	0.007	84	27	29.6		345	1223	3725	638	4860	6699	1839
	911112		18/20	0.008	58	15	30.3		212	638	5101	9	3612	4926	1314
	911112		21/23	0.003	17	6.9	28.8		103	191	3912	80	2099	2680	581
	911113		24/28	0.002	16	4.7	27.1		53	64	2654	75	1235	1445	210
_	_		_			_	_			_					

### APPENDIX C (CONTINUED)

EVENT	DATE	TIME	SN	FLOW	55	TURB	COND	TPF	pp	TPU	NO3	NH3	KNF	KNU	PN
9	911114	19.24	1	0.002	16	4.2	33.6	122	67	189	3580	19	1283	1489	206
	911115	3.51	2	0.002	13	3.2	30.8	75	2	77	3287	12	938	1211	273
	911115	8.29	3	0.027	53	8.7	27.4	87	219	306	2741	12	878	1634	756
	911115	8.5	4	0.061	254	29	19.1	138	117	255	1860	12	932	2421	1489
	911115	9.15	5	0.026	406	73	27.1	786	1204	1990	3108	34	2179	5811	3632
	911115	10.08	6	0.016	194	48	27.8	724	449	1173	2888	31	2567	4479	1912
	911115	11.48	7	0.007	50	16	40.9	796	326	1122	4283	50	3414	5085	1671
	911115	14.12	8	0.008	36	12	43.6	592	445	1037	4650	44	3196	4600	1404
	911115	16.32		0.007	16	7.8	37.9	347	170	517	3745	53	2143	3208	1065
_	911115		11/12	0.006	8	4.5	29.3	202	44	246	3010	50	1308	1544	236
	911116		13/14	0.003	8	4	29.2	128	39	167	2741	44	1084	1211	127
	911116 911117	_	15/17	0.002	13	3.9	30.3	131	27	96	2692	44	950 678	1029	79
	911118		18/20 21/24	0.003	4	2.9	27.3	17	34	51	2472	128	714	754	40
	911119				5		31.9	22	45	67	3108		630		62
	DATE	TIME	25/28	0.002	55	2 TURB	COND	TPF	PP	TPU	NO3	69 NH3	KNF	692 KNU	PN
10		13.59	SN	FLOW 2E-04	23	2.7	40.9		93	135	5309	11	the second second	11111	446
10		_	6		1860	75		42		4105			665		
	920101	19.24		0.142			13.4		3933		1550	337	1066	13720	12654
	920101	19.33	8	0.142	2312	140	10	758	6141	6899 7567	1362	746	1551	23527	21976
	920101 920101	19.41	9	0.185	2628	150	9	1097	5969	7066	1128	540 597	1306	21643 19758	20337
	920101	19.48		0.196	1552	160	9.4	935	3375	4310	3523	609	1439	19/58	18319
	920101	20.03	11	0.175	1046	140	12.2	1525	2310	3835	2584	631	1/18	9155	7293
			_				14.7	2052		3655					
-	920101 920101	20.13	13	0.151	658 728	80	14.7	2052	1603	4150	3805	617 563	2564	8140	5576
							_		2005	2306		437		5266	
	920101	20.33	15	0.085	415	39	11.2	1363			2795	_	1590	3484	3676
	920101	20.5	16	0.064	198	28	8.6	1306	631 391	1937	2490	366 237	1395	2421	1026
	920101	21.13	17	0.038	80	15		629		679	1292		1751	2566	815
	920101	_	18	0.027	51	15	9.3	451	228		940	209			
	920101	and the second se	19/20	0.024	36	7.5	12.4	278	144	422 310	2607	220	1840	2494	654
	920102 920102		21/22	0.013	18	8.2	14.9	260	50	239	3195	166	1885	1890	669
	920102		23/25 26/28	0.008	33	4.7	19.8	77	134	170	3735	9	1211	1479	406 268
	DATE	TIME	20/20 SN	0.003 FLOW	55	TURB	COND	TPF	PP	TPU	NO3	NH3	KNF	KNU	200 PN
11	920301	7.25	3	0.001	748	130	40.3	37	3016	3053	285	12	996	15652	14656
	920302	1.51	4	6E-04	195	41	45.9	12	455	467	7445	12	949	3676	2727
	920302	22.42	5	0.004	576	170	30.8	31	2399	2430	1567	12	806	12332	11526
	0.0.0.0 M													1.0.000	
	920303						27.7	37	1832	1860	21371	12	830	9960	9130
	920303	8.29	6	0.003	310	63	27.7	37	1832	1869	2137	12	830 4585	9960 11621	9130 7036
	920303	8.29	6	0.003	310 492	63 190	40.6	249	1620	1869 1869 841	8125	156	4585	11621	7036
	920303 920303	8.29 11.49 16.19	6 9 11	0.003 0.01 0.005	310 492 96	63 190 61		249 270	1620 571	1869	8125 9477	156 12	4585 3874	11621 6462	7036 2588
	920303	8.29 11.49 16.19 19.46	6	0.003 0.01 0.005 0.004	310 492 96 47	63 190	40.6 47.8	249	1620	1869 841	8125	156	4585	11621	7036
	920303 920303 920303	8.29 11.49 16.19 19.46 0.2*	6 9 11 12 13/14	0.003 0.01 0.005 0.004 0.004	310 492 96 47 20	63 190 61 33	40.6 47.8 47.6	249 270 156	1620 571 327	1869 841 483	8125 9477 5291 4741	156 12 87	4585 3874 3059 2158	11621 6462 4506 4506	7036 2588 1447 2348
	920303 920303 920303 920304 920304	8.29 11.49 16.19 19.45 0.2* 8.2	6 9 11 12 13/14 15/16	0 003 0.01 0.005 0.004 0 004 0.003	310 492 96 47 20 29	63 190 61 33 71 33	40.6 47.8 47.6 47.4	249 270 156 100	1620 571 327 539 231	1869 841 483 639 312	8125 9477 5291 4741 5454	156 12 87 12	4585 3874 3059 2158 2964	11621 6462 4506 4506 4506	7036 2588 1447 2348 2016
	920303 920303 920303 920304	8 29 11 49 16 19 19 46 0 2* 8 2 22 19	6 9 11 12 13/14 15/16 17/18	0 003 0.01 0 005 0 004 0 004 0 004 0 003 0.003	310 492 96 47 20 29 33	63 190 61 33 71 33 27	40.6 47.8 47.6 47.4 47.8	249 270 156 100 81 44	1620 571 327 539	1869 841 483 639	8125 9477 5291 4741	156 12 87 12 587	4585 3874 3059 2158	11621 6462 4506 4506 4980 2585	7036 2588 1447 2348 2016 1067
	920303 920303 920303 920304 920304 920304	8 29 11 49 16 19 19 46 0 2* 8 2 22 19	6 9 11 12 13/14 15/16	0 003 0.01 0.005 0.004 0 004 0.003	310 492 96 47 20 29	63 190 61 33 71 33	40.6 47.8 47.6 47.4 47.8 47.8 47.8	249 270 156 100 81	1620 571 327 539 231 280	1869 841 483 639 312 324	8125 9477 5291 4741 5454 5535	156 12 87 12 587 18	4585 3874 3059 2158 2964 1518	11621 6462 4506 4506 4506	7036 2588 1447 2348 2016
12	920303 920303 920303 920304 920304 920304 920304 920305	8.29 11.49 16.19 19.45 0.2* 8.2 22.19 17.05	6 9 11 12 13/14 15/16 17/18 19/20 <b>SN</b>	0 003 0.01 0 005 0 004 0 004 0.003 0 002 0 001	310 492 96 47 20 29 33 52	63 190 61 33 71 33 27 22	40.6 47.8 47.6 47.4 47.8 47.4 47.8 47.4 47.4	249 270 156 100 81 44 25	1620 571 327 539 231 280 349	1869 841 483 639 312 324 374	8125 9477 5291 4741 5454 5535 8031	156 12 87 12 587 18 16	4585 3874 3059 2158 2964 1518 972	11621 6462 4506 4506 4980 2585 16897	7036 2588 1447 2348 2016 1067 15925
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12	920303 920303 920303 920304 920304 920304 920304 920304 920304 920304 920304 920304 920304 930210 930211 930211 930211 930211 930211 930211 930211	8.29 11.49 15.19 19.46 0.2' 8.2 22.19 17.05 TIME 9.49 20.33 20.37 20.4 20.43 20.43 20.43 20.44 20.43 20.44 20.43 20.45 120.55	6 9 111 12 13/14 15/16 17/18 19/20 <b>SN</b> 1/2 1/2 3 4 4 5 5 6 7 7 8 9	0 003 0.01 0 005 0 004 0 004 0 003 0 002 0 001 FLOW 8E-04 0 076 0 156 0 156 0 175 0 19 0 19 0 19 0 217 0 241 0 26	310 492 96 47 20 29 33 52 \$5 2 6888 4450 2760 2116 14854 1354 13572 1638 1350	63 190 61 33 27 22 <b>TURB</b> 2.5 1500 1300 1050 850 650 570 560 480	40.6 47.8 47.6 47.4 47.8 47.4 47.4 COND 38.6 8.05 5.08 4.89 4.89 4.72 4.47 4.18 4.83 5.48	249 270 156 100 81 44 25 7PF 15 5 5 14 32 24 38 42 24 38 42 44 94 121	1620 571 327 539 231 280 349 <b>PP</b> 92 6646 4252 2137 2268 1678 1573 1897 2288 2241	1869 841 483 639 312 324 374 <b>TPU</b> 107 6853 4206 3169 2292 1716 1615 1941 2382 2362	8125 9477 5291 4741 5454 5535 8031 127 137 2958 456 448 541 431 636 613	156 12 87 12 587 18 16 NH3 57 333 370 302 134 198 149 201 107 139	4585 3874 3059 2158 2964 1518 972	11621 6462 4506 4506 4980 2585 16897	7036 2588 1447 2348 2016 1067 15925
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