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Remote Sensing of Bathing Water Quality

A Thesis Submitted to Middlesex University in Fulfilment of the Requirements
for the Degree of Doctor of Philosophy

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ACKNOWLEGEMENTS

Abstract

The European Union (EU) has openly solicited advice on the development of EU bathing water quality policy and made calls for the development of remotely sensed operational real world solutions. This research demonstrates a new approach to estimating water quality using remote sensing and specifically to monitoring bathing water quality by using remote sensing to "flag" failing areas for manual survey. This method meets the environmental demands of the EU, the tourist industry, the water industry and environmental monitoring agencies throughout the world. The results show the genuine potential for a remotely sensed monitoring system that could, with further research, lead to an efficient and effective method of monitoring bathing water quality. These findings are particularly important given the imminent changes in EU Bathing Water policy, an expected increase in monitoring costs (currently estimated by the EU to be 15 million euros for 2001 (EU, 2002)) and the widespread availability of airborne sensors and satellites.

Simultaneous water quality and spectral data were collected at Southend-on-Sea pier with a Natural Environment Research Council (NERC) loaned spectroradiometer and water sampling equipment. Simultaneous data enabled the accurate analysis of the relationship between water quality and reflectance, avoiding the normal delays experienced with flown or satellite data. The thesis successfully proposes and investigates a remotely sensed flagging system for bathing water quality monitoring using both statistical and visual analysis to identify optimum wavelengths which identify threshold levels of E.coli, suspended sediments, low pH, nitrates, chlorophyll, faecal coliform and temperature.

The findings demonstrate that remote sensing could be used to monitor several of the water quality parameters that are relevant to the EU Bathing Water Directives and, in particular, the monitoring of effluent in bathing waters through the successful identification of high E.coli counts. Through the creation and integration of a localised water quality model, it demonstrates that it is possible to predict when water quality parameters exceed a threshold level through direct remote sensing or through the use of remotely sensed indirect water quality parameters. The success rate of remotely sensed "flagging" of samples above a threshold level was tested and used to yield a "predictor" rating for each parameter. Finally, a spectral physical model was constructed that identifies the parameters, wavelengths and secondary parameters that could be used to flag failing water quality areas. This model could be used to improve monitoring coverage and reduce overall costs. The application of the model, which was based on Case 2 coastal water, to other types of coastal area is suggested as needing further research before it could be widely exploited.

Remote sensing information could lead to a greater understanding of the coastal environment and offers potential near real time monitoring, allowing for the first time reactive management of coastal water quality in failing water quality areas. This would provide a solution to many of the issues raised by the EU regarding the current bathing water quality directives and provides the remote sensing community with a practical solution to a real world problem.

Dedicated to both my Hatsie, with love ....

and to the memory of my father, grandfathers and Pam Ings

who I hope would have been proud of my work ......

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CHAPTER 1

Introduction

Publicity from pressure groups campaigns such as Surfers Against Sewage's Clean Water Initiative (Surfers Against Sewage, 1999) and the availability of water quality information through local authorities, the Environment Agency, the EU and guides like 'The Good Beach Guide' have dramatically increased public awareness of bathing water quality issues. This has increased public expectation for the provision of bathing water quality information and it is now a regular topic covered by both national and local newspapers during the holiday season. In the last two Department of Environment, Food and Rural Affairs (DEFRA) surveys of 'Public Attitudes to Quality of Life and the Environment' (1996 and 2001), pollution in bathing waters and beaches was shown to be in the public's top four greatest environmental concerns in England and Wales which was higher than concerns over ozone depletion, climate change and traffic pollution Wales (DEFRA, 2002).

The number of designated beaches varies throughout Europe as well as the parameters[1] actually assessed. For Example in England and Wales, monitoring and compliance with the European Union (EU) Bathing Water Directive (1976) is currently undertaken and enforced by the Environment Agency (EA) who assess compliance with just the coliform standards (Environment Agency, 1999). Although the number of designated beaches has generally increased over the last decade (Surfers Against Sewage, 1999: EU, 2002c (see Table 1.1)), under the existing EU Bathing Water Directive, there has

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[1] *The current EU Bathing Water Directive refers to parameters as being the water quality determinands that are included for monitoring and therefore the term parameter will be used throughout this study.

been an inevitable political resistance to increase the number of beaches monitored. The current variation in numbers of designated beaches is eloquently illustrated by a comparison of the number of designated beaches and number sampled that do no not comply between Italy, France, Portugal and the UK (Table 1.1). The number of French designated bathing areas has actually fallen (with an increase in pass rate which may in part be due to selective designation) but this is still more than three times the number designated in the UK with just 564 designated areas (551 in 2000, 447 in 1997) and 342 Portugese designated areas despite their enormous coastlines. These low numbers of designated beaches are put into perspective when compared to Italy's 4820 designated beaches. This disparity whilst being due to differing geographies is also a consequence of the high political and economic costs involved with monitoring bathing water quality. Designating additional beaches that could fail, implies costs for the water industry responsible for sewerage, individual governments, their monitoring agencies, and have a detrimental effect on the tourism industry. Thus it is perhaps not surprising that there is a lack of political will to increase monitoring unless forced to do so through legislation. This is illustrated by the fall in numbers of designated beaches in France and possibly by their failure to submit figures for 1999 and 2000 due to industrial disputes.

Table 1.1 Figures from the Online EU bathing Water Reports 1992-2000 (EU, 2002c)

Country	No. Designated Beaches 1992 (% passing Guide Values)	No. Designated Beaches 1998 (% passing Guide Values)	% Designated 1998 Beaches that DO NOT comply with mandatory values or were under-sampled
FRANCE	1932(49.8%)	1856(72.2%)	5.5%
ITALY	4034(85.4%)	4868(90.3%)	4.9%
UK	455(35.6%)	496(44.2%)	11.3%
PORTUGAL	227(58.1%)	342(77.2%)	10.5%

The political repercussions have been for the EU to revise its bathing water quality directive. This revision in policy accepted the need to encourage and broaden monitoring within the EU. In European Commission communications in 1994 and 2000 it was stated that "every stretch of water in the EU could potentially be used for bathing and should thus be monitored and managed under the Bathing Water Directive" (EU COM(2000)860 Final, p7). This was seen as unobtainable so in operational terms, the new directive will include a definition of bathing water, removing the opportunity for interpretation. This will inevitably increase the numbers of designated bathing water areas.

The EU has openly solicited advice on the development of a new bathing water policy to "streamline the European environmental water legislation....that will ensure the same environment ... but at the same time will take into account new approaches and new science and technologies" (EU COM(2000)860, p4) in order to accommodate the increasing numbers of coastal areas that need to be monitored. Indeed, as already indicated, the EU 2000 policy document COM(2000) 860 Final specifically refers to an ideal but unobtainable objective for all coastal waters to be monitored. Remote sensing has the potential to make this an obtainable objective.

Furthermore, this EU document also states that the considerable time taken in microbiological analysis was a significant criticism of current monitoring and that there was a need for good quality information to be available in near real-time to allow management reaction to non-compliance. Near real-time monitoring is potentially possible through the application of remotely sensed monitoring.

Remote sensing itself has been rapidly changing over the last decade. Past research in remote sensing has been restricted to the use of data from a handful of wavebands provided by existing sensors. Typically, programmes such as SPOT, Landsat, and ERS were designed for terrestrial applications such as crop identification (Lillesand and Kiefer, 1994). This has been an underlying cause for the slow progress of research into marine applications. This situation has been changing with the emergence in available sensors with narrower spectral bands suitable for marine applications (e.g. (Coastal Zone Colour Scanner (CZCS), MOS (launched March 1996), SeaWiFS (launched August 1997) and MERIS on board Envisat launched March 2002) and an increasing interest in the use of airborne spectroradiometers such as CASI (Canadian Airborne Spectrographic Instrument). The Natural Environment Research Council (NERC) and the Environment Agency (formerly NRA) have already used planes with on-board spectroradiometers in studies of sediment load in the Humber estuary (NERC, 1999) and for chlorophyll identification in other UK coastal areas (Groom, 1991; NERC, 1999). There have been numerous remote sensing projects involving individual water quality parameters e.g. chlorophyll level (Groom, 1991) and sedimentation (Buchroitner, 1991; Rahman *et al.,*1996) in a variety of environments, but few have investigated overall water quality with most exceptions relating to freshwater lake environments such as Dekker and Peters' (1993) study of eutrophication of dutch lakes using Landsat TM data. Airborne instruments have been used throughout North America in marine and fresh water studies to study sediment load, and chlorophyll levels (Roberts *et al.,* 1994). Relatively low-cost airborne spectroradiometers have the potential to provide a cost effective method of monitoring coastal areas, especially if they are of particular scientific, economic or environmental interest such as bathing waters. The increasing choice in wavebands that can be selected for data collection

using these new airborne instruments has meant that there is a need to ascertain the potential of wavelengths for monitoring water quality parameters. The launch of SeaWiFS provided the first dedicated sensor to marine remote sensing since the CZCS in the late 1970s. This has now been followed by the MERIS instrument on ENVISAT (March 2002) which offers 15 targeted narrow channels in visible light specifically aimed at maximising opportunities for remote sensing of the aquatic environment therefore compared to previous decades, there's now a relative abundance of operational satellite data.

Environmental remote sensing's ultimate goal must be to produce reliable, routine information that assists and improves the management of the environment. This objective was supported in EU policy concerning funding and development of EU space policy through the 1992 EU communication document COM(92) 360 Final which placed strategic emphasis on the "operational uses of earth observation data that assist in the development of policies and procedures for the effective deployment and use of resources in the environment" (Sloggett, 1994, p26). This thesis aims to progress the role of remote sensing in monitoring coastal water quality, specifically the water typical of Northern European coastal waters which are typically 'murky' high load waters, referred to as Case 2 waters (Lahet *et al.* 2001). This research is one step to wards the development of remote sensing towards a practical purpose where it can provide reliable routine information that will assist the management of the environment. The economic implications of an effective remotely sensed monitoring system that could flag failing areas to be manually sampled would allow both the number of bathing areas to be increased without risk of onerous monitoring costs or administration. In short this research addresses both the objectives of EU bathing water policy and remote

sensing need for cost effective operational applications of environmental remote sensing.

This research seeks to identify which wavebands show the potential to allow remote monitoring of coastal waters and how reflectance could potentially be used to flag bathing areas that are exceeding EU guidelines. This research hopes to show that remote sensing could potentially offer a wide coverage (answering the EU Com 860 Final Paper suggestion that the perfect system would monitor all EU coastal areas), cost effective monitoring system that would potentially allow an improvement in overall sampling quality. Indeed while manual sampling will give accurate localised sample results, it is just that, a localised result. Remote sensing could potentially highlight any problem zones within a coastal region. The problems with localised sampling were illustrated in 1993 when I was involved in a sailing competition where the competitors had to sail through a visually obvious slick of sewage outfall which was less than one kilometre from designated bathing beaches. The local authority published general water quality information on the local beaches for public information and on that day, the water quality was described as "good/excellent". This experience illustrates that the spot sample monitoring being carried out can be misleading and actually led to the development of this research thesis.

Chapter 2 discusses in full the aims and objectives of this research which can be summarised as the identification of the most appropriate wavelengths for remote sensing of bathing water quality; the development of a model that demonstrate how these wavelengths can be applied in an operational system; and to make recommendations on how remote sensing could be effectively implemented as a

flagging system of failing water quality and consequently its implications on the future development of EU policy. The literature review (Chapter 3) discusses the current understanding of coastal water quality, marine remote sensing research, it's application and current levels of achievement and future directions of research. This also clearly demonstrates that the application of remote sensing to a multi-parameter practical coastal marine application has not been developed and that this research's approach and results are both original and significant in remote sensing research and application. The data collection methodology, including identification of equipment, (a NERC loaned Spectroradiometer) and site selection (Southend-on-Sea), are discussed in Chapter 4 while the data pre-processing, identification and removal of spectral data errors are discussed in Chapter 5. The data analysis is separated into three chapters. The first of these (Chapter 6 preliminary analysis) includes statistical analysis and graphical visual analysis used to identify areas of the electromagnetic spectrum for more detailed analysis undertaken in the second stage visual analysis. In Chapter 7, the first component of a spectral physical model is developed through the construction of a water quality model for the Thames estuary using data collected for this research. The results of the preliminary analysis (Chapter 6) are used for the final detailed visual analysis (Chapter 8) and the results are evaluated using regression analysis where appropriate and tested against the data to produce an estimate of accuracy in Chapter 8. The results of Chapters 7 and 8 are then used in Chapter 9 to estimate, and evaluate the accuracy of prediction for the remaining water quality parameters that cannot be identified directly through remote sensing. The final results are summarised through the production of a predictor rating for each water quality parameter in Chapter 10. Chapter 10 also includes the supporting evidence, final spectral physical model (Figure 10.3) and limitations, recommendations and full discussion of results and conclusions.

CHAPTER 2

Aims and Objectives

2.1 The Research Setting

As discussed in the literature review (Chapter 3), past research in remote sensing, particularly those investigations using satellite data, have traditionally been restricted to the use of data from a handful of wavebands provided by existing sensors (e.g. Dekker *et al.*'s(1993) study of eutrophic lakes using Landsat TM data). Typically, the wavebands collected by sensors were broad and designed for terrestrial applications (Lillesand and Kiefer, 1994). This has been an underlying cause for the slow progress of research into marine applications. In recent years, however, there has been a gradual increase in available sensors with narrower spectral bands suitable for marine applications (e.g. MERIS, SeaWiFS) along with an increasing interest in the use of airborne instruments (such as CASI (Canadian Airborne Spectrographic Instrument)) as costs have fallen with advances in technology. SeaWiFS provided the first dedicated satellite for marine remote sensing for several years, and the launch of MERIS (Envisat) (March 2002) offering 15 channels (see Table 2.1) will provide a wealth of new data with narrow spectral wavebands suitable for aquatic applications including coastal remote sensing. In the UK NERC and the Environment Agency have used planes with on-board spectrometer for use in studies of both sediment and chlorophyll loading estimation (Groom, 1991; NERC, 1994,1995,1998). Roberts (1994) and others have used airborne spectroradiometers throughout North America in marine and fresh water studies. The use of relatively low-cost airborne spectroradiometers could provide a method of monitoring local coastal areas effectively, especially if these areas are of particular scientific, economic or environmental interest, such as bathing waters.

Table 2. 1 ENVISAT MERIS Wavebands (launched 2002) (Doerffer *et al.*, 1997)

Band centre (nm)	Bandwidth (nm)	Potential Applications
412.5	10	Yellow substance, turbidity
442.5	10	Chlorophyll absorption maximum
490	10	Chlorophyll, other pigments
510	10	Turbidity, suspended sediment, red tides
560	10	Chlorophyll reference, suspended sediment
620	10	Suspended sediment
665	10	Chlorophyll absorption
681.25	7.5	Chlorophyll fluorescence
705	10	Atmospheric correction, red edge
753.75	7.5	Oxygen absorption reference
760	2.5	Oxygen absorption R-branch
775	15	Aerosols, vegetation
865	20	Aerosols corrections over ocean
890	10	Water vapour absorption reference
900	10	Water vapour absorption, vegetation

This advance in technology means that airborne spectroradiometers such as CASI allow the collection of spectral data within a number of very narrow wavebands down to 1.8nm if required.

A method of monitoring water quality in Case 2 waters can be set against a background of increasing usage and potential of airborne spectroradiometers, as well as new data available from SeaWiFS and MERIS. The increasing choice in wavebands that can be selected for data collection has meant that there is a need to understand the potential of wavelengths in marine applications in order to pinpoint which wavelengths will be genuinely useful for monitoring bathing water quality. This research thesis intends to identify those wavelengths which could allow the identification of levels of EU bathing water parameters when they exceed the directives guidelines.

Many studies into water quality parameters have been concerned with a single parameter such as chlorophyll (Matthews and Boxall, 1994) or sediment load (Chen *et al.*, 1992; Stewart *et al.*, 1993). For a monitoring system to be useful and cost effective, it must consider all parameters required by the various organisations involved in water quality assessment to ensure the water quality is acceptable. While this requirement does add complexity to a potential remotely sensed monitoring system, multi-parameter studies have been successful, as in Dekker *et al.*'s 1993 study of Eutrophic lakes and the work done by Doeffer and others for the MERIS specification (Doeffer *et al.*, 1999).

2.2 Requirements of a Remotely Sensed Bathing Water Quality Monitoring System and its Advantages

This research thesis aims to provide a basis for monitoring bathing water quality using remote sensing. Currently this is achieved through a system of manual spot samples taken by regulatory bodies throughout Europe. For example in the UK samples are taken at designated EU beaches at a depth of 30cm and taken for analysis in the laboratory. The

frequency of testing varies depending on parameter (see Appendix 1A1). Mounting political pressure to include all areas used for recreation from groups such as SAS (Surfers Against Sewage), Friends of the Earth, and commercial pressures to attract tourism has led to ever increasing numbers of bathing water beaches being designated in most countries. The EU's recent communication document specified that "the public has a basic right to use surface water...this implies that every stretch of water in the EU could potentially be used for bathing and thus should be monitored" (EU COM2000(860) Final, p7). While the EU acknowledged that this was impossible, a new directive will leave less room for interpretation in the definition of bathing water. This inevitably implies a significant rise in costs of monitoring with traditional manual spot sampling and laboratory analysis. Inevitably in the future, relevant monitoring authorities will need to economise on frequency of sampling; or reduce the number of parameters monitored (e.g. the UK EA only regularly records seven of the seventeen parameters specified in the current legislation), avoid the designation of beaches (France reduced its number of designated beaches as discussed in Chapter 1); or have their monitoring budgets raised. Economising on monitoring will be particularly true in the poorer EU countries. This research provides an alternative by investigating a cost effective way of identifying areas whose water quality are failing.

A remotely sensed warning system would allow improvements in overall monitoring standards to be achieved whist potentially lowering costs to the authorities in the longer term. Whilst it would be advantageous for a remote sensing monitoring system to simulate the manually sampled water quality parameters, even the EU has acknowledged in its COM2000(860)Final paper that the actual parameters sampled, or how this is

achieved, may need to adapt so long as it can offer a system that will result in the same standards of water quality :

"ensure the same environment ... but at the same time will take into account new approaches and new science and technologies" (EU COM(2000)860 p.4)

The currently identified EU directives (Johnson *et al.*, 1989; Department of Environment, 1989; EU, 2002) are therefore the best starting point for the development of a monitoring system since they provide a limited number of parameters with recommended or required levels and instructions on how and when these should be monitored. This gives a clear indication of what would be required for a remote sensing monitoring system and are specified in detail in Appendix 1A1. The main water quality parameters of current interest to the EU are set out in Table 2.2. The actual selection of water quality parameters for this research is discussed in further detail in Chapter 4.

For remote sensing to achieve it's full potential in the field of near-coastal monitoring, it will have to provide a standard method of monitoring. This must yield reliable information on a range of water quality parameters to a known, satisfactory level of accuracy, using as little field measurement and human decision making in the process as possible in order to minimise cost.

Table 2. 2 Main bathing water quality parameters identified by EU Bathing Water Directive

PARAMETER
Total coliform
Faecal coliform
Escherichia coliform (E.coli) Not in current spec but included in proposed changes (EU, 2000) and has been used in the US (Kay, 1992). One of only two microbiological parrameters included in the EU COM 2002 which has been adopted for introduction in 2004.
Faecal Streptococci
pH
Colour
Mineral oils
Phenols
Transparency
Dissolved oxygen
Tarry residues and floating debris
Nitrogen
Nitrates and Phosphates
Suspended solids
Salinity
Petroleum hydrochemicals
Temperature

The perfect remotely sensed product would be a method by which remotely sensed data can be gathered and the water quality automatically determined allowing individual areas to be monitored through time and different areas to be compared. However, remote sensing can only provide an estimated parameter concentration. For this reason, effort should be directed at developing a remote sensing flagging[2] system that will highlight areas that have potentially exceeded EU guide values so that targeted manual spot

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[2] A flagging system is based on a pre-defined threshold level above which an environmental monitoring body cannot allow a water quality parameter to exceed. A flagging system will therefore only seek to identify when a parameter has exceeded that threshold level and therefore does not need to be able to quantify the exact volume of that that parameter.

samples could be collected in the field for laboratory analysis. This would not only allow the broadening of EU policy to potentially cover all coastlines but it would also reduce the number of manual laboratory samples required to just those areas that fail. This could lead to large financial savings whilst ensuring water quality standards over much wider areas of coastline. For example, in Italy according to EU bathing water reports, 95.6% of the 4820 areas manually sampled in 2000 passed the minimum standards required thus if just those 4820 areas were monitored remotely only 4.4% or 213 areas would have required manual monitoring (EU Bathing Water Data, 2002).

The second advantage of a remotely sensed system is that it would produce a library of water quality data for the whole coastal area allowing greater understanding of sources and distribution of pollution in local areas. This is again important because one suggested requirement in the EU COM2000(860) document was for the development of beach profiles incorporating all potential pollution sources in the vicinity and to gain a better understanding of the bathing water. A remotely sensed database could provide information on the sources and distribution patterns that would facilitate genuine management of the water quality.

Finally the ability of remote sensing to cover large areas of coastline would allow improvements /control of regional or even national coastlines allowing the standard of water quality to possibly exceed that currently offered by manual monitoring. COM2000(860)Final also criticises the current directive for the delay in laboratory analysis methods preventing managerial reaction to non compliance. The near real time potential of remote sensing would allow reaction to pollution incidents rather than simply reporting them.

2.3 The Application of Remote Sensing to Water Quality and the need for Secondary Water Quality Parameters

2.3.1 Overview

It would be ideal if the water quality parameters could be directly identified from remotely sensed data and this would be the principal aim of a monitoring method. However, this may not always be possible because the effect on spectral reflectance of a water quality parameter may be small or indistinguishable from the effects of other parameters. Nevertheless, in many cases, it is likely that secondary characteristics of a pollutant could be identified using remote sensing which would then indicate the presence of the pollutant. For example, in a study of the Dnjepr, Dnjestr Southern Bug and Danube river systems, the German Remote Sensing Centre showed a relationship between river run off containing high levels of sewage, agricultural and industrial waste with algal bloom patterns in the Black Sea (DFD, 2002).

Figure 2.1 shows a fictional diagrammatic representation of the type of relationship between the spectral and physical aspects of water quality that could be developed. Indeed, the use of secondary characteristics is essential, as "many important water characteristics such as dissolved oxygen, phosphorous and salt concentration cannot be observed directly through changes in water reflectance...... such parameters sometimes correlate with observed reflectance. In short, there are many complex interrelationships between the spectral reflectance of water and particular characteristics" (Lillesand *et al.*, 1987, p604). Traditional manual water quality monitoring uses indicator parameters to imply high levels of pollution. For example, total coliform and faecal coliform has/is used as an indicator of sewage effluent (EU, 2002), the accuracy of this relationship is open to debate

(Fleisher, 1992; Kay *et al.*, 1999). In considering the use of remote sensing, it may be possible for example, to monitor oxygen level by the use of an indicator water quality variable such as change in chlorophyll-a (see Figure 2.1).

Figure 2.1 Fictional example of a relationships between water quality and reflectance

Power station cooling
water (filtered before
entry into station)

Thermal Infra Red reflectance

Decrease in blue reflectance (0.45-0.5 um)
decrease in reflectance at 0.68um

Temperature rise

Increase in chlorophyll
and phytoplankton due
to warm clear water

Decrease in
Phosphates

Decrease in sedimentation due to
filtration of water but increase due
to increased biomass, therefore little
change in overall sedimentation levels

2.3.2 Specific Aims of the Research

In summary, this research aims to:

1. Identify the most appropriate wavelengths for research into monitoring EU bathing water quality parameters by remote sensing.

2. Propose a model relating reflectance to bathing water quality parameters within EU directives concerning bathing water quality or parameters related to bathing water quality parameters

The first objective of the research is to propose a set of wavelengths and water quality parameters that can indicate threshold concentrations/loads of key water quality parameters. These would allow monitoring agencies to flag coastal areas that are failing EU bathing water directives. This flagging could allow manual samples to be taken in those areas for detailed laboratory analysis. This fulfils two communities goals:

1. The need for the EU to use technological advance to facilitate the broadening of bathing water monitoring whilst potentially reducing implied costs to national agencies/governments and assist in the management of our bathing areas

2. The need for remote sensing to develop real world solutions that can lead to a better environment at possibly less monitoring cost

This research study is limited to Case 2 coastal and estuarine waters. Case 2 waters are the highly turbid (typically turbidities of 2m or less) water found around the south-eastern coastline of the UK and other northern european countries. This research will identify (using a spectroradiometer) the optimum wavelengths for future research and possible operational use. The optimum wavelengths can be used in research systems using airborne, field or laboratory spectroradiometers to allow increased spatial resolution and/or eliminate data redundancy in both data collection and analysis. Airborne instruments collect large volumes of data very quickly when a wide range of wavelengths are collected at high spatial resolution. Identification of wavelengths that show potential would allow a significant reduction in data redundancy which would reduce storage requirements and data processing time. Subsequently, the knowledge of optimum

wavelengths could allow collation into optimum wavebands. These can be used by researchers to select data from current satellites/sensors which provide the closest fit to the wavebands identified, and subsequently to assist the development of future sensors which require optimal wavebands for Case 2 water quality. The derivation of optimal wavelengths and wavebands for monitoring EU water quality parameters in Case 2 waters can then be used as guidelines for future research to develop an eventual system that will allow bathing water quality to be monitored using remotely sensed data.

The second primary aim of this research is to propose spectral/physical models for each of the water quality parameters selected. In some instances a parameter may be identifiable directly though its effect on reflectance at a wavelength or waveband. In others it may be through a secondary water quality indicator that can be identified directly through its effect on reflectance. Each model specifies the relationships between each parameter and the physical appearance/state of the water body and their combined effect on the spectral characteristics of the water (a fictional example of this is illustrated in Figure 2.1). Where possible this would produce an expected spectral signature for each parameter and may be based on both established research and this research results.

This research provides a basis from which a standard method of monitoring water quality from remotely sensed data could be developed to identify coastal areas that are failing expected EU bathing water standards so that detailed analysis can be implemented. Ultimately this could reduce monitoring costs and allow targeting of human resources and monitoring to those areas that are potentially failing standards specified in EU directives.

2.3.2 Beyond this Research: The Future for Remote Sensing of Bathing Water Quality

This research aims to identify both potential water quality parameters and wavelengths that could allow a remotely sensed flagging system or warning system for poor bathing water quality. The conclusions and results of this research provide a basis to identifying bathing water pollution and could eventually be incorporated into a commercially viable method of flagging the failing EU water quality parameters in the near coastal zone.

CHAPTER 3

Literature Review

3.1 The development of water quality understanding and modelling

Seawater is a highly complex dynamic solution containing 80 out of the 92 naturally occurring elements with an approximate salinity of around 35 parts per thousand by weight (dissolved salts) (Open University, 1978). However, this does not mean that some aspects of seawater cannot be modelled or understood. Indeed, Alexander Marcet in 1819 showed that the percentage relationship between some of the major parameters and salinity are a constant i.e. A/S=k (where A is the concentration of some of the major parameters, S is the salinity and k is a constant whose value varies with the major parameter involved) (Open University, 1978). This was further tested by experiments in the 19th century by G.Forchhammer1843-1863, W.Dittmar 1872-1876 and the 1960s at the University of Liverpool and Institute of Oceanographic Sciences (Open University, 1978). These are termed conservative water parameters and include (with some minor variations) chlorine, sodium, potassium, bromine, strontium, boron and flouride (Open University, 1978). In coastal and estuary areas, increases in freshwater input do affect the ionic ratios (Open University, 1978) and therefore increase their complexity. Parameters that vary due to environmental factors such as biological activity and temperature are termed non-conservative and generally these are the parameters that are of interest when monitoring bathing water quality. Coastal areas are likely to have additional inputs such as treated or even untreated sewage and domestic, industrial, and agricultural waste. Effluent discharge (even treated) will lead to enrichment with nitrates and phosphates and other nutrients which can lead to increased micro organism production, especially algae (Warren, 1971). Warren (1971) and Groom (1991)

suggested these blooms will disappear if the discharge of nutrient input ceases but in inshore waters these bloom can become a nuisance in coastal waters. Biological Oxygen Demand (BOD) of most waters can be as high as 5mg/l but with discharge levels can reach hundreds of mg/l (Warren, 1971).

Water quality models have used the relationships of conservative parameters and non conservative parameters identified by Marcet and others (James, 1978; James, 1984). Initially models tried to understand the distribution of water quality within an environment. These were followed by models that were used to explain the ecological and physical relationships of water quality (Biswas, 1981). The earliest attempts at this were based around temperature variation and included the Massachussetts Institute of Technology (MIT) Model and the Water Resources Engineers Inc. (WRE) model (Biswas, 1981). Orlob(1981) developed a water quality ecologic model on which he implied any water quality parameter can be modelled entitled the 'General Mass Conservation Equation'. The general mass conservation equation for an element j of a stratified impoundment is shown in equation 1 below (Biswas, 1981):

$$\frac{\partial(V_j C_j)}{\partial t} = -Q_j C_j + Q_{j+1} C_{j+1} + \left(Ea\frac{\partial C}{\partial z}\right)_j - \left(Ea\frac{\partial C}{\partial z}\right)_{j+1} + C_j \frac{\partial V_j}{\partial t} \pm V_j \frac{dc}{dt}$$

$...............(advection)..................(diffusion)...............(vol.\Delta)..(local.derivative)$

$Where: C_j = concentration\_of\_any\_quality\_constituent$

$\frac{dc}{dt} = all\_processes(except\_advection/diffusion)\_that\_\Delta\_the\_concentration.$

$V_j = control\_volume$

$t = time$

$Q = Flow$

$E = Evaporation$

$a = surface\_area$

$z = Thickness\_of\_surface\_element$

$\partial = Cons\tan t$

<div align="right">Equation 1</div>

The principle of the general mass equation can be applied "to any number of water quality parameters, either independent or coupled through the definition of the local derivative" (Biswas, 1981, p.297). However, Biswas (1981) suggests that twenty two parameters (some of which are coupled) can be solved using the mass balance equation when developing water quality models. Biswas also suggested that in order to solve the equations in a model it is necessary to begin with temperature, followed by conservative substances then non coupled non conservative substances.

The 1925 Streeter-Phelps model uses the mass balance equation to evaluate effluent discharge effect on oxygen and biological oxygen demand (Biswas, 1981; Chapra, 1997). This model was used in subsequent model development to cover estuary and stream water quality and to include bacteria models in the 1960s (Chapra, 1997). Prior to computers, models had to be simple closed systems but in the 1960s models could become progressively more complex as represented by Thomann's model for estuaries and bays (Chapra, 1997; Thomann and Mueller, 1987). Thomann et al.'s estuarine and harbour models incorporate variables such as flow distribution and mixing as well as water quality variable models of both conservative and non conservative substances from point, multi-point and non point sources (Thomann and Mueller, 1987). Later models in the 1990s such as those by Harris et al.(1993) at the Plymouth Marine Laboratory have produced estuary specific models taking into account different types of estuary (Harris et al.,1993; Plymouth Marine Laboratory, 1998). The 1970s led to the development of interest in water quality problems such as eutrophication (Chapra, 1997) and models that could address water quality issues rather than specifically dissolved oxygen such as Orlob's impoundment model and ecologic model (Orlob, 1981). Others have developed specific variable software models (typically for river catchments or

groundwater) such as Whitehead *et al.* (1999)'s QUASAR model for nitrogen modelling within rivers and the Integrated Nitrogen in Catchments model (INCA) which simulates nitrate-nitrogen and ammonia-nitrogen concentrations along a river leading to greater understanding of each element of water quality.

During the 1980s and 1990s water quality modelling continued to address the need for complex water quality modelling for areas such as bays, harbours and estuaries and Thomann's models included the development of understanding of flows and transport (Thomann and Mueller, 1987). Chapra summarises that the 1980s models used the understanding of water quality in closed systems but also recognised the importance of "solid matter in the transport and fate of oxidants"(Chapra, 1997p.20). Chapra (1997, p20) summarised that by the 1990s water quality models had reached the point where they "can be effectively integrated into water- quality- modelling frameworks". The 1990s had lead to the possibility to buy cost effective out of the box water quality simulation modelling software such as the Estuary Simulation Shell (ECOS) (Harris *et al.*, 1993) and the F.D.Masche and Associates enhanced QUAL-II model (QUAL2E) software for stream water quality modelling used by the US Department of Environment (Chapra, 1997).

The 1990s also saw a rise in interest in the coupling of models to gain a greater environmental understanding. The Land Ocean Interaction Study (LOIS) was a collaborative study between the Natural Environment Research Council and Higher Education Institution laboratories. One of the LOIS aims was for the "development of coupled land-ocean models to predict the impacts of environmental change in the coastal zone"(Lois Science Plan, 1992, p.Aim). LOIS was the umbrella study of four

core research programmes; the River Basins, Atmosphere, Coast and Estuaries Study (RACS); the North Sea Modelling Study (NORMS); Shelf Exchange Study (SES) and the Land Ocean Estuary Particulate Study (LOEPS). The River basins , Atmosphere, Coast and estuaries Study (RACS) led to the development of the ECOSII water quality modelling software by Harris, Bartlett and Gorley at the former Plymouth Marine.

3.2 The development of marine remote sensing and atmospheric correction

Remote sensing of the aquatic environment especially coastal waters has lagged behind that of its terrestrial equivalent. One difficulty is the diversity of coastal water with the composition of both dissolved and particulate matter being "both optically active and highly variable in kind and concentration"(Lahet *et al.*, 2001, p.1639). The low levels of reflected energy from water means that the proportion of this energy that is atmospheric noise and deflected light is far greater than for land applications. At depths greater than 20 metres below the water surface, there is a near total absorption of the wavelengths above $0.68\mu m$ i.e. IR and longer wavelengths (Mather, 1989). In fact "the proportion of information contained in the signal received by a sensor can be as low as 20%" (Mather, 1989, p33). This makes the removal of "noise" from satellite data an essential element. Therefore a major barrier has been the effect of atmospheric interference and because of this "the oceanographic remote sensing community has been most active in developing techniques for the removal or reduction of atmospheric effects from remotely sensed imagery" (Mather, 1989, p.33).

All current and future research into the use of remote sensing of coastal area relies heavily on the ongoing research into atmospheric correction. The better atmospheric correction

becomes the more detailed and accurate models can be developed for coastal monitoring. Atmospheric correction is highly complex and essential to all applications of remote sensing and is an entire remote sensing research field of its own. To gain some understanding of this area of remote sensing research, research into atmospheric correction can be categorised into two sections, the Rayleigh component and the aerosol component.

Atmospheric interference correction using the Gordon model (atmospheric correction algorithms) was developed primarily for Case 1 waters in the late 1970s. Since then H. Gordon of the University of Miami has criticised and improved the model (Bottrell et al., 1994). Bottrell and Matthews (1994) suggested that it can be assumed that most aerosols are located below an altitude of 2km and therefore satellite data and flown data such as CASI (normally flown at 3km) can be treated in the same way. Much of the progress in atmospheric correction was based on research found from CZCS (Coastal Zone Colour Scanner on the Nimbus-7 satellite (late 1978 to 1986)) data by Gordon, Sobolev and others (Sturm et al., 1999) based on models for Case 1 waters. These processes were incorporated in software (OCEANcode) to automate the calibration and correction of CZCS data. Empirically derived corrections have been developed based on the case 1 models for Case 2 waters (Sturm et al., 1999). In a joint project, as part of the COAST GIS development to show sediment dynamics and concentrations around the UK coastline, Bottrell of the Plymouth Marine Laboratory and Matthews of Southampton University continued work on the earlier algorithms to make them more accurate for UK waters. Simplistically the models are based on the principle that water absorbs nearly all light in the NIR, therefore any backscatter and reflection in this waveband can be assumed to be atmospheric interference. They found that the atmospheric interference at other wavelengths can be correlated to this. All the atmospheric correction algorithms combine

to produce a very complex process, but they would suggest that the final result is successful but does require powerful computing ability (Bottrell and Matthews. 1994).

Effectively the "Rayleigh contribution is the largest component and is the most easily and accurately calculated"(Bottrell and Matthews, 1994, p.5). This is because the effect can be assumed to be homogenous over the study area and therefore one algorithm can be applied to the whole image. This is not the case for the aerosol component because they vary significantly within very small areas. The aerosol component algorithms have to be calculated for each part of the image. Its calculation is almost entirely based on the previous assumption that water absorbs nearly all light in the NIR, therefore any backscatter and reflection in this waveband can be assumed to be atmospheric interference and the Rayleigh contribution is relatively constant throughout the image. Therefore any change in the reflectance of the NIR can be assumed to be the aerosol component. This means that in effect every individual pixel will have to be separately processed (Bottrell and Matthews, 1994).

3.3 Remote sensing advances in identification of water quality variables

Water in whatever form absorbs energy in the near IR wavelengths. However, as one moves into the visible spectrum water's characteristics change with a wide variety of different factors. Clear fresh water absorbs little of the wavelengths of less than about $0.6\mu m$ in the visible spectrum. In fact relatively high transmittances of the blue/green portion of the spectrum are typical. As loads change in the water body (i.e. turbidity changes) the reflectance and transmittance of the water body changes in a relatively large

way. Therefore load quantities in water can be detected and estimated by studying the reflectance changes in the visible spectrum (Mather, 1989; Dekker *et al.*, 1993).

The level to which different water parameters can be detected varies; some cannot however be realistically monitored or measured. Lillesand *et al.* (1987, p 604) stated that "many important water characteristics such as dissolved oxygen, phosphates, and salt concentration cannot be observed directly through changes in water reflectance......such parameters sometimes correlate with observed reflectance. In short there are many complex inter-relationships between the spectral reflectance of water and particular characteristics". Whilst the inter-relationships will offer a simple way of monitoring such "hidden" characteristics, and may well provide the best way of doing so, studies since the early 1990s have shown the opportunities of uncovering information (e.g. Dekker *et al.*,1993). As technology has advanced some of the individual parameters previously undetectable by direct remote sensing have become possible such D'sa *et al.* (2000) who used NOAA's Low Frequency Microwave Radiometer at 1.43Ghz to detect surface salinity and also showed a relationship between salinity and chlorophyll level.

A broadly generalised summary of Dekker's study of eutrophic lakes in the Netherlands (Dekker *et al.*, 1993) to show the potential of wavelengths for water quality/content that could be generated from the respective wavelengths has been summarised into Table 3.1.

Table 3. 1 Dekker's Study of Eutrophic Lakes (Dekker, 1993)

•	450nm	absorbed by chlorophyll A and humus backscatter main reflectance
•	500nm	lower chlorophyll absorption
•	550nm	reflectance mainly due to sediment
•	600nm	no discrimination possible
•	630nm	is at peak of cynobacteria absorption
•	650nm	
•	680nm	strong chlorophyll A absorption/chlorophyll concentration
•	700nm	peak of reflectance
•	750nm	surface vegetation
•	800nm	
•	850nm	loss of subsurface information
•	10.5-12.5μm	surface temperature.

Initial projects that intended to identify and quantify parameters in water from satellite data were concerned with large algal blooms. For example, Ulbricht (1983) first identified areas of algal bloom, and in 1991, NERC commissioned a study to monitor coastal algal blooms off the UK coast using AVHRR data (Groom, 1991). During this time there have been sporadic projects. The first study to successfully identify (using Landsat data) the estuarine region with the highest biological activity and to analyse associated parameters such as turbidity and suspended solids was by Khorram (1980). In the early 1990s, Dekker *et* al. (1993) completed a project in the Netherlands which successfully analysed the levels of chlorophyll and general levels of biomass in a study of eutrophic lakes using Landsat TM data. In this study, Dekker *et* al. monitored the water quality of fifteen lakes to a satisfactorily high standard of accuracy demonstrating and supporting the findings found in earlier studies. The success of their results led them to call for a standard approach in the method of correction, data extraction, and model adopted so that comparisons could be made between any data set of inland water bodies which would allow the creation of a data base library of water quality (Dekker *et* al., 1993). In contrast to this, however, Jorgensen (2000) compared OCEAN (CZCS) algorithms using historical CZCS data in a study of

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Danish coastal waters. Jorgensen found that the established CZCS pigment algorithms did not take into account the fact that gelbstoff absorb radiation in the range 400-500nm and these waters typically had high gelbstoff levels present which meant that gelbstoff disguised the levels of chlorophyll when using the ratios of 520/550nm or 443/550nm. Despite the limitations of CZCS data, Kogeler and Rey (1999) using CZCS data to show the potential for satellite imagery to allow the temporal monitoring of phytoplankton blooms.

Several studies have monitored outfall systems and plumes and by 1985, Davies recognised that this would be possible once improvements in image enhancement were achieved e.g. destriping (Bowker, 1985; Davies et al., 1985). Following this conclusion. . Davies et al. (1986) carried out a study using SPOT data on coastal discharges and demonstrated that it was possible to identify sources of effluent discharge in shallow coastal zones and in the deeper regions of a tidal.

Changes in chlorophyll levels can be detected using the ratios of 443nm and 550nm. Therefore an increase in just sediment load can be differentiated from an increase in biomass due to chlorophyll carrying phytoplankton or algae. Research into the study of both these factors has been carried out in various studies (Khorram, 1980; Groom, 1991; Davies et al., 1986; Hernandez-Guerra, 1993;Vinchon, Dupont et al., 1993; Matthews, Boxall, 1994; Kogeler and Rey, 1999; Siegael et al.,1999, Allee, 1999 and others) where detailed results have been achieved particularly in studies since 1990 e.g. Dekker et al. (1993) which differentiated between chlorophyll types. Research in the mid to late 1990s at Southampton University into the chlorophyll fluorescence peak i.e. a peak of reflectance caused by the presence of chlorophyll-a, showed that the peak can vary in position in the

spectral range quite significantly from 680 to 710nm in laboratory experiments through the life cycle of phytoplankton. They found that this shift in peak as the phytoplankton mature is due to a shift in the dominance of the pigments chlorophyll-a and phaeophytin-a (phaeophytin-a increases with maturity). The maturity of phytoplankton populations tends to increase with the time of year i.e. mid summer tends to support more mature populations. Stress also causes change in the position of the fluorescence peak and the changes in peak fluorescence make it possible to assess the health of the phytoplankton population (Matthews and Boxall, 1994).

Typically Case 2 waters are near coastal and estuarine water bodies with high suspended load. The reduced light penetration was suggested by Lahet *et al.*(2001) to reduce the success of the blue green ratio (proposed by both Morel *et al.*(1977) and Andre *et al.*(1991)) for identifying chlorophyll load due to an increase in other influences particularly the absorption by yellow substance and overlapping of spectral signatures. Chen *et al.* (1992) showed with studies of suspended load in Case 2 waters that it was still possible to apply derived signatures from laboratory analysis using reflectance at 560nm and 727nm.

The classification of Case 1 and Case 2 waters is based on suspended matter and was put forward by Morel and Prior in 1977 (Lahet *et al.*, 2001). Typical clear ocean waters are Case 1 and most research over the past few decades has concentrated on identification of chlorophyll or other water parameters within these clear ocean waters with low suspended sediment content. Another avenue of research has concentrated on wave identification and size estimation for shipping and other commercial objectives (Hesselmans *et al.*, 1997). Case 2 waters are influenced by phytoplankton, particulate and dissolved organic matter of

local and terrigenous origin and mineral particles (Lahet *et al.*, 2001) and are inherently more variable and complex. However, Case 2 waters are "disproportionately important for human interest"(Lahet *et al.*, 2001, p.1648). Gower Doeffer and Borstad (1999) showed in a study related to MERIS using aircraft flown and boat mounted spectroradiometers that the peak at 685nm is a linear indicator of chlorophyll a.

Despite the barriers to its use, research has continued into the application of remote sensing to marine / water environment and gradually the impediments have been eroded. Major advances into the study of contents of aquatic environments have been made since the mid 1980s. Despite this, by 1989 it was still true to say that "operational methods for routine identification and quantitative measurement of suspended sediment and chlorophyll concentration levels from remotely sensed imagery are still some way off" (Mather, 1989,p.33). In the last few years (from the very late 1980s and 1990s to the present) there have been several projects with the specific intention of trying to use remote sensed data to identify sediment, phytoplankton and chlorophyll loads. Now research has brought the remote sensing world to the stage where methods of identifying chlorophyll loads, sediment loads, oil slicks, surface temperature and algal blooms can all be quantified and loads or levels compared. Although, their application to Case 2 waters can sometimes yield unsatisfactory results (Sathyendranath, 1994; Aguirre-Gomez, 1999; Lahet *et al.*,2001). Lahet *et al.* (2001, p1641) showed that "derivative spectra can be used to eliminate background signals and to resolve overlapping spectral features" found in Case 2 waters allowing satisfactory results in some Case 2 waters. Temperature detection has been shown to be possible in all waters with research projects spanning the decades with successful results in operational studies concerning seasonal variation fisheries etc (Murty

et al., 1998; Sasamal, 1999; Parada and Canton, 1998; Steyn-Ross *et al.*, 1999; Van der Piepen *et al.*, 1999).

A major catalyst to progress in recent years has been the impending and subsequent arrival of two instruments: SeaWiFS (1999) and very recently MERIS (2002). SeaWiFS provided the first new spectral data of wavelengths suitable for oceanographic study. This data along with flown data from scanners such as CASI was used to help in the selection of wavebands for the new MERIS instrument. The technical document number PO-TN-MEL_GS-005 by GKSS/Institute of Hydrophysics by Doerffer (1997) set out a water quality reference model specifically targeted at Case 2 waters where characteristics of a water body could be described by a model. Doerffer highlighted the importance of Yellow substance and its ability to mask other relationships. Doerffer identifies 550nm for non chlorophyllus suspended matter, and Yellow substance or Gelbstoff absorption peaks at 440nm (Doerffer, 1997) within Case 2 waters. The European Space Agency (ESA) is obviously confident of the reliability of the technical document and believe they will be able to offer a set of ocean products based on the MERIS data. The ocean products that are expected to be available are chlorophyll concentrations, algal pigment, total suspended sediment (coastal only), and gelbstoff (yellow substance) (ESA, 2001). They will also provide the raw reflectance spectra available for other products to be produced (ESA, 2001) by other researchers. A recent ESA study found that the ocean product produced a 70% over prediction but with the use of some in-situ measurements for calibration, very good results could be achieved (ESA, 2002). The ESA technical document number PO-TN-ESA-GS-00701 also identifies peak optimised wavebands (centred at 753.75nm and 760nm) for oxygen absorption (ESA, 1997).

There have been several studies into the use of remote sensing in the aquatic environment over the last decade (including estuaries) investigating its ability to derive sediment load. Lake water quality and sediment load studies have been carried out (Chacon-Torres *et al.*, 1992) producing alternative predictive models to process data and produce comparable results to allow result comparisons over time and between areas. Reedy's (1993) set up a model for the estimation of suspended sediments in an estuarine environment using Landsat MSS data. The study was intended to produce water quality maps but illustrated that it was possible to accurately estimate estuarine loads and proposed a simple, but reasonably accurate model. This model could again be adapted into a general method of monitoring, rather than specific to a particular study. Forster *et al.* (1994) showed the possibility of modelling suspended sediment in near coastal waters where they showed the possibility of monitoring distribution by identifying particle size. Aguirre-Gomez (2000) used AVHRR data to detect total suspended sediment in Case 2 waters (the North Sea) and found that in spring/summer good results could be achieved but in winter period results were not as successful and summarised there was a need for greater understanding of Case 2 waters. Moore *et al.* (1999) showed that using flown CASI data sediment level could be successfully retrieved although this depended on the type of Case 2 water with waters with low yellow substance content proving more successful. In another study Kratzer *et al.*(2000) used raft based sensors in Case 2 waters (Menai Straits) successfully measuring suspended sediment in a study monitoring seasonal changes in optical properties including chlorophyll, total suspended solids and yellow substance. Jorgensen and Edelvang (2000) again proved the potential of suspended sediment measure in a plume mapping project using CASI data at 550nm.

3.4 The application of remote sensing to water quality modelling

The need to identify relationships between reflectance and levels of parameters so as to be able to differentiate between the different applications is essential for remote sensing to become a useful medium for the monitoring of Case 2 water of coasts and estuaries. There have been a number of studies dating back to the mid 1980s which look at particular applications e.g. thermal or sediment plumes or sediment load such as Charlton and Davies, 1986;Gibbons *et al.*, 1989; Cambell and Essias, 1985. However there are few studies that examine several variables involved in the study area, with the exceptions typically involving only two parameters such as chlorophyll and temperature. For example, Cambell and Essias (1985) investigated the relationship between chlorophyll and other parameters. Most studies use more than one waveband to study a single criteria, a few have shown the potential for one wavelength to be used. For example it is possible to study changes in sediment levels by just studying changes in the reflectance of a single waveband (Bhargava and Mariam, 1990, 1991; Collin and Pattiaratchi. 1984; Mayo *et al.*, 1993). However to allow bathing water quality monitoring more detail would be required such as the percentage of this load that is organic. inorganic, the chlorophyll load etc. within the total sediment load. To allow this, studies such as Dekker's (1993). and Doerffer's (1997) have shown the need to differentiate using additional wavebands. The wavelengths that provide the maximum detail and data on the distribution and concentration of water quality parameters have, in the main, been determined by a variety of different projects. Baban (1993) showed that there was a correlation between several water quality parameters so that it was possible to use a "simple relation to predict various parameters" (Baban, 1993,p.1252) which also meant that there was no need for atmospheric correction. (The conclusions were that Landsat TM band one was best

correlated for secchi disk depth and suspended solids, band 2 for total phosphorous, band 3 for chlorophyll a and salinity, and band 6 for temperature). Baban created predictive models that could be applied to other study areas of a similar nature. Forster *et al.* (1993) proposed what they believed to be a satisfactory methodology for the determination of seawater quality parameters including turbidity, chlorophyll a, chlorophyll b, phaeopigment and total pigment, although they did not adequately prove the accuracy of this method. Solanki *et al.* (2001) used operationally derived sea temperature from NOAA AVHRR and SeaWiFS derived chlorophyll concentration and found that there was a similarity in both pattern and distribution features between temperature and chlorophyll concentration along the North West coast of the Arabian Sea. Solanki (2001, p.3881) also suggests that chlorophyll concentration is a convenient and appropriate "index of phytoplankton biomass". The relationship between surface temperature and chlorophyll concentration was inverse and Solanki *et al.* (2001,p.3881) concluded there was a "close coupling between the physical and biological processes". The Solanki *et al.* study also incorporated fish catch data and found there to be a significant relationship between the high fish catch point locations and the distribution features identified by the surface and chlorophyll concentration.

The relationship between different water quality components will inevitably lead to a complex model of different parameters being built up, and will require that multiple wavebands be monitored and their relationships compared using a simplified model of the

Table 3. 2 MERIS Band Set Centres

- centre 412.5nm   Yellow substance and turbidity
- centre 442.5nm   Chlorophyll absorption maximum
- centre 490nm   Chlorophyll
- centre 510nm   Turbidity, suspended sediment
- centre 560nm   Chlorophyll reference, suspended sediment
- centre 620nm   Suspended sediment
- centre 665nm   Chlorophyll absorption
- centre 681.25nm   Chlorophyll fluorescence
- centre 705nm   Atmospheric correction
- centre 753.75nm   Oxygen absorption reference
- centre 760nm   Oxygen absorption
- centre 775nm   Aerosols, vegetation
- centre 865nm   Aerosols correction over ocean
- centre 890nm   Water absorption reference
- centre 900nm   Water absorption vegetation

aquatic system of each of the parameters that need to be monitored. Dekker et. al. (1993, p819) called for "predictive modelling ....in order to estimate the range of reflectance values to be expected" and used an understanding of the main optically active water parameters to interpret the spectral signatures of the water in the eutrophic lakes that they were trying to study. Ultimately, remotely sensed monitoring of estuaries or any large water mass will lead to "the possibility of an archive or library ... of water quality status. The continuity in data gathering with new satellites being launched to replace existing satellites is also important" (Dekker *et al.*, 1993,p.819). 2002 brings the possibility of the Dekker's archive closer with the MERIS operational band set shown in Table 3.2. The European Space Agency's MERIS should allow a set of proposed ocean products that include corrections for sediment loaded waters, algal pigment indexes that indicate concentration, suspended matter concentration, and glebstoff (ESA, 2001).

CHAPTER 4

Methodology

4.1 Strategy

Three approaches to data collection were considered. These were to analyse simulated water quality in a laboratory environment; to carry out a full field study using flown data; or to use surface based field equipment for analysis in the environment. The advantages and disadvantages of each are discussed below.

1. Laboratory tank experiments.

A laboratory tank can be set up with manufactured 'standard' coastal water and each parameter of interest could be individually manipulated while controlling other related parameters. This approach has a number of advantages in that the data set is free from changes in the available light source; varying light levels; height above water level, surface roughness (which itself affects the water content); surface glare; radiometric and atmospheric problems; and each parameter can be controlled exactly. This allows easier interpretation of the data and analysis can be sure that changes in reflectance of the water are due to one parameter alone.

However, there are many disadvantages which render this the weakest option in terms of data quality. The principal drawback is that the artificially manufactured coastal seawater is a major simplification of the water and that the complex relationships between the parameters concerned cannot be artificially simulated. Although ocean sea water can be

generally described as water with an approximate salinity of around 35 parts per thousand by weight (dissolved salts), in reality sea water is a complex solution containing 80 of the 92 naturally occurring elements (Open University, 1978). The actual composition of seawater varies with location, climate and time. Coastal waters are invariably more complex with sediments from both natural and human sources. This is compounded by the fact that many of the parameters are at such low levels e.g. erbium (Er) 8×10^{-7} mg L^{-1} (i.e. PPM), that they would be impossible to simulate (Open University,1978). These small parameters cannot be ignored as they may have an important limiting or accelerating effects on the chemical and biological processes in our coastal waters (Open University, 1978; Kay, 1992; Laws, 1993). There would also be an increased dependence on the accuracy of the water quality process models which will inevitably exclude minor side effects which may have profound spectral significance and which are predominantly based on closed systems. These factors alone render this approach as impractical.

Many models concerning water quality work poorly when relating them to real life situations due to the complexity of currents, storage and mixing of the water bodies unless they become exceptionally complex such as the one developed by Harris *et al.*(1993). Without a greater understanding of water quality and its spectral reflectance, this method of data collection would not provide an acceptable standard of data on which any further work could be based to investigate the possibilities of a bathing water monitoring in complex Case 2 waters. Studies that have used this method have tended to concentrate on a single specific parameter. For example Matthews' experiments with algal blooms which analysed the change in reflectance with the maturity of the bloom (Matthews and Boxall, 1994). Matthews' study showed some quite detailed information about the spectral response of a species of algae as described in the previous review section. It is debatable

that the relationships identified would be present in the real world due to a multitude of real world environmental factors. These may include depleting nutrients, temperature fluctuations, and affects of water parameters not included in the synthetic seawater and i.e. there must be doubt over the validity of the spectral responses of the algal blooms when observed in the real world. It would obviously place a massive dependence on the accuracy of simulated pollution model.

II Flown CASI data with simultaneous water sampling.

The use of a plane flown over an area of estuary or coastline carrying a spectroradiometer such as the CASI or even the GER SIRIS with a ship below recording simultaneous water truth data provides the most realistic approach including all atmospheric problems and data collection errors. Indeed in a real working monitoring system, it would seem likely that this would be the approach for data collection. Flown data has the obvious advantage of removing any uncertainty over the realism of the water quality models or obtainable changes in reflectance.

The foremost difficulty would be to find the funding to provide a plane flown on several days with a ship or boat collecting simultaneous water quality data. Even if funding is not an issue, such data have many practical problems for establishing potential relationships. One major problem is the difficulty in obtaining simultaneous water quality data. Even if it was possible to fund the use of a plane and ship collecting water quality data, a ship cannot travel at the same speed as an aeroplane and therefore there has to be a significant

delay in water quality data collection and spectral data collection. It would also have to rely on the water quality samples taken some distance apart to provide water quality data via interpolation for the areas of spectral data collection.

The second major issue is that the effects of surface glare, radiometric and atmospheric interference would mean that the spectral data collection would require considerable pre-processing and the opportunity for error is higher. These factors could easily disguise spectral signatures observed under more restricted conditions.

The only solution to the costs would have been to use a limited data set collected by another project but then the range of water quality data available would also be limited as only selected parameters would have been recorded such as the LOIS Humber estuary study where sediment and chlorophyll and temperature were being collected NERC,1994; Plymouth Marine Laboratory, 1998). To fund such an approach outside an existing study would be prohibitively expensive as it would not only involve a plane crew but also a boat (with onboard laboratory), available at short notice for the occurrence of a cloud free period. Even if necessary funds could be raised, the high cost and complexity of co-ordinating the teams of people involved would inevitably result with a limited number of data collection periods. This would in turn have the effect of reducing the variation in water quality to a very small and unpredictable range and would produce a handful of data sets which would reduce the validity of any correlation found between a water quality parameter and its spectral signature. The only affordable option would be to acquire data from as many sources as possible (namely NERC via Plymouth Marine Laboratory and the Environment Agency, Bristol) limiting the water quality parameters

selected by those organisations, typically chlorophyll and sediment load and therefore of limited use to this study.

III Field spectroradiometer with on site water sampling from a pier or boat.

A field spectoradiometer such as the GER SIRIS (the type of equipment that could also be flown) can record close to the water's surface. This can be achieved by suspending it over the target area of water and recording reflectance in a similar way to those used in laboratory experiments. This allows water samples to be taken from the water at very nearly the same moment of reflectance recording. This approach allows the use of genuine coastal water with the sun as the light source, but removing most problems with atmospheric and radiometric noise. Most significantly this approach eliminates the problems in simulating coastal water that would occur in laboratory simulation (such as Matthews laboratory simulations (Matthews and Boxall, 1994)), and minimises delays in water quality parameter collection when compared to flown data. Surface glare that can change with the azimuth of the sun can be reduced to low, or insignificant levels by using a constant shadow such as that given by a pier or boat with calibration based on the incoming radiation in the target area. Water quality samples can be taken within minutes of spectral readings which is impossible using flown data.

This approach to data collection avoids most of the problems of laboratory or flown data, and should therefore provide a higher quality of data. It also has several practical advantages because local resources can be used for the laboratory analysis of water samples thus ensuring that samples are uniformly analysed within suitable time periods after each sample. This has the real world advantages of a flown exercise but without

many of its disadvantages and removes the need for any simplification of water parameter relationships that would be required to be simulated in a laboratory experiment. This approach allows greater flexibility in terms of dates and periods allowing more data to be collected and covering a greater variety of water qualities.

In conclusion, this approach has the advantages of both laboratory and flown data collection, but without many of the significant disadvantages. Therefore this approach to data collections was adopted for the current project.

4.1.1 Site Selection

The site chosen for data collection needed to include EU designated coastal bathing water within the vicinity in Case 2 waters (turbid waters). If data were to be collected over a period of weeks, then the area needed to show a history of variable water quality to ensure a variety of water quality for data collection. This variation was required to allow samples to be included that show low and high levels of each selected water quality parameters (indeed an ideal data set would include some samples that exceed EU designated guide or mandatory values). In order to measure reflectance, data can only be collected in daylight hours and therefore access to suitable water at every tidal state was essential to maximise the number of samples collected. The site itself needed to be free of obstacles and preferably relatively sheltered to prevent both significant surface roughness and equipment damage. Finally, there had to be rapid access to both local microbiology laboratories and the laboratories at Middlesex University to allow water analysis to be carried out within five hours from the first sample for microbiological parameters and

eight hours for chlorophyll. The sample analysis time limits were based on advice from both the Middlesex and independent professional laboratories on sample handling. On this basis the selected site had to be within one hour of a microbiology laboratory, and one and a half hours from Middlesex University at any time of day to ensure water samples could be analysed and allow reasonable time in the field. This inevitably resulted in only a handful of locations being suitable (see Figure 4.1).

Figure 4.1 Potential Sites for data collection
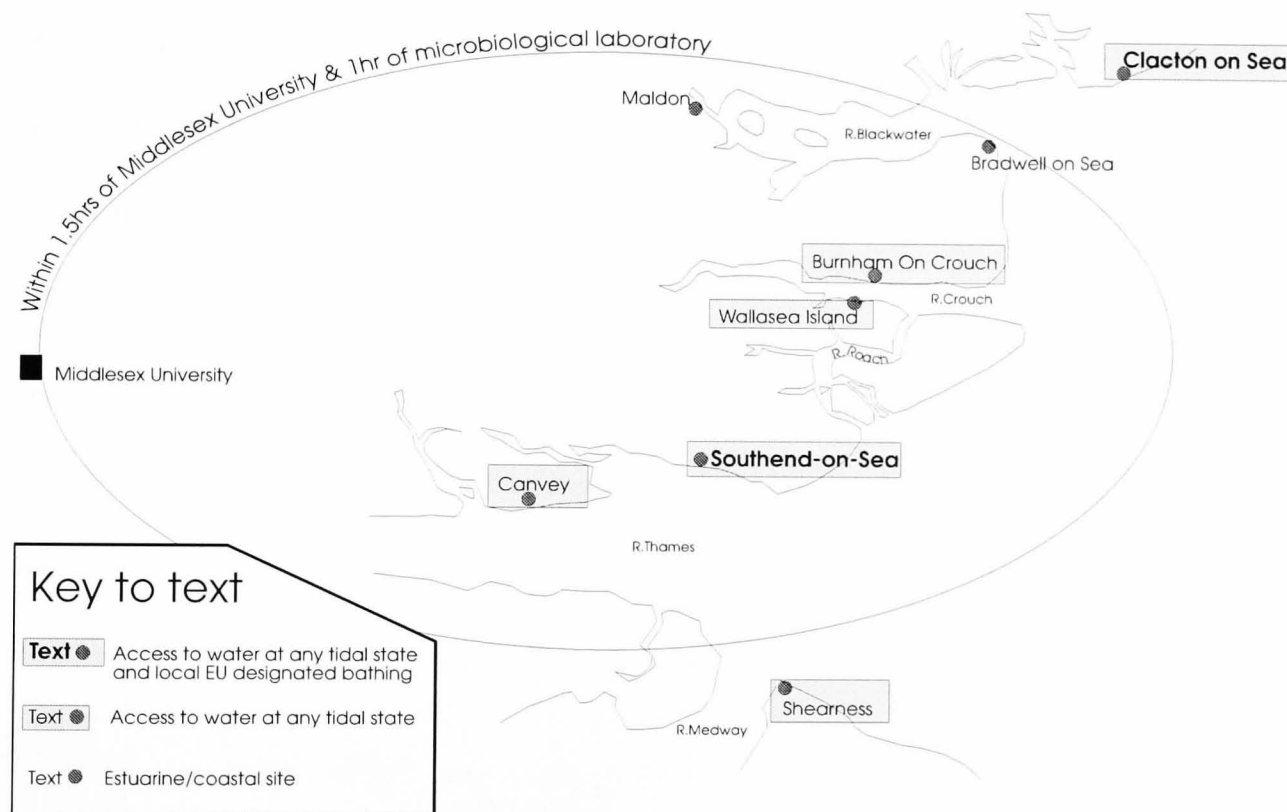
Only Southend-on-Sea possessed a designated EU beach, with access to the water at any tidal state for either inshore boats or via the pier or sandbanks without any need for offshore boats. Southend-on-Sea also has the added advantage of being at the entrance to the Thames Estuary. There is therefore, a strong tidal effect which causes significant changes in water quality during the tidal cycle. This was confirmed by study of NRA (now EA) data on the beach sampling and river sampling points (five in total) around the

area for the previous two years (1993-1994). These data confirmed that the greatest variety in water quality occurred in spring and late autumn. This is because of the enhanced levels of nutrients in the water and the significant climatic changes (Biswas, 1981). In addition, theses estuarine/coastal Case 2 waters experience variations in water quality over short periods of space and time due to discharge of treated sewage effluent in close proximity to the pier. In fact, in August 1994, coliform levels were 60000 times higher to the west of Southend pier than they were to the east of the pier. The pier has a convenient location which:

- Reduces travel time and costs to a minimum

- Within fifty minutes of the Micro-biology laboratories based at Burnham on Crouch which was required as microbiological parameters had to begin analysis within six hours

- Within ninety minutes of Middlesex University's laboratories again allowing a minimum of delay between data collection and laboratory analysis

Figure 4.2 Southend-on-Sea Pier.

At the Southend site, it was possible to:

- Gain access to launches or Southend Pier

- Wade from the beach or sandbanks

Wading was not a practical option due to risks involved to the equipment in even mildly windy conditions, uncertainty about bottom reflectance at the sample points and obvious difficulty in taking simultaneous water samples. When comparing the use of launches or the pier, the pier had the following advantages:

1. It's height above sea level gives a significant increase in the field of view (FOV). For the instrument finally selected (see later) this FOV was calculated as being 34cm by 13cm at 1.5m above sea level increasing to 263cm at 12m above sea level (pier height at a mid point in the tidal cycle (see Figure 4.4).

2. It offers a stable platform with permanent access to coastal water at any tidal state (2.14 km offshore at high tide) which is unaffected by adverse weather conditions removing problems that would occur on a floating platform because a vertical position could be guaranteed. It provided a safe location above the waters surface so that equipment would be unaffected by sea spray and salt if conditions became poor.

3. It has two EU bathing beaches within 1km East (Southend on Sea) and 1km West (Thorpe Bay) which had both shown significantly differing water quality over the previous four years period. There are also four other popular bathing beaches within 5km as well as numerous water sports activities around the pier (see Figure 4.3) which would be included as bathing water if current EU recommendations are developed and accepted.

4. It reaches permanently deep water which avoids both interference from bottom reflectance and means that data can be collected at any tidal state. (A launch would be limited by slow access to laboratories especially at low tide limiting field collection time).

5. A sewer outfall pipe ends further offshore, within 1km South/East of the pier head (see Figure 4.3) and obviously can have a strong effect on bacterial counts as shown by the contrast in coliform counts on either side of the pier from previous Environment Agency data. This study requires high and low levels of parameters during data collection including microbiological counts.

6. It offers a constant and predictable level of shade over the water, which would assist in the avoidance of problems with variation in surface glare which is likely to vary depending on the positioning of the sun (i.e. time of day) and surface conditions (Tassan, 1994).

7. The pier has a time tabled railway running to the pier head which allows easy access with all the equipment, and rapid departure with the collected water samples maximising sampling time.

8. Piers have been used successfully by other projects as suitable platforms for recording wave patterns and other factors e.g. the U.S. Army Corps of Engineering Field Research Facility Data Program pier at Duck, North Carolina (NOAA Coastal services Center, 2001).

Consequently, it was decided to use Southend on Sea pier for all data collection. Due to the period of time scheduled for the field work (i.e. late summer) and the quantity and value of the equipment, it was necessary to gain access to secure areas on the lower deck and flanks of the pier which were beyond normal public access areas. Therefore, approval was acquired from the Director of Engineering, Southend Borough Council.

Figure 4.3 Entrance to the Thames Estuary
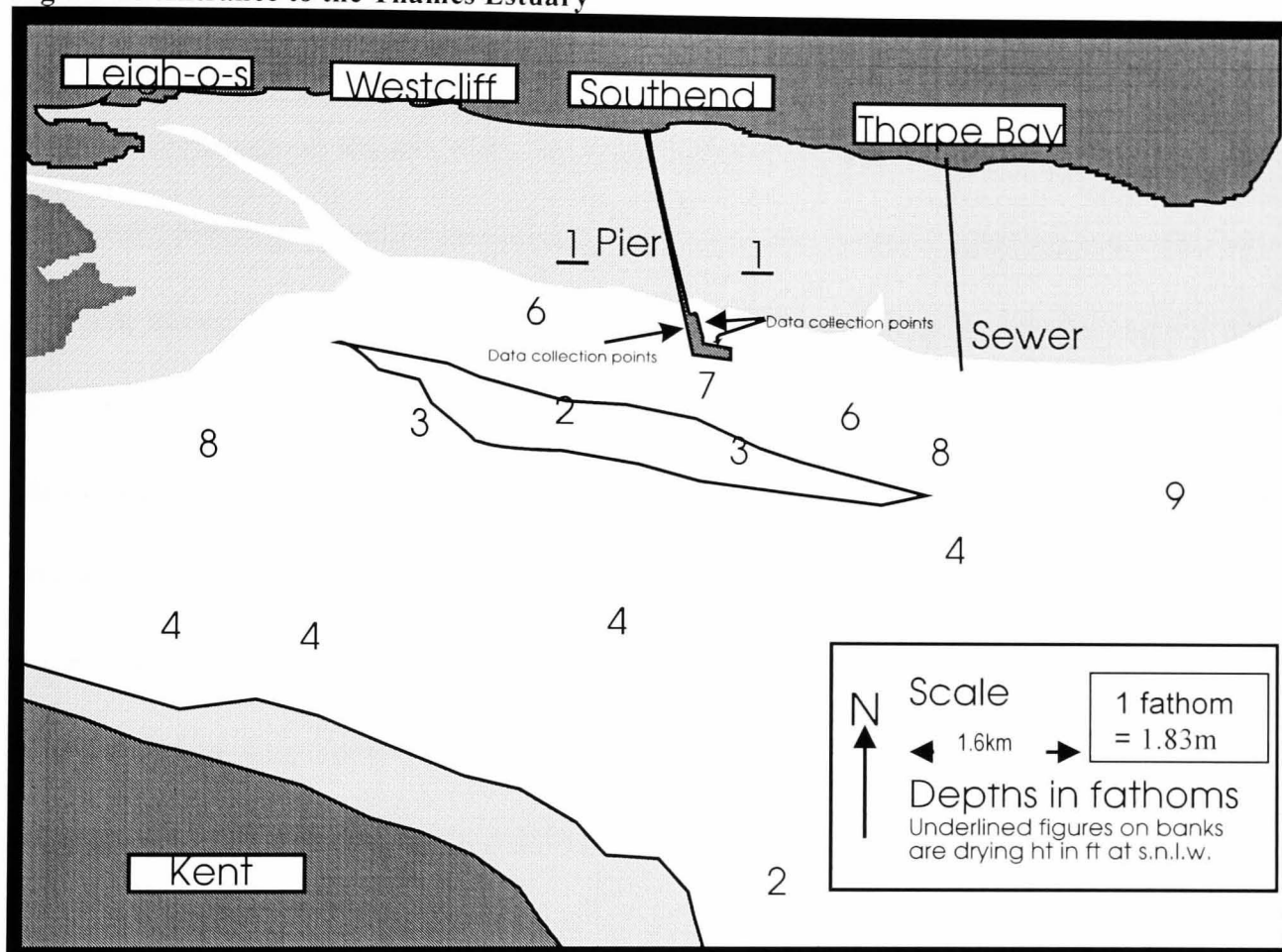
4.1.2 Selection of Water Quality Parameters

The water quality parameters of initial interest were those identified for monitoring by the EU Bathing Water Directive. The EU have two lists of water quality parameters that are relevant to the near coastal zone, specifically the directives (1976) concerning bathing

water quality (EU, 2002) and shellfish water quality (1979) (EU, 2002). The bathing water quality parameters are currently under review (European Commission, 2000; EU 2000) (see Appendix 1A1 for a full listing of EU directives). As already stated this thesis aims to address the need for a remotely sensed flagging system for bathing water quality and as such the parameters currently monitored for bathing water by the environmental agencies within Europe are those of interest to this study. However, these parameters such as faecal coliform are used as indicators of effluent i.e. faecal coliform was seen as a good indicator of human effluent and therefore generally indicate the presence of other microbiological parameters such as viruses and specific bacteria that are equally, or often more, dangerous (Kay et al., 1992; Fleisher, 1992, EU 2002). This is why the EU have specifically been reviewing the directive (COM1994 onwards) and acknowledged that the parameters selected may need to take advantage of technological advances (European Commission (EU COM(2000)860). Some of these parameters have a genuinely significant effect on the spectral reflectance of water. Others involve such low levels that they have little significant effect, except perhaps in controlled laboratory experiments. However, some parameters with low quantity levels are likely to have strong effects within the ecosystem of the near coastal water. In other words, there may be side-effect parameters (to be referred to from now on as secondary parameters) which do have a significant effect on the reflectance of the water at certain wavelengths. For example, chlorophyll is not cited as an EU water quality parameter but it is indicative of nutrient and oxygen levels which are EU parameters. Therefore, the parameters of interest to the current study inevitably include some that are not EU parameters and exclude some which are EU or are proposed EU parameters. Indeed the EU has suggested taking the idea further by using change in salinity or turbidity to indicate change worth investigating rather than solely relying on microbiological

parameters that take time to analyse (12 to 24 hours) to allow rapid reaction to contain or control a pollution event (European Commission COM (2000) 860).

4.1.3 Selection of water quality parameters for research

Only three of the 19 parameters (total coliform, faecal coliform, and transparency) specified in the 1976 Bathing water directive should be sampled every two weeks. All others fall into the following categories, either:

1. to be checked by the competent authorities when an inspection in the bathing area shows that the substance may be present or that the quality of the water has deteriorated

2. must be checked when there is a tendency toward eutrophication (very unlikely in most coastal bathing areas)

The National Rivers Authority (NRA) (now Environment Agency) have consistently sampled for eight parameters in bathing water sampling areas that are listed in Table 4.1 and some of these, most notably E.coli are not listed on the 1976 EU directives. The new proposals for bathing water (COM2000) do include both these microbiological parameters.

Table 4. 1 Water quality parameters sampled by the Environment Agency at bathing water sample points and estuary river water sampling points

Bathing water sample points
Total Coliform
Faecal Coliform
E.coli
Enteroviruses
Transparency
Salmonella
Faecal Streptococci
pH
River water sampling points
pH
Suspended solids
BOD
Temperature

Other parameters traditionally viewed as important measures of water quality include pH, suspended solids, Biological Oxygen Demand (BOD). All are routinely sampled by Environment Agency for river water quality sample points in river and estuary areas such as the Thames.

Several parameters were excluded from the directive that could not be directly monitored because their levels are so low that it really would be futile to expect direct

changes in spectral response except in extreme laboratory conditions and these included all the specific micro- parameters such as salmonella, cyanides, entero-viruses, phenols, pesticides, substances that react with methylene blue and heavy metals. None of these are indicator parameters in the way that E.coli is an indicator of recent untreated human effluent (Fleicher, 1992; EU, 2002) nor are they directly related to nutrient levels. The only way such parameters could be monitored is by relating them to other secondary parameters (e.g. its effect on the ecosystem increasing/decreasing algal growth). None of these excluded parameters are categorised by the EU as being necessary to monitor unless there is a change of water quality or there have been previous failed samples. From EU and Environment Agency data the substantial majority of European bathing water samples currently undertaken have not been required and have not been included by the relevant authorities in fortnightly sampling. These do not, therefore, need to be included in a remotely sensed flagging system as they would only be sampled if there was an obvious decline in water quality which would be shown by other water quality parameters. The remaining parameters total coliform, faecal coliform, pH, transparency, ammonia, nitrogen, nitrates, dissolved oxygen were included for data collection though only the micro-biological parameters (total coliform and faecal coliform need fortnightly sampling). E.coli was also included as it was widely supported in the U.S. as a good raw sewage indicator (Fleicher, 1992) and for that reason had been included in discussion for the revision of the EU directives (EU, 2000) alongside faecal streptococci. Faecal streptococci was not included because with three microbiological indicators whose main role is to identify effluent levels, it was:

1. Unnecessary as the other indicators should provide enough evidence (particularly E.coli and faecal coliform)

2. All micro biological samples had to be processed by an independent commercial laboratory and its inclusion was not financially arguable as the existing three parameters were adequate and faecal streptococci is not currently included as a compulsory parameter by the directive.

The other water quality parameters for selection, needed to be used as secondary parameters i.e. those that are related to a number of water quality parameters as described earlier. This meant that interpretation of models such as Biswas's (1981) general mass conservation equations had to be applied. As shown in the summary diagram of the general mass balance equation in Figure 4.4 some parameters such as algal level have a central role in the water quality model while others such as sediment load can change the water quality balance. The growth of algal blooms in coastal areas is raised as a future requirement for bathing areas in the EU COM(2000) document. Chlorophyll-a has been shown by Matthew and Boxall (1994), Groom (1981) and others to be a good way of estimating algal levels that can be monitored by remote sensing. Figure 4.4 shows chlorophyll to be an ideal candidate as a secondary parameter as it displays relationships with a number of other water quality parameters including nitrates, phosphates, oxygen levels, temperature and turbidity. Therefore chlorophyll was included in this investigation to assist in the development of water quality relationships. In the case of chlorophyll the optimum wavebands have already been identified by Groom (1981), Matthews *et al.*(1994), Dekker *et al.* (1993), Kogeler *et al.*(1999) and several others and its relationship to other water quality parameters is established so chlorophyll represented a potentially reliable secondary parameter. In a similar way, BOD (a widely acknowledged important water quality indicator currently

collected at river sampling points rather than bathing water) was also included because of its potential to help develop the relationships between water quality parameters.

Figure 4.4 General Mass Equation adapted for illustration by Biswas (1981)

Light   Oxygen CO_2 Sediment   Nutrients,Nitrogen, phosphorous etc.

Aquatic plants   Algae   Zooplankton   Pelagic fish

O_2 Toxicity

Bacteria CO_2

O_2 Detritus

Thermocline _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _ _

NO_3

Ecologic Relationships as described by the General Mass Equation. Adapted Illustration from Biwas.

Organic sediment CO_2 NO_2

NH_3 Rough fish   Toxicity

Bacteria   Toxicity

Benthic animals

Source adapted from modified Odum [1971] diagrams for the water quality ecologic relationships in a stratified impoundment.

While models such as Biswas (1981), Street-Phelps(1925), Chapra (1997) and Thomanns (1987) can be used where inputs are known in ideally a closed system such as a lake or harbour, modelling becomes increasingly more complex when involving the coastal zone and simulation models such as Harris, Gorley and Bartlett with their ECoS software (1993) illustrate the complexity of this issue. However with all the models the relationships between parameters do remain consistent, it is just the number of inputs and mixing that increase in complexity. Thus if nutrient levels are increased then algal levels will also become higher (EU, 2000). In order to develop a flagging system, it is simply this relationship that is required.

As Figure 4.4 illustrates suspended sediment, nitrates (an EU bathing directive parameter already included), phosphates (an EA river water sampling parameter) and temperature were also included as secondary parameters (temperature is not illustrated but affects oxygen levels and biological activity). This is because they affect the water quality equilibrium when their levels are increased through discharge. Suspended sediment and temperature have, like chlorophyll, also been widely used in other remote sensing projects with good results and these relationships to reflectance can be used to benefit this research. Table 4.2 summarises the water quality parameters selected and a brief explanation of their reason for inclusion

Table 4. 2 Reasons for inclusion of each water quality parameter.

Parameter	Effects and Importance	Relations
Dissolved Oxygen	It is effected by temperature, organic matter, photosynthetic activity, bacterial activity. It has dramatic effect on fish populations. If very low can promote anaerobic respiration and production of noxious gases such as methane and hydrogen sulphide. Oxygen required for oxidation of sewage, ammonia to nitrogen etc. Levels below 5mg/l are dangerous to fish. The effect of low levels of oxygen can mean that water is pumped over gills faster with the result of any poisons (even at normally safe levels) being concentrated in the fish blood stream. Similarly some sewage discharges are supersaturated with oxygen through treatment. (Laws, 1993; Tebbut 1992)	Photosynthesis Bacterial levels Temp (high temperature results in high DO) nitrate levels oxidation
BOD	Decomposition by aerobic bacteria of organic (including sewage), and nitrogenous material requires oxygen - this means a high BOD. A high BOD is a very good indicator of high levels of pollution, particularly sewage. (EU, 2000; Kay, 1992; Open Univesity ,1978)	High levels of organic material Sewage results in high BOD Nitrogenous material
Nitrogen	Indicative of high levels of agricultural pollution. It has a negative effect on oxygen levels due to its oxidisation. (EU, 2000; Open University, 1978)	Oxygen Organic matter

Alkalinity	High alkalinity complexes heavy metals with carbonates and bicarbonates reducing their toxicity. Very high alkalinity can indicate high levels of human effluent and chemical pollution. (EU, 2000)	Heavy metals Ammonia
Ammonia	Excellent Indicator of domestic, agricultural and industrial waste. (EU, 2000)	Nitrogen, BOD, fertilizers
Temperature	Rise in temperature will increase bio-degredation of organic material. Therefore will increase BOD. The higher the temperature the lower the capacity of the water to hold oxygen. (Laws, 1993; Tebbut 1992)	Oxygen, BOD Bacterial levels
Suspended solids	Detrimental to aesthetic enjoyment. Chemically they can reduce the DO content of water if it is predominantly organic. If inorganic, it can reduce the BOD by effectively smothering the biomass. Light penetration is reduced and therefore primary production. (Open University, 1978)	Colour BOD Chlorophyll Turbidity
Nitrates	It is a nutrient and therefore high levels will promote primary production will higher levels of chlorophyll and algae. May have been created by the oxidation of Ammonia and therefore could be related to the DO. It is a primary sewage indicator/index. (EU,2000, Laws, 1993; Tebbut 1992, Open University 1978)	Agricultural pollution Chlorophyll Ammonia Bacterial levels
Phosphates	Sewage produces high levels of phosphates and it is therefore connected with faecal coliforms. It is a nutrient and therefore will increase biological primary production, therefore related to chlorophyll and algal activity. It was high as a consequence of sewage as will nitrates. (Laws, 1993; Tebbut 1992, Open University 1978)	Chlorophyll Algal growths Nitrates Faecal Coliforms
Total Coliform	Largest bacterial group indicator for sewage/human effluent. It has been used as the sole indicator in the past around the world. It does however include large groups of naturally occurring bacteria. (EU,2000; Fleicher, 1992)	
Faecal Coliform	A more specific sub group of total coliform, used as an effective bacterial indicator. Thermo-tolerant faecal coliform are highly correlated with high levels of	Salmonella human effluent Ammonia Oxygen

	Salmonella (>100 organisms per 100ml). They increase BOD, and increase the rate of biochemical breakdown. (EU,2000; Fleicher, 1992)	BOD
Escherichia Coli (E.coli)	A highly specific indicator of untreated human effluent. Will provide the most effective indicator if levels were high. As a singular group it will have little effect on other parameters, but parameters it is related to will have strong effects on other water quality parameters is has been included in the revisions of EU directives and is widely regarded as an accurate indicator of human effluent . (EU,2000; Fleicher, 1992)	Related to all biological parameters
Turbidity	Inevitably related to suspended sediment, chlorophyll via algal blooms, and other loads in the water although Case 2 waters are naturally highly turbid.	Chlorophyll effluent
Chlorophyll	Increase in algal growth through increase in nutrient availability therefore related to phosphates, nitrates, sewage effluent and weather conditions (EU,2000; Tebbut 1992, Open University 1978)	micro biological nitrates phosphates

4.1.4 Spectral Data Collection Equipment Selection

The research required the collection of spectral data, with as wide a spectral range as available, with simultaneous water truth data with a field operable instrument. At the time of data collection (1995) the NERC EPFS (Equipment Pool for Field Spectroscopy) advised that it held only one spectroradiometer, the GER SIRIS that was suitably weather proofed. The GER SIRIS (GER Single Field of View IRIS) has a narrow spectral bandwidth of just 2nm and wide spectral range (0.3μm to 2.5μm) with a spectral bandwidth of 2nm in the field (this nearly matches the widely used CASI resolution which is 1.8nm and offered a broader range than CASI's range of 0.4-0.9μm). It was inclusive of the range of the MERIS sensor (ESA, 2001). The reason for including a wider spectral range is to allow potential comparison with other instruments such as CASI (see Table 4.3). The GER SIRIS also had the largest field of view which meant the field of view of the GER SIRIS at a height of 10m was comparable to that of more recent airborne instrument such as CASI.

Table 4. 3 Comparison of spectral instruments (sources: NERC EPFS, RICHARDS(1997))

Instrument	Spectral range (μm)	Spectral bandwidth (nm)
Geoscan II	0.49-1.09	17-24
GER	0.499-1.083	25.4
MONITEQ	0.43-0.805	2.6
CASI	0.4-0.9	1.8
HIRIS(NASA)	0.4-2.5	10
AVIRIS	0.4- 0.72	9.7
MIVIS	0.433-0.833	20
MEIS FM	0.38-1.00	6+
MAIS	0.45-2.45	21-25
GER SIRIS	0.30-2.5	2-4nm in the field
GER 3700	0.3-2.5	3-16
Source for information: NERC EPFS and Richards J.A.(Remote sensing digital Image analysis)		

Due to longer wavelengths being absorbed by water, it can reasonably be assumed that substances that cause a change in reflectance in the NIR are only detectable up to a limit of 1.0μm. Beyond this limit the levels of light reflected back are too low to warrant any practical information on water content except for surface debris. However, information obtained on surface materials possibly including algal blooms could affect reflectance in the longer wavelengths as no water penetration or little penetration would be necessary. Therefore the full spectral range of the GER SIRIS was recorded allowing recording through a wide range up to 2.5μm. The GER SIRIS bandwidth increases to 4nm for the range 1000nm-2.5μm but this was not seen as a disadvantage as the longer wavelengths above 1.0μm were unlikely to provide relevant data due to their absorption by water and 4nm was still very narrow. One waveband of interest is the Thermal Infra-Red (3.0-15μm) for surface temperature (Mather, 1987), but available field spectroradiometers at the time of data collection (1995) did not cover this range. Remotely sensed surface temperature estimation has been widely accepted and so results found in projects such as Li *et al.* (2001) and others dating back to the 1970s. A list of spectral ranges and resolutions of several current airborne spectroradiometers in Table 4.3 illustrate that most do not include any range above 1.1μm.

4.1.5 Selection of data collection points on Southend- on Sea Pier.

The most essential element of selecting suitable sampling points was to ensure that no part of the pier or under water features obstructed or could be included in the field of view of the spectroradiometer at any tidal state. This was because the obstacle would affect the recorded spectral reflectance. The field of view was calculated by measuring the height of the pier above the water surface at low tide and adding another (as mean

turbidity according to the NRA data for 1993-94 was less than 1m and maximum turbidity was 1.5m over the previous year) 2m to account for sub-surface obstruction of the pier legs. Finally, the field of view of the spectroradiometer was calculated using a geometrically correct diagram (Figure 4.5). This maximum field of view was used to measure the overhang and spacing between the pier legs. This meant that many parts of the pier were unusable due to the distance between legs or angle of entry to the water (in fact this excluded the area with deepest water at the far end of the pier). In addition to this, some platforms overhung the pier base. As an additional measure the spectroradiometer was hung over the edge using a specially constructed boom (built from an aluminium pole, bolted to a steel box, drilled to seat the recording head) securely set up on a camera tripod and counter-balanced using the equipment carry box and batteries (see Figure 4.6). The length of the boom was limited by the length of the cable connecting the spectroradiometer to the batteries and laptop computer.

Figure 4.5 **Sample Area on ground of the GER Single Field of View IRIS.**
    Sample area based on the widest dimension using the 13 degree angular field of view.   The full field of view is 13 x 5 degrees.

Approx. level of instrument on pier

1metre

2
2.5
3
3.5metres

FOV approx.
1m wide

Approx. level of estuary below pier

5
5.5
6
6.5

2.21   10metres
              10.5
2.42   11
              11.5
2.63   12
              12.5
2.90   13

3.11   14

3.37   15

3.58   16

17metres
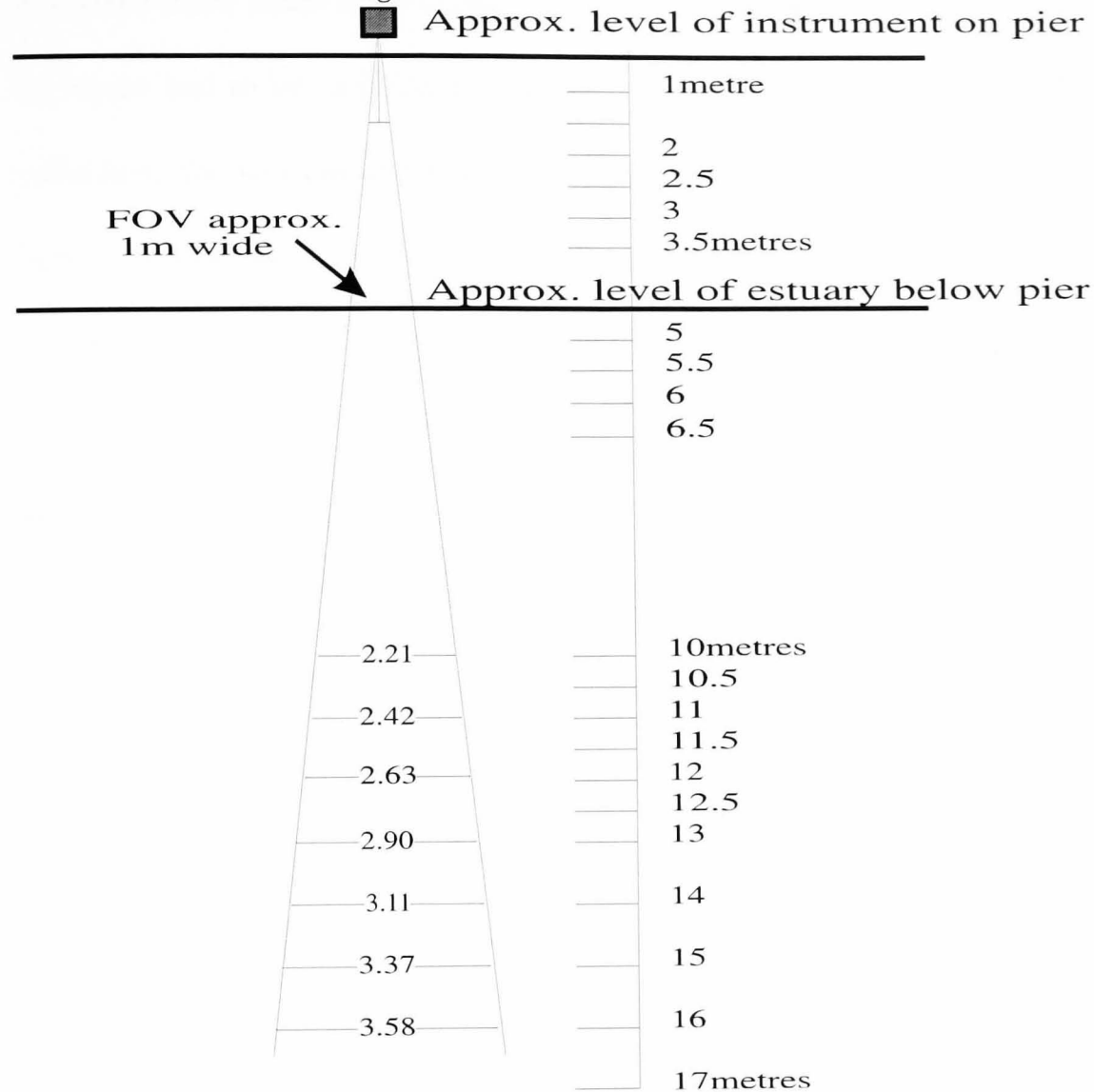
Surface glare was an expected potential source of error and was the second major problem to be avoided as much as possible prior to data collection by careful site location. In an effort to reduce glare, the shade of the pier was used to avoid direct sunlight and this was supported as an appropriate and acceptable solution by both the NERC EPFS and through personal communication with Professor Cracknell (June 1995) from the University of Dundee. This inevitably meant selecting two points for data collection depending on the time of day because the east side of the pier is shaded in the mornings and the west is shaded from midday onwards. Two secure overhanging platforms were available on each side of the pier just prior to the head (see Figure 5.0 and

Appendix 1A2) and these provide the perfect conditions except from 1 hour either side of low water mark when water depth fell below the minimum level (3.5m). The shadow over the water had to be identical to that available to the reference panel. Prior to the data collection, this was ensured through numerous checks with a light meter that the level of light available below the deck (i.e. as close to the target water as possible) and the area available to calibrate the spectroradiometer at the pier deck level were the same. This was possible because all sites were beneath or behind permanent structures (buildings or upper deck) whose shadow continued over the deck and water. The level of light was confirmed to be constant prior to the field study using a light flux meter held close to the water's surface and at the pier deck on bright spring days at three times of the day 0930 1200 and 1400hrs for each one of the potential sites during April 1995.

It was also essential to avoid bottom reflectance by ensuring that water depths always exceeded light penetration which equals turbidity in the visible sector and longer wavelengths should be absorbed at lower depths (Lillesand, 1987; Mather, 1985). An optimum minimum water depth of 3m was used based on the turbidity data from the NRA (whose river sampling point at Southend (69.7km below Teddington) and EU beach sample points at Thorpe Bay and Westcliff never rose above 1.5m and averaged <1m in the two years (1993-4) prior to data collection). This was shown to be correct in the current study because turbidity never rose above 1.5m throughout the data collection period in 1995. A third site for low water was used on the lower deck on the north side of the pier head (an area submerged at high water). This site is permanently shadowed by the upper deck of the pier and water depth never fell below 3 metres. The point in the tidal cycle could be very accurately observed as the NRA depth measurement for the Thames is taken and is visible at the pier head.

4.2 Operation of Field Data Collection.

4.2.1 Spectral Data

The data were collected from the three selected points at the head of Southend on Sea pier approximately 2.14km offshore. The spectroradiometer was held by a tripod and boom arrangement (constructed for this purpose) clear of obstruction at an approximate height of between 4-8 metres over the water (see Figure 4.6) depending on tidal state.

Figure 4.6 The placement of the GER SIRIS at Southend on Sea Pier

Calibration carried out in situ or with sensor swung within reach of pier edge

Overhang beyond pier legs
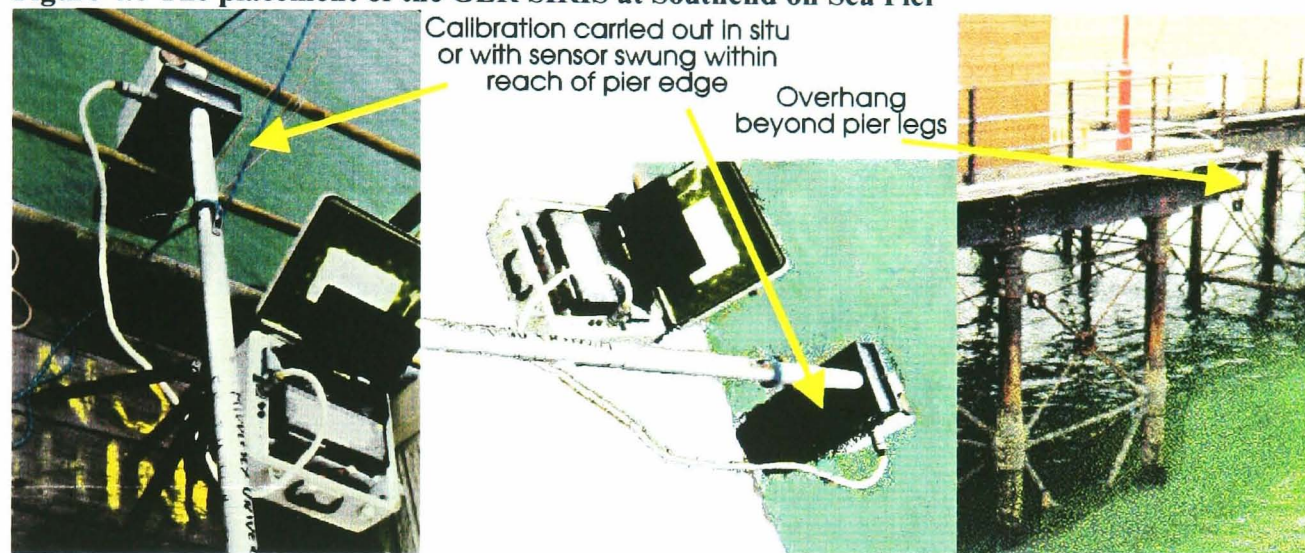
The GER SIRIS requires sequential measurement of the target and reference panel and the boom allowed the spectroradiometer to be swung slightly into a position where the reference panel (SRT4240A) could be suspended under the spectroradiometer for calibration. For each of the reference data sets collected, a sequence of readings were recorded over the water. Each reading took around 90 seconds with a minimal delay of less than 20 seconds between the reference set and the first data collected. The recording time varies with battery power which decreases with temperature and with time in the field. The period of time over which further readings were taken was dependent on the weather/cloud conditions. If conditions were good and there was no change in light conditions (according to the light meter) then a sequence of up to ten recording were

made. More usually, however, only four recordings were made for each reference set and frequently only one recording could be made.

The general weather and surface conditions were noted and cloud conditions recorded using the EPFS sky codes (shown in Table 4.4) for every sequence of recordings. Each data set was stored within a computer file (on a laptop computer connected to the equipment) with filenames consisting of the day number, a letter referring to reference set (and water quality sample) and a number referring to the number in sequence of that recording.

Table 4. 4 EPFS sky codes

0	clear sky
1	haze
2	thin cirrus - sun not obscured
3	thin cirrus - sun obscured
4	scattered cumulus - sun not obscured
5	cumulus over most of sky - sun not obscured
6	cumulus sun obscured
7	complete cumulus cloud cover
8	stratus - sun obscured
9	drizzle

Several sets of recordings (including recalibration) with approximately 5 minute intervals were taken for each set of water samples. The number of recording varied with conditions.

4.2.2 Pre-processing of spectral data

The spectral data sets were saved direct onto a laptop PC in the field as binary format files. These files contained the brightness value for each of the wavelengths recorded for the target (water reflectance) and reference reflectance (calibration panel reflectance). At the end of each data collection day, the files were processed in three stages using the software provided by the NERC Equipment Pool for Field Spectroscopy (EPFS) for the GER SIRIS.

1. The spectroradiometer management software (Master) was used to convert the SIRIS format file to a readable binary file format. In the process the reflectance values were converted to percentage reflectance. No corrections were made to the data in terms of ambient brightness, predictable atmospheric and mechanical errors, etc.

2. The reference data set was used to calibrate the spectral signatures recorded in accordance with the available light at the time of the recording. The next stages of pre-processing were completed after the fieldwork period because there was not enough time to complete these processes after data collection. Each file already contained reference data and target data, and by running the NERC Multicaldo software and entering the reference panel code each individual binary format file was converted to a normalised file containing simply the normalised percentage reflectance values for each wavelength recorded (creating a series of identically entitled files with the extension .abs).

3. The normalised files were converted to CSV format containing normalised reflectance values with corresponding wavelengths. The GER SIRIS records in three sequences using three separate gratings (2nm in the range 0.3-1.0μm, 4nm in the

range 1.0-1.8μm and 5nm in the range 1.8-2.5μm) and each time the gratings are changed there is some mechanical interference with the recorded reflectance. The final conversion process to CSV format files. also completed corrections for the change of gratings in the GER SIRIS. It was also possible to remove the atmospherically effected channels but this option was not utilised in case some data of interest were lost.

Appendix 2A2 contains the NERC EPFS literature on the GER SIRIS pre-processing and gives full details of the procedures involved.

The final stages of data collection involved entering the water quality data by hand and importing the ASCII format CSV files containing the spectral data into a spreadsheet.

4.2.3 Water Quality

Each of the water samples were separated into sterilised (by steaming) containers as follows:

- 500ml for chlorophyll analysis

- 500ml for suspended solids, nitrates, phosphates

- 250ml for microbiological analysis (the container was pre-sterilised by steaming the previous night)

- 150ml for BOD

- Approximately 500ml for the field analysed water quality parameters which included DO, Ammonia. Temperature, salinity. These parameters were immediately tested.

The water was collected using a water sampler capable of holding 500ml suspended on a rope with the 1 metre depth clearly marked. A limit of six hours was placed on work in the field because the biological water quality parameters need to be analysed within strict time limits of 8 hours following advice from the microbiology laboratory. All biological samples (BOD, chlorophyll, and the microbiological samples) were stored in a cold storage bag out of the sunlight to prevent the bacteria being killed by UV light and to slow biological growth.

The majority of the water quality parameters (pH, temperature, dissolved oxygen, ammonia, salinity and turbidity) were analysed on the pier in-between spectral recordings. This was important as laboratory time was limited to normal working hours (see Appendix 2A1). Laboratory analysis of the water samples at Middlesex University allowed collection of water truth information on chlorophyll, BOD, Phosphates, Nitrates and suspended solids. The microbiological parameters (E.coli, faecal coliforms, total coliforms) were analysed by a commercial laboratory (The Micro Biology Laboratory, Burnham On Crouch) using the membrane filtration method to give counts per 100ml of each bacterial type. This results in 810 sets of spectral data with 90 corresponding water quality samples for water truth data. The laboratory methods carried out were standard methods and are listed in Appendix 2A2 which contains the methods used for the laboratory analysis carried out at Middlesex University.

The water samples were taken from the first 1m below the surface and were taken 2 hours before high tide, at high tide and 2 hr after high tide whenever possible to attempt to increase the variety on water quality. The tidal state of the water was viewed as important for water sampling as there is a net influx of sea water prior to high tide along with

potentially increased sewage input (both of the sewer outfalls are east of the pier and one is 0.5km (approximately) East/out to sea (see Figure 4.3). Spectral data were recorded at least every 30 minutes between these times. Time practicality implications of carrying out more than three water samples for laboratory analysis means that many of the spectral data sets do not have a corresponding full set of water truth data i.e. micro-biological, BOD, chlorophyll, phosphates and nitrates. The water quality for these recordings had to be estimated on the basis that water quality changes gradually during the 1.5-2 hours between the water samples unless there was a change in tidal flow direction. The water quality parameters measured in the field (temperature, turbidity, pH, ammonia, salinity and dissolved oxygen) were recorded between water samples and provide supporting evidence of the gradual change in water quality. This assisted with the estimation of the water quality for spectral recording between water samples.

4.2.4 Data collection timing issues

Pier opening times (8 a.m. to 6 p.m.) onto the pier and tide times are not always compatible, therefore, it was necessary to vary the times of data collection accordingly, perhaps switching to the low water period. This meant that it was not always possible to record over a change in tidal flow. Water quality estimation was only done during one tidal flow direction. Data collection was repeated for a period of one month from the 22nd August to the 22nd September 1995 and the dates and times of data collection are listed in Appendix 2A1.

Water quality data for the microbiological parameters were limited by the time required to process the water samples and available times due to the tides and laboratory work

required at the Microbiology Laboratories in Burnham on Crouch. Samples had to be with the laboratory by 5.00p.m. and samples should not be kept for more than 6 hours from collection to analysis. This resulted in 48 samples for the microbiological parameters being collected and analysed (see Appendix 2A1).

Chlorophyll was limited by travel/tide times from site to Middlesex in order to complete the analysis by 5 p.m. when the laboratories close. BOD was limited by a 5 day analysis process (see Appendix 2A2) which meant that samples could only be analysed from 3 days of the week (Mondays, Thursdays and Fridays) (see Appendix 2A1) and had to be frozen for all other days. Limited access to the laboratories at Middlesex University meant that samples for BOD and chlorophyll could not be analysed for the first two weeks of data collection. Microbiological samples cannot be frozen following advice from the microbiology laboratories at Middlesex University and three pilot tests (carried out in June/July 1995) to test the possibility of freezing samples for BOD and chlorophyll showed that samples for chlorophyll could not be frozen. The exception to this was the BOD which showed that there was no significant variation in the results and so could be frozen without a marked detrimental effect to the result so 14 samples could be included in the first two weeks to increase the number of BOD samples. This was not the case for chlorophyll which was found to change significantly in two pilot tests. On advice from Middlesex University laboratory suspended sediments, nitrate, and phosphate samples were all frozen and all were defrosted and analysed within four weeks of collection i.e. by late September 1995.

4.2.4 Estimation of water quality

Although the majority of the spectral data did not have simultaneous water quality data, no set of data were more than 60 minutes from the next and previous water quality sample. Changes in overall water quality will inevitably be slow: changes will not happen instantly as water is continually mixing. This assumption has been depended upon in other flown remote sensing studies such as those carried out by Roberts *et al.* (1994) or Dekker (1993) or any of the studies carried out by NERC in the Humber estuary which used a ship to collect water quality data. In this study's case the delays in water samples were reduced to a maximum of half an hour from a water sample being taken. This allows the average water quality to be estimated with an acceptable degree of accuracy for each of the spectral data sets between the water quality samples. The water quality between two samples on the same day in the same tidal flow were assumed to gradually change along a linear relationship (see Figure 4.7). Therefore water quality at the mid point of these two water samples was the mean of both samples results. This is obviously a potential source of error, but turbidity, ammonia, dissolved oxygen, temperature, salinity and pH were all recorded more regularly and were used to check that there was no sudden change in water quality when calculating the estimated water quality. If a sudden change had been found in the other parameters a missing value would have been inserted rather than an estimated value but this was not found to be necessary. This is additionally supported by the fact that the Thames is a well mixed estuary (Harris *et al.*,1993) and therefore it is reasonable to expect changes to be gradual so long as tidal direction does not change. The regularity and accuracy of sampling location relative to the reflectance recordings make this approach more accurate than a larger scale study using boat and plane sampling. The spectral data were collected continuously with an equal interval

between samples so that water quality could be calculated on the basis of the linear relationship. Water quality was only estimated between water quality samples on the same day and on the same tidal flow. Missing quality values that had no preceding data from the same day were entered as a missing value. Estimated water quality was calculated and entered manually because of the complexity of including or excluding an estimated value. Exclusion was on the basis of tidal flow for the sample. change in other parameters and day of sample.

Figure 4.7 Assumed relationship between water quality samples on any one day.
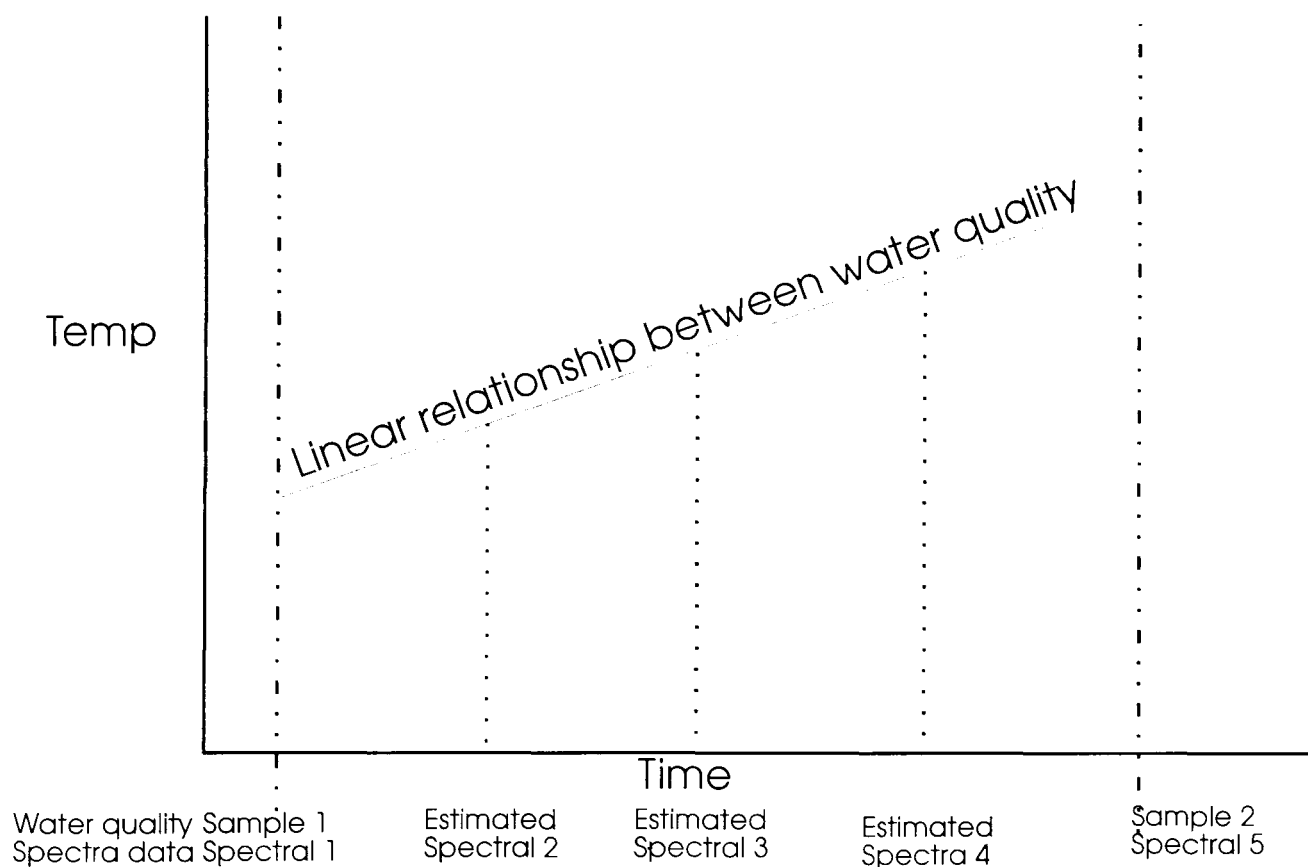
The water quality data collected supported a gradual but significant change in water quality over the sampling period and the regular testing of water quality over the short 4 hour period proved very beneficial in estimating water quality and confirmed the use of non airborne data collection was the best approach to data collection. The use of flown data with water quality collected by ship would have produced a significant delay between obtaining water quality data compared to spectral data.

4.2.5 Understanding water quality data in the study area

Prior to the initial data collection period water quality data were acquired from the National Rivers Authority (now Environment Agency) for all surrounding sampling points. This thesis's research sampling site at Southend-on-Sea Pier was at the extreme end of the EA river sampling region and therefore their river sample data was also obtained. The Environment Agency (EA) bathing sampling points (pttb0001, pttb0002, pttb0003, pttb0004, pttb0005, pttb0006, pttb0008) are shown on Figure 4.8, with the river water sampling points (pttr0024, pttr0025, pttr0026). The river sampling points provided additional information on chlorophyll, BOD and ammonia/nitrogen which are not recorded at bathing water sampling points (Figure 4.8). Only pH, temperature, coliforms (total), E.coli, and faecal streptococci have been collected at the bathing water points as these were the minimum range of parameters required by the EU bathing water directives, though E.coli was also usefully included by the EA. EA bathing water quality samples are recorded at standard 30cm depth in 1m of water within one hour of high tide. The EU does not stipulate times of sampling, and therefore the Environment Agency do not consider the tidal state in their water quality data although times are recorded i.e. samples can be taken prior to, after or before high water.

The data collected prior to 1995 showed a dramatic variation in water quality throughout the season (as do subsequent year's data) and Table 7.1 shows the summary of water quality data for some of the beaches around Southend pier over the period 1993-1994 (the years prior to data collection). The EA data showed that large variations

in levels of parameter occur between consecutive days of sampling. Consecutive days water quality data showed no relationship to one another. e.g. July 15th 1996 coliform levels at Westcliff passed all requirements with a count of just 40/100ml but on the 16th July it failed with a count of 3700/100ml. This significant variation showed that each days samples could be regarded as independent of one another. The variability of water quality in the study area meant that the site was suitable for this study because a wide range of different water qualities could be expected in water quality samples over a month period. This variability in water quality was necessary for this study when considering the relationship between changes in spectral reflectance of the estuary and change in water quality. These significant changes in water quality are the result of tidal flows and changing of the water body within change of tide.

Table 4.5 Summary (minimum and maximum recorded values) of EA water quality data for beaches in Southend - on - Sea area over two years (1993-1994).

EA Beach/ sample point	pH		Temperature (centigrade)		Coliforms /100ml		E.coli /100ml		Chloro -phyll-a (ug/L)		BOD 5day (mgl-1)		ammonia nitrogen (mgl-1)	
pttr 0025	7.8	8.6	3.9	22	*	*	*	*	4	17	1.2	2	.016	.62
pttb 0004	*	7.3	11	24	100	65500	10	29000						
pttb 0005	*	7.3	11	24	10	5800	10	3400						
pttb 0003	*	7.3	11	27	10	4100	10	2700						
pttb 0002	*	7.3	11	24	20	4300	10	2700						

Figure 4.8 Southend Bathing water Study Area EA Sampling points (not to exact scale (Southend Pier is approximately 2.14km long))
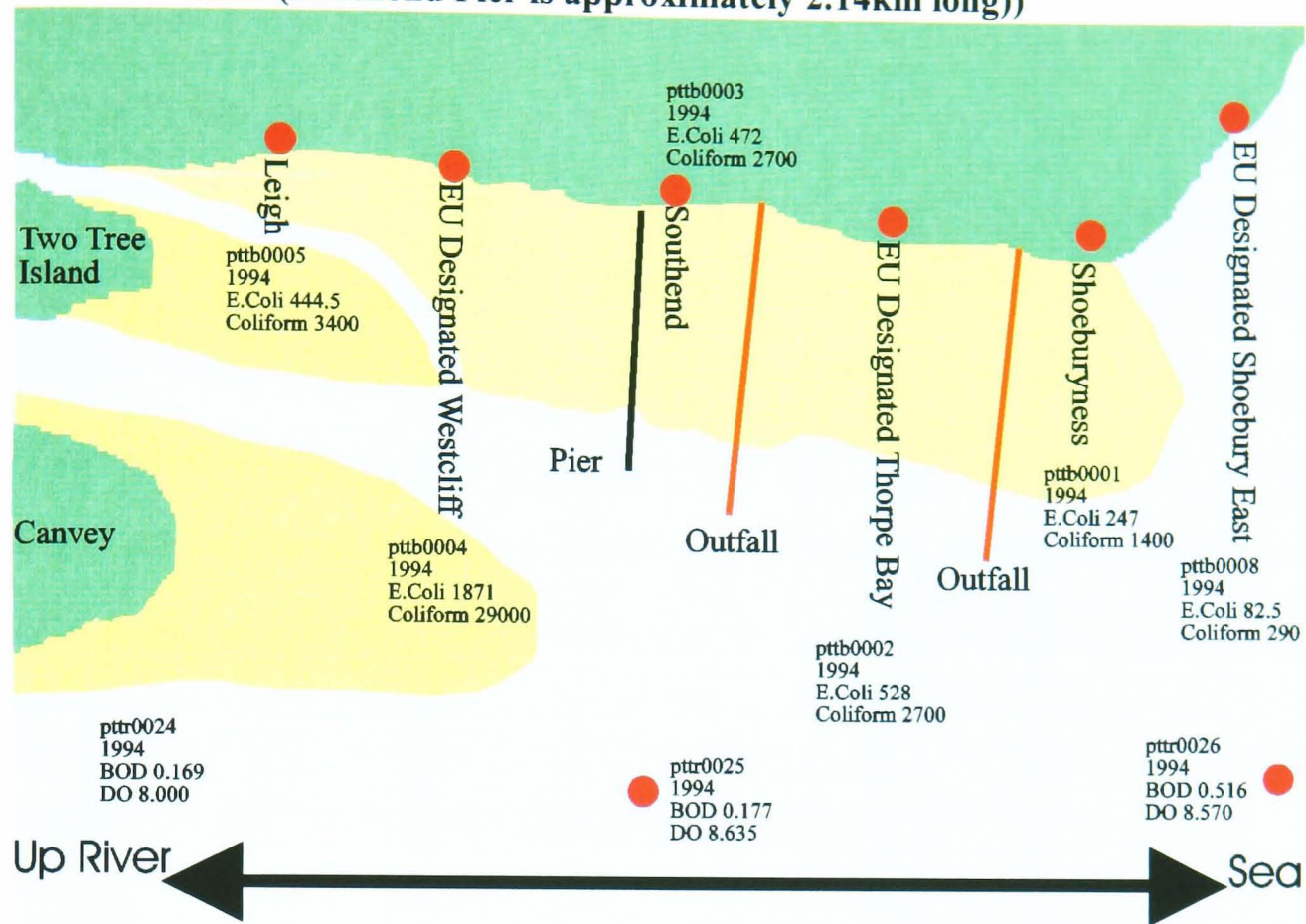
● Sampling point

The sampling points at Westcliff (Environment Agency sample point pttb0004) illustrate the variation in water quality as it failed on the bacterial levels on several occasions during 1993-94, as well as 1995 while Thorpe Bay (pttb002) passed on the corresponding days (subsequently pttb0002 has failed the directive in 1995 and 1996. The bacterial levels were sometimes higher at Westcliff and sometimes at Thorpe Bay. It should be noted quality variation may be different following subsequent upgrades in 1997 to the treatment works to allow further treatment to the sewage prior to release and changes to storage to prevent storm overflow of raw sewage. The two sample points (Thorpe Bay pttb0002 and Westcliff pttb0004) are either side of the pier and tidal flows (Figures 4.9 and 4.10) must move water through and past the pier, this produced a variety of water quality levels in the field data. A sewer outfall, which released primary treated sewage in 1995 on a constant basis, was between the two sample point near to

the pier head (see Figure 4.8). This was likely to increase the number of high bacterial count samples. At Southend, sewage is pumped into holding tanks which are then allowed to flow out through the outfall pipes. The lack of any mechanical pumping of the sewage means release from the sewer is greater at low water when sea pressure is reduced due to lower water depth and therefore less resistance to the outflow of sewage (Anglian Water, 1998). The outfall pipes release the sewage into relatively sheltered waters which reduces the breakdown rate of the discharged matter (Grantham, 1992). The outfall pipes have been the source of some extremely high bacterial counts at the EA sampling points in the early 1990s prior to upgrades to treatment in 1996. The localised tidal flows of the area (Figure 4.9 and Figure 4.10) considerably influence water quality and ensure a large variation in water quality at the pier head.

Data collected were used to estimate water quality between samples on the basis of a gradual linear change in water parameter level. The use of a linear relationship is supported by the continuous and controlled supply of the local inputs from two known sources.

1. Continuous flow of gravity fed (un-pumped) sewage outflow that prevents a sudden surge in effluent unless there was a rain storm (of which there were none during the data collection periods).

2. Data collected in an undergraduate study of water quality in the area in 1998 (Diprose, 1998) highlighted a potentially large phosphates and nitrates input source to the water from a refuse land fill site on marshland approximately 5km up stream from Southend-on-Sea on Two Tree Island (see Figure 4.8). The land fill site is

surrounded by two tributaries that pass either side of land fill site and have themselves passed through an agricultural river catchment. Therefore, this is a significant source of nitrate and phosphate input into the study area. Again these will be continuous and constant inputs that will increase or decrease gradually over time so a linearly related change is a reasonable expectation over the short time scale involved of 4 hours per day.

Figure 4.9 Tidal Flow in the Southend-on-Sea bathing water area with flood (incoming) tide (not to exact scale (Southend Pier is approximately 2.14km long))
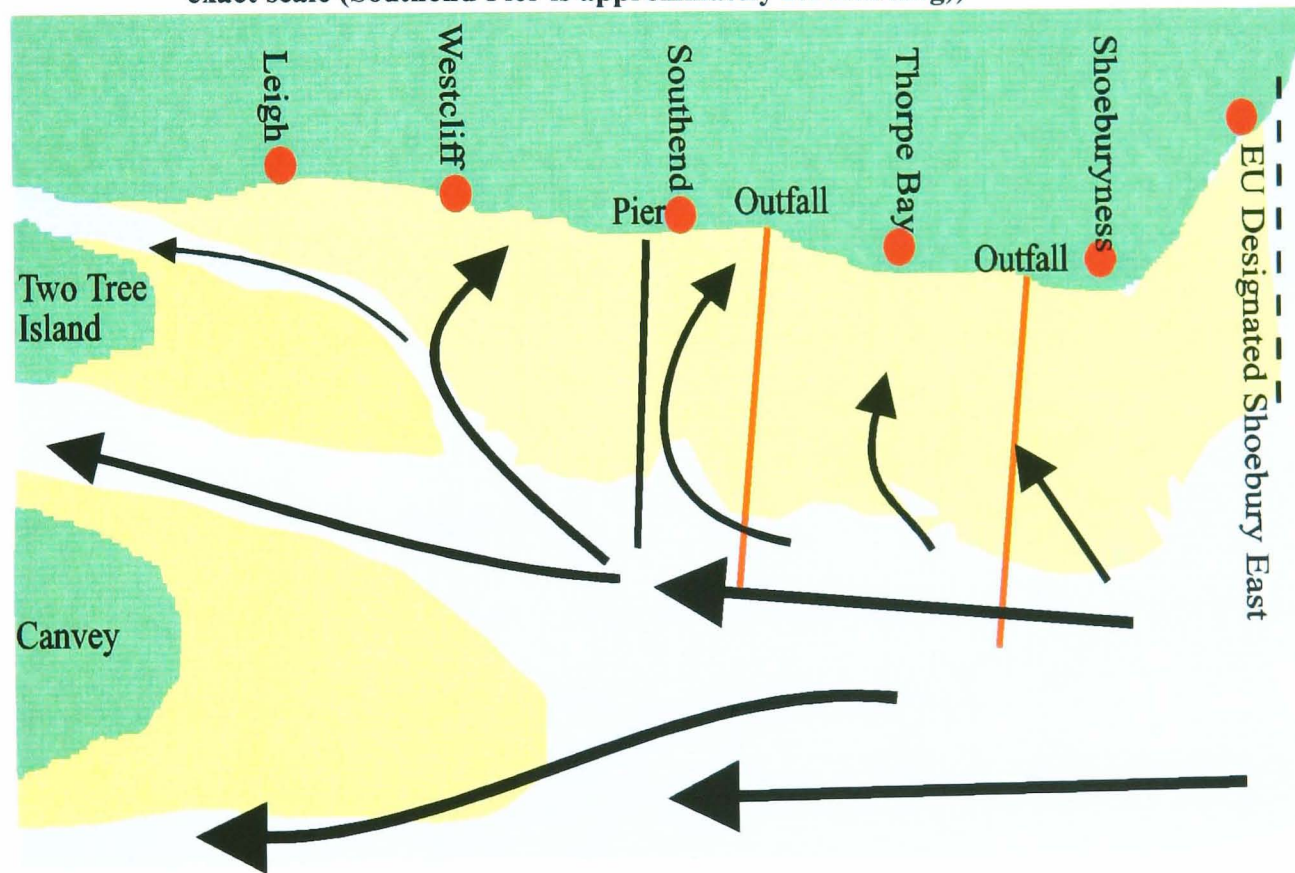
The water quality variation was maximised by trying to complete data collection over a change in tide, from 2 hours before to 2 hours after low water or high water to try to take advantage of these potential local inputs. Water quality was only estimated whilst the tidal direction was constant i.e. ebb or flood tide.

Figure 4.10 Tidal Flow in the Southend-on-Sea bathing water area with ebb (outgoing) tide (not to exact scale (Southend Pier is approximately 2.14km long))
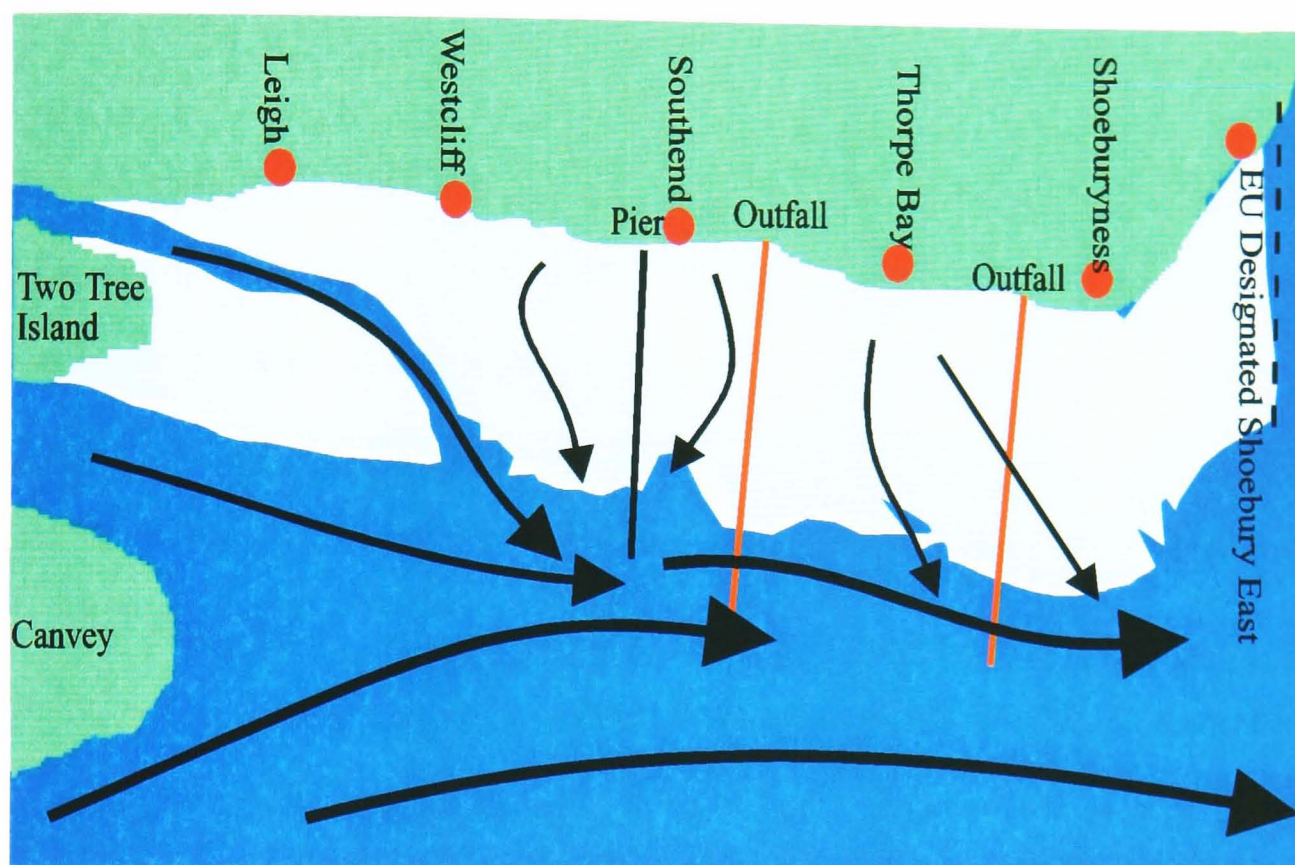
4.3 General Chapter Summary

After consideration outlined in this chapter, Southend-on-Sea pier was selected for data collection using a GER SIRIS spectroradiometer. This allowed:

- The use of genuine coastal Case 2 water in a bathing recreational area that includes two EU designated bathing beaches

- The proximity of the surface in comparison to flown data collection to reduce the influence of atmospheric interference

- The stable structure of the pier to remove problems of roll, pitch and yaw that would be experienced in data collected from a boat and from a plane

- A reduction in the potential influence of the sun position and potential problems with surface glare by using the structure of the pier to provide a permanent shade from direct sunlight.

The water quality parameters selected (see Table 4.2) were initially based on the current EU bathing water quality directive but some were excluded and some additional parameters included. This was because of:

- EU expectation that there will be a new directive that will include E.coli amongst other parameters

- Cost of microbiology analysis capped the number of samples and number of parameters that could be tested. However three major indicators were included (faecal coliform, total coliform and E.coli)

- Currently only eight (8 EU) parameters are collected by the EA in the UK

- Some parameters such as salmonella were unlikely to be directly visible and would be indicated by the presence of E.coli

- Some parameters were included due to their potential as secondary parameters. Secondary parameters are parameters that may be good indicators of changes in water quality, specifically those in the EU directive e.g. chlorophyll is likely to be an indicator of high levels of phosphates or nitrates

The water quality samples were taken at approximately ten minute intervals alongside calibration of the spectroradiometer for all parameters that could be measured in the field. Field measurement of microbiological, chlorophyll, BOD, nitrates, phosphates, suspended sediment was not possible so samples were taken every two hours. Where

possible these were taken once prior to high water, once at high water and once after high water when laboratory opening times and tide times permitted. Estimated values of concentration level of these parameters was required based on a linear relationship to provide data for the intervening periods. This still offers greater accuracy than a comparable study using flown data and water samples collected by boat.

Spectral data were collected using a GER SIRIS through the range 300-2500nm. The spectroradiometer was calibrated every ten minutes for changing illumination between samples using a reference panel (SR4240A). The instrument was held over an overhanging part of the pier where interference from the pier structure was not possible. Pre-processing of the spectral data produced normalised percentage reflectance.

CHAPTER 5

Spectral Data Error, Interpretation and Solutions

Following spectral data collection, an understanding of the problems encountered in the field and their effect on the data was needed to allow the development and application of explicit and objective error removal before any analysis of the data could be performed.

5.1 Spectroradiometer calibration issues and interpretation of unexpected reflectance (probable error)

The data collection from Southend-on-Sea pier presented some problems involving the calibration of the field spectroradiometer. These problems were a mix of both instrument design and field operation of the spectroradiometer.

1. It was not practical to record the level of light at water level for calibration because of the physical distance from the surface of the water (ranging from 2.5m to approximately 8m) therefore there was a possibility of error with calibration. However, had significant problems with calibration occurred they would have been visible during pre-processing of the spectral data. During pre-processing, there were no detected problems with calibration.

2. The calibration panel had to be held under the spectroradiometer optical head for the calibration. This meant that on some sampling points (specifically the lower deck sites), the sensor had to be swung to within arms reach to place the panel underneath the spectroradiometer, carrying a possible risk of the reflectance being affected by the upper deck. A hand-held light meter was used to check for changes in

reflectance during the initial site location studies undertaken prior to site selection and these gave no indication that there would be a problem with shadowing of the calibration panel. The results obtained in the different locations also showed no significant differences.

3. There was a delay in recording from the calibration panel and recording from the estuary. This was partly due to use of the spectroradiometer on the pier, with the delay in placing the panel below the optical head and then placing the head securely over the estuary water (see Figure 4.4). This delay was also due to the instrument itself, because it took one minute for each recording, thus giving a practical delay of 3 minutes from the beginning of the calibration recording and the end of the first estuary recording. This meant that it was not practical to use the calibration panel for every recording.

The alternative method adopted was to record a sequence of recordings after the first calibration until the light meter indicated a change of lighting, or until it became evident that cloud cover was approaching. This was not ideal but again the practicalities of field measurement necessitated its use. Analysis of the data indicated stable reflectance readings for all sequences except where cloud cover had changed and had been noted. This indicated the suitability of the approach to calibration that was adopted. The spectroradiometer was re-calibrated at least every 10 minutes or whenever conditions changed. This varied from day to day with clear ideal conditions allowing five, six or more recordings in a sequence while cloudy days sometimes allowed only individual recordings before re-calibration was necessary. Readings were discarded prior to pre-processing where changes in ambient light had been noted. Minor effects of changes in ambient light will

inevitably have caused some variation in spectral recording, but these were not considered to be significant.

4. The instrument used, a GER SIRIS, had a minimum scan time of 30 seconds. On colder days this scan time could increase to a minute per scan because batteries perform better when warm. Although in the field it is better to have a rapid scan time to avoid environmental variation, this can only be said to be true for land/static surfaces. Water is dynamic and hence an averaged reflectance of the surface is required, not a point sample. The duration of the scan allows minor changes on the surface of the water to be evened out in a similar way to that found when using an aeroplane that allow the coverage to be very large so that, for example, surface foam is averaged over several square metres. The length of the scan time increases the possibility of errors incurred due to changes in atmospheric conditions such as wind, moisture and light conditions/cloud cover. However, the careful use of the light meter and using cloud free periods when possible reduced this potential error to a minimum. Wright (1986) took the idea of longer scan times even further by proposing that the longer scan time leads to time averaged recordings. These are similar to a spatially averaged measurement with a larger field of view, even on static surfaces, in that it accounts for atmospheric conditions such as wind disturbance (Wright,1986; Analytical Spectral Devices, 1996).

Different field environmental factors, particularly cloud cover, have led to significant variations in recorded reflectance, which implies a deterioration in the quality of recorded data. An understanding of these factors is essential to the interpretation of the data. Environmental factors operate in several ways to affect the quality of reflectance data:

1. It is physically more difficult to record in adverse conditions (wind/rain) both for calibration and target measurement due to difficulties in steadying equipment, fatigue and keeping equipment such as the calibration panel dry and clean.

2. Rough seas will create more diffuse reflectance and consequently more diverse reflectance spectra for a given water quality i.e. poorer recordings.

3. Poor weather conditions (high wind, rain) can cause far more surface foam, and dramatic changes in height of the water from the spectroradiometer. The foam levels/horses on the waves were increased by waves breaking through and onto the pier structure itself.

4. Rough conditions cause surface debris to become common for some time post storm.

5. Abnormal tides cause very high levels of surface debris, resulting in extreme reflectance values when this debris is included in the field of view.

6. Cloud cover of any description will considerably affect the available light (Milton *et al.*, 1995). This is illustrated in Figure 5.1 which shows the effect that different cloud conditions can have on normalised reflectance during a two minute period (the GER SIRIS could take 1 minute for a single scan). Cloud cover is never homogenous. Every effort was made to avoid the effects of cloud cover with frequent calibration and careful selection of recording periods when cloud cover was not present or was as low as possible. On two days, weather conditions included drizzle and high

levels of water vapour which caused variation in the recorded light (Gao and Goetz, 1990) and thus very frequent calibration on these days was required. Calibration will be affected dramatically by such weather conditions, particularly of longer wavelengths. It would be nonsensical to exclude any day with imperfect conditions because a monitoring system would have to be operated through a workable range of weather conditions. However, data collected on very poor days were likely to be impossible to use.

7. On low-tide sampling days, there was a significant increase in the possibility of bottom reflectance, especially at low tide itself. Water depth fell to as low as 2.5m on two occasions, which was more than double the depth of turbidity indicated by the Sechi disk at those times. However, the Sechi disk inevitably only involves the use of visible light. Infra red light should theoretically penetrate to less depth but there is a risk some bottom reflectance could have played a role.

8. Surface glare was reduced to a minimum by using the pier structure to remove direct sunlight and the effect of changing sun height as discussed in the data collection methodology but inevitably there will still be some instances of glare. However these values will be very high and explain some of the extreme anomalous data values where reflectance was much higher than all surrounding recorded values.

Figure 5.1   Effect of sky cloud cover (Milton, Rollin, Emery 1995)
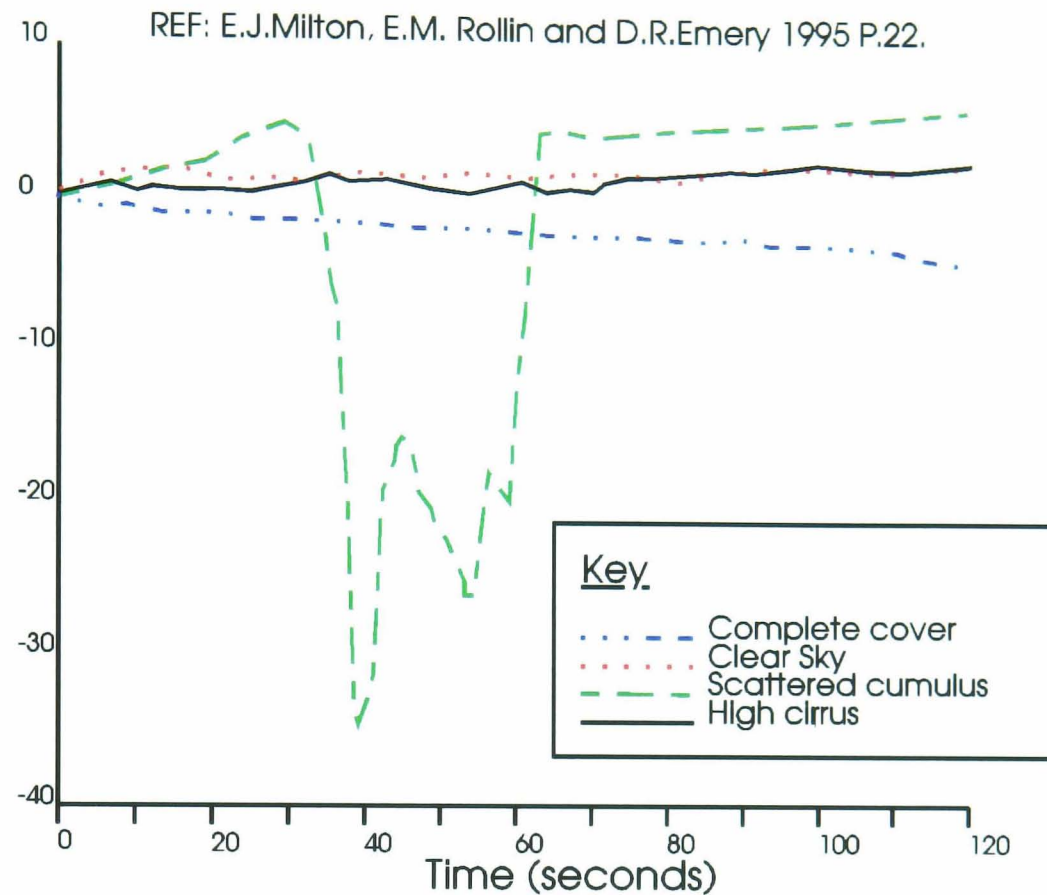
Figure 5.1 illustrates the percentage errors associated with different cloud cover. Understanding of the effect of different types of cloud condition on spectral recordings allowed more care to be taken in conditions such as cumulus clouded days to avoid any cloud contamination and also to assist in the exclusion of samples on the basis of the cloud cover present. This information was used to select the better samples for analysis when appropriate for some analytical approaches.

5.2 Error and unexpected reflectance as a result of the field environment.

As expected the weather conditions had an effect on the quality of the data with high winds and cloud cover causing wide variation in the recorded spectral reflectance of the water. Figure 5.2(a-d) shows examples of the variations found in recording for each calibration through a range of conditions from a clear day which yielded good quality data, to a windy, cloudy day where the quality of the data has to be questioned.

Figures 5.2a-5.2d show the reflectance curves recorded for one calibration on an individual day and each reflectance curve on each graph should therefore show reflectance from similar water quality. The reflectance curves in Figures 5.2a-5.2b are similar with minimal variation especially in Figure 5.2a when conditions were very good. However, the series of graphs in Figure 5.2 clearly illustrate the dramatic variation that can occur when atmospheric conditions significantly deteriorate in e.g. wind in Figure 5.2c and the wide variation caused by variable cumulus cloud cover in Figure 5.2d.

Figure 5.2(a-d): Variation in reflectance with field conditions
**Figure 5.2a Reflectance of estuary on day 28 with excellent conditions (clear sky and calm water).
These data were recorded from the optimum sample site on the upper deck, west side facing west.**
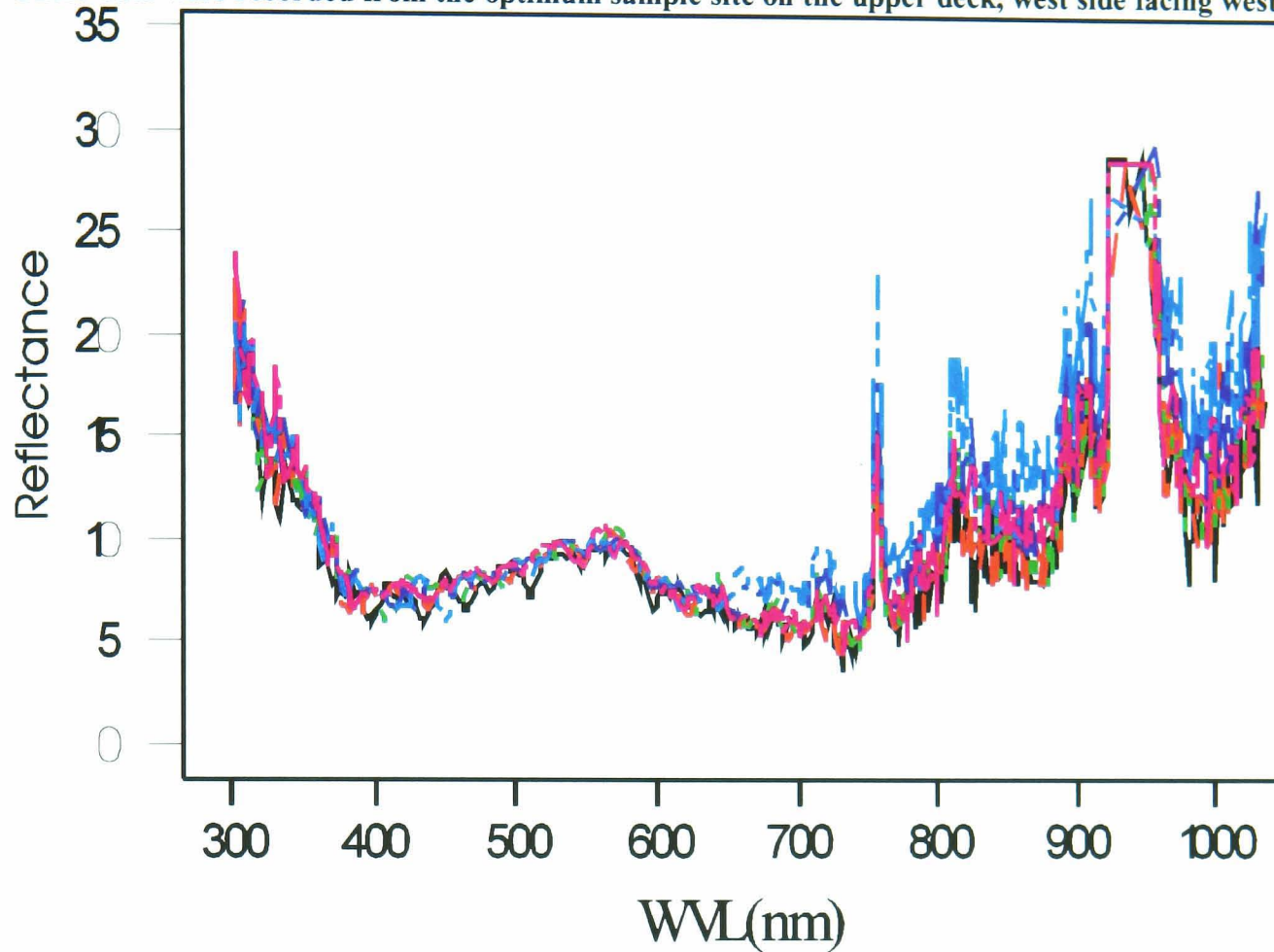
**Figure 5.2b Reflectance of estuary on day 22 with good conditions with some clear sky and calm
water. Recorded from the low water sample site on the lower deck, east side facing north.**
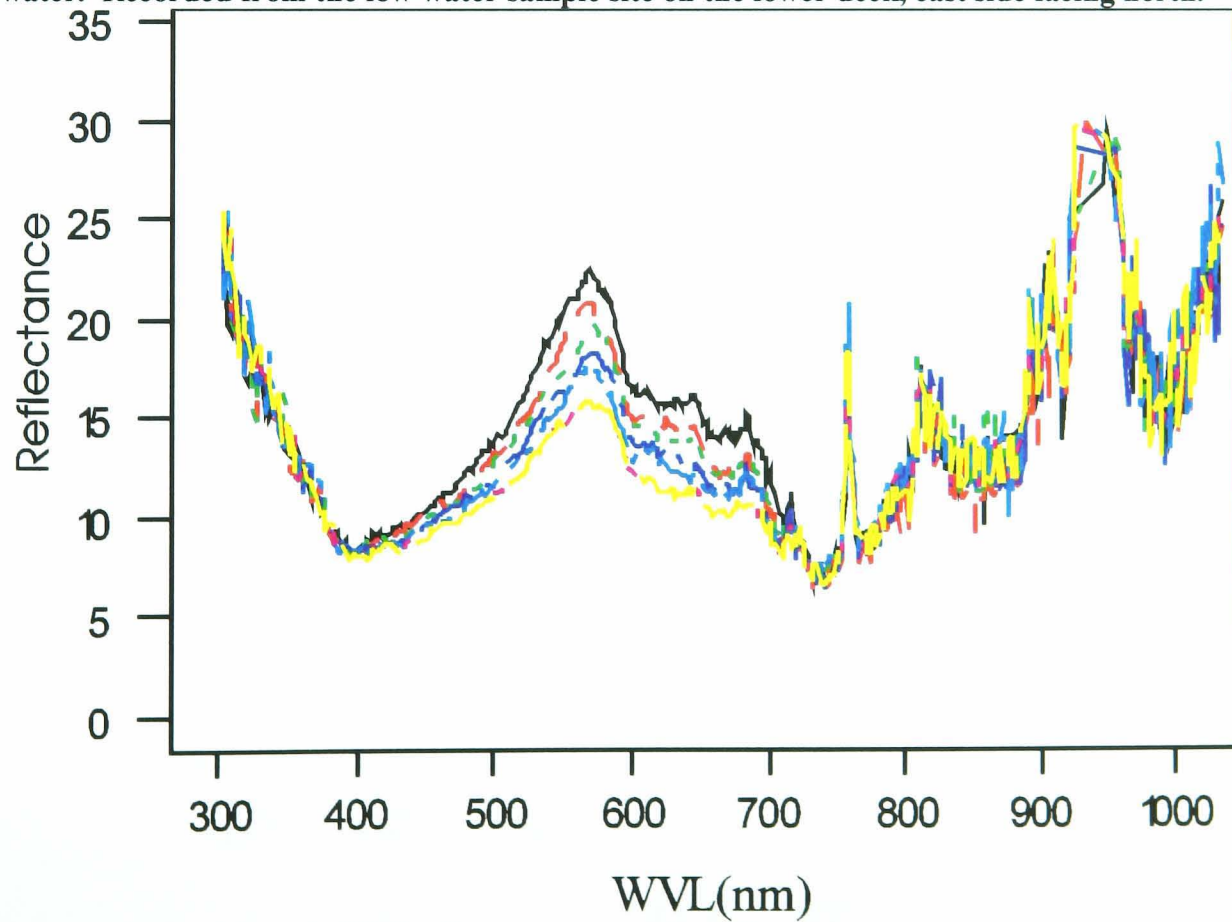
Figure 5.2c Reflectance of estuary on day 4 with average conditions with some cloud cover but very rough sea. Recorded from the sample site on the upper deck, west side facing west.
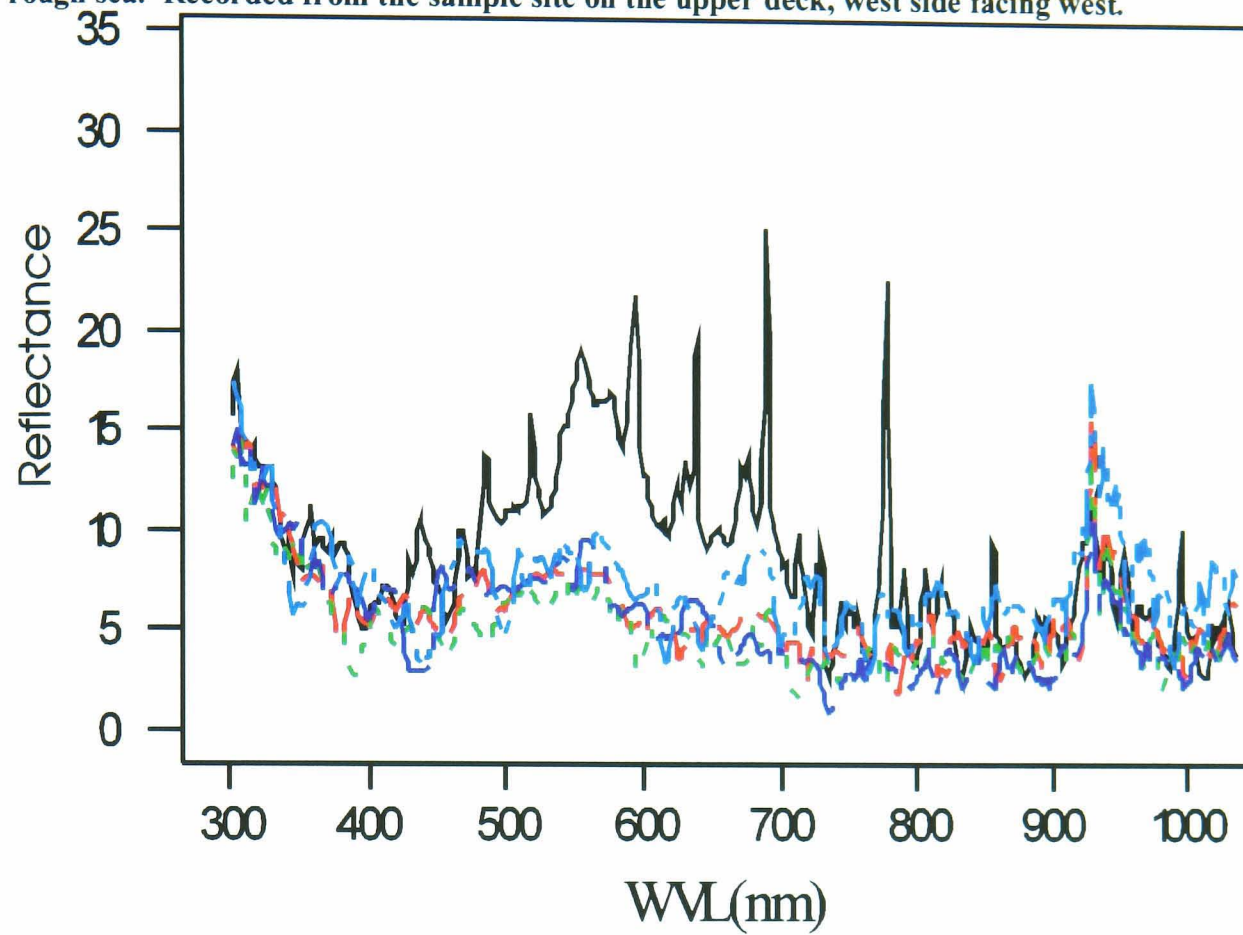
Figure 5.2d Reflectance of estuary on day 21 under poor conditions with broken cloud cover but calm sea. Recorded from the optimum sample site on the upper deck, west side facing west.
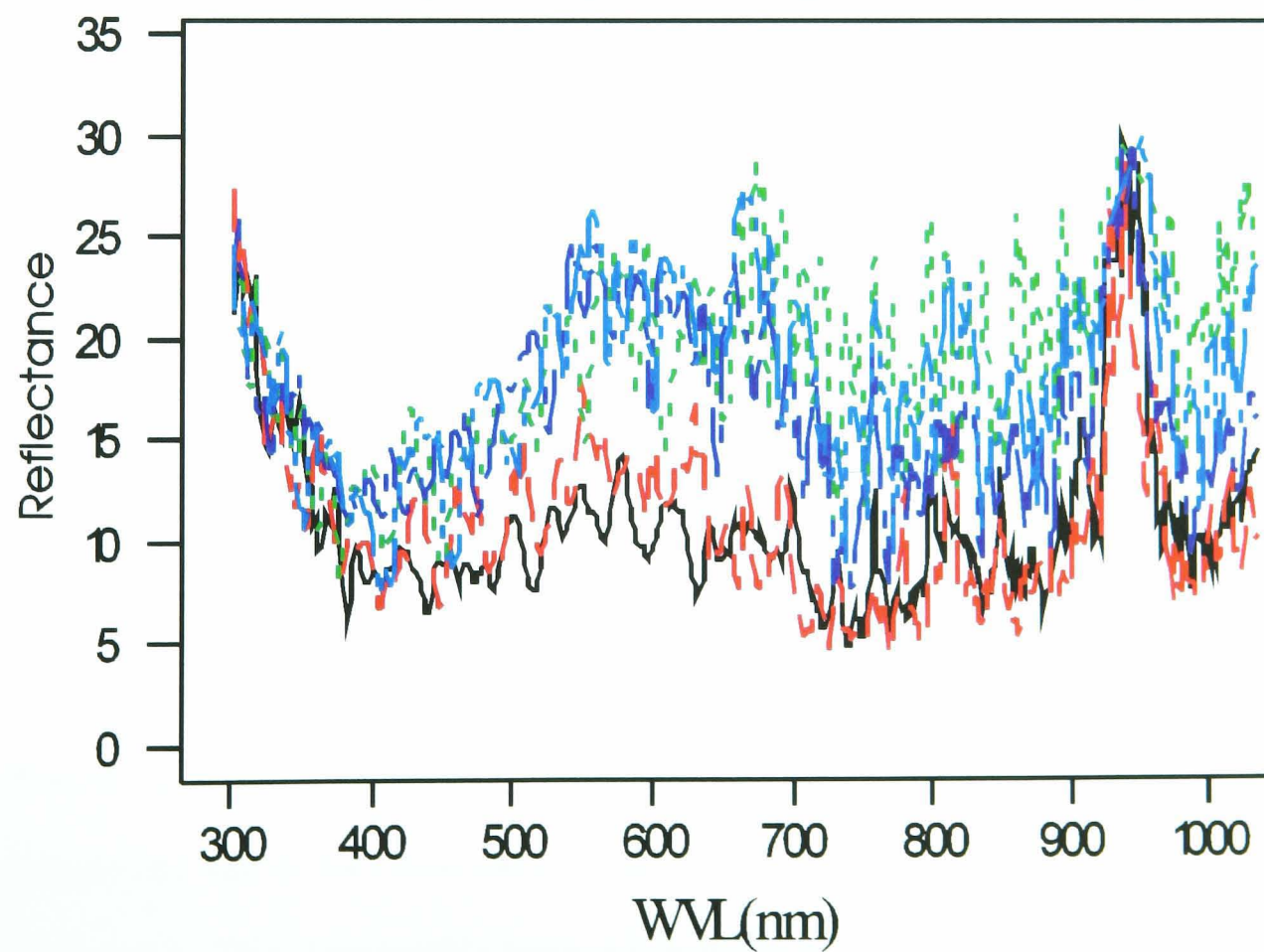
5.3 Approaches to account for error in the spectral data

Land-based studies can rely on recording a static surface. In contrast, an estuary water's surface is dynamic; during the time a recording is made, the surface will be a mix of several parameters that vary constantly and the surface height and angle is constantly fluctuating. Inevitably, the reflectance signatures recorded will vary during the measurement period despite there being no significant change in water 'quality'. In many respects, this issue is of central importance to this study.

If remote sensing is to be used to monitor water quality, then the relationships between reflectance and each water quality parameter must be robust. i.e. they can be identified, despite small changes in the real world environment. The dynamic nature of the estuary and subtle changes in atmospheric conditions mean that some variation in the reflectance for each recording following a calibration is to be expected. It is the general reflectance of the area that is important because point water quality is neither necessary nor useful. The aim of a monitoring system should be to break up the water body into 'tiles' of homogenous water quality determined by the resolution of the instrument used. Thus, a remote sensing monitoring system will always result in the spatial averaging of water quality over a known surface area. Therefore any minor fluctuation within the field of view of the sensor will be averaged out by the recorded reflectance within the whole field of view. The wide field of view of the GER SIRIS assisted this process.

However, it would be naive to expect it to be possible to include all data collected in the analysis and still extract reasonable results. Therefore, any obvious anomalies have to be removed. This is acceptable because it is reasonable to expect a monitoring system to identify large anomalous fluctuations. Very poor quality data have been excluded

from all the analysis through the implementation of several filtering procedures. A potential approach would be to replace poor data values by a mean value of reflectance from the neighbouring wavelengths. Poor data is any data value affected by interfering environmental factors other than changes in water quality such as cloud cover, surface debris, glare or other similar factors. Poor data will usually be identifiable by being significantly outside the normal radiance range recorded. However, these data will be used for further analysis and so any poor values were removed and left as missing to avoid statistically contaminating the data. Data were removed if:

1. there was a dramatic change in reflectance between some of the recordings for a single calibration then, that recording can be presumed to be caused by sudden change in illumination or glare from the water's surface. Values affected by glare or changes in illumination are typically very high multiples of neighbouring reflectance values usually by multiples of ten or more e.g. % reflectance values of 70 when normal values are between 5-20.

2. a particular wavelength recording has an extreme value, for example values greater than 300 when values were usually less than 20, then a temporary, pre-processing, mechanical, and/or electrical interference can be presumed and that single value removed.

3. foam or surface litter can have a profound effect on reflectance. This is not important where a larger area is being recorded because these exceptional values would be averaged out. However because the surface area being recorded was in the region of 1m x 1m (see Figure 4.3), these values cannot be averaged out. Therefore

these values were removed by setting a realistic maximum Figure based on the usual range of the % reflectance values (5 up to 25). Based on this range, the threshold value was set to a % reflectance value of 30 using a filter to remove any greater value from the data set, leaving it as a missing value.

4. any visual change such as foam was recorded in the field to aid the explanation and interpretation of reflectance anomalies. This was important because some spectral data were visually poor at the time of recording in the field because of visible changes in illumination or the water's surface. These recordings which were identified as being collected at the same time as the presence of surface foam were excluded manually before analysis.

5. the influence of minor fluctuations in the data caused by minor changes in atmospheric conditions was significantly reduced by averaging the spectral recordings for each calibration (Wright, 1986). For example, 4 recordings were taken on day 2 (coded as 2A1-2A4) and the standardised value used for analysis was the mean of these four values. The only cautionary element of this procedure is that the better recordings (i.e. those taken on good clear days in ideal conditions) were averaged despite the low level of error, as illustrated in Figure 4.1(a). Therefore this approach ultimately reduces the number of good recordings available for further analysis and in poor conditions, it was sometimes only possible to collect one recording for each calibration. On these poor days, the data should be excluded to prevent inflating the effect of the poor quality data that cannot be averaged. After studying the data only data with three or more recordings per calibration were included in this process of data cleaning.

6. Some subjective judgement needed to be applied to establish which recordings were acceptable, reserving the possibility of being selective with the days that were averaged using subjective qualitative evaluation of the data for each day. These subjective judgements were based on the weather and cloud cover information recorded in the field. This was to prevent the loss of the best quality data because otherwise days with excellent conditions will be reduced in number and consequently the proportion of recordings used with calibration errors could be increased not decreased. This judgement was based on cloud and weather conditions recorded. If the sun was completely obscured by cumulus cover or the conditions were hazy with drizzle the recording were averaged.

5.4 General Chapter Summary

There was a delay between calibration and recording because the calibration of the spectroradiometer had to be done in sequentially rather than simultaneously. The solution to this was to take a sequence of spectral recordings until either light conditions or cloud cover conditions changed (using a light meter) or ten minutes had elapsed. This usually allowed five or six recordings per calibration. Each spectral recording had a corresponding cloud cover code assigned based on the EPFS scale 0-7 as well as weather and sea conditions. This allowed the selection of best sample day data and the exclusion of poor samples. The entire data set was 'cleaned' to produce the 'full data set' by:

- Removal of extreme values caused by glare, surface debris, or mechanical or electrical interference

- Averaging of data on days with poor cloud cover conditions for each calibration to reduce the influence of changing cloud cover

CHAPTER 6

Preliminary data analysis

6.1 Overview

The preliminary data analysis were performed on the pre-processed, filtered data (i.e. the full data set) as previously described in Chapter 5 which removed obvious anomalies and problems from variation in cloud cover and will from herein be referred to as the 'full data set'.

The purpose of the initial spectral data analysis was twofold:

- Reduce the volume of data collected (total of 682773 data values);

- Narrow down the analysis to smaller succinct parts of the spectrum that were likely to yield information on water quality i.e. wavelengths that require more detailed analysis.

Two approaches were taken to determine the relevant areas of the spectrum: statistical analysis and graphical visual analysis. The results of these preliminary analyses were then used to target wavelengths in later analysis to study the relationship between reflectance and water quality parameters in the secondary analysis (Chapter 8).

6.2 Statistical Analysis

Correlation analysis was undertaken between the 840 different wavelengths and the water quality parameters using all 793 field data records in the full data set to try to identify any potential relationships. Due to the large number of wavelengths involved a

preliminary investigation into the linearity of relationships between reflectance at each wavelength and each water quality parameter level was not practical. Therefore, where a significant relationship was shown a scatter plot was produced to ensure that the relationship was reasonably linear. The spectral data were correlated against each water quality parameter using the Pearson product moment correlation method to see if there was any indication of a relationship.

$$ r = \frac{\sum (x - \bar{x})(y - \bar{\bar{y}})}{(n - 1) s_1 s_2} . $$

Where $\bar{x}$ and s_1 are the sample mean and standard deviation for the x variable, $\bar{y}$ and s_2 are the sample mean and standard deviation for the y variable. Where there were missing values, then that pair was excluded from the calculation (pairwise deletion) (Minitab 1996).

The results of these calculations are provided in Appendix 3A1. Correlation coefficients over +/-ve 0.115 are all significant at the 0.01 level (Bryman *et al.*, 1996). In order to identify the wavelengths of optimum interest for further investigation, very low correlation coefficients (<0.2) were excluded from further consideration. In addition where correlation coefficient values were >0.2 (e.g. for E.coli and Total Coliform) a threshold of coefficient value of 0.35 was used. These have been separated for each water quality parameters at the end of Appendix 3A1. Though the resulting coefficients produced should be viewed as low or modest (based on the definitions of Cohen and Holliday (Bryman *et al.*, 1996)), the correlation coefficients do show statistically significant evidence (at the 0.01 level) of a relationship at several wavelengths. Later analysis will concentrate on individual parameters, and the wavelengths with the strongest 'suggested' relationships shown by the correlation calculations will be used

within this analysis along with others identified through the initial visual analysis approach. Inevitably, there were no outstanding correlation coefficients but the figures do suggest possible relationships between reflectance within ranges of wavelengths and each of the parameters. Noise is more significant with spectral reflectance data from water because of the low levels of percentage reflectance. Therefore correlation analysis was carried out on the standard normalised data and not on first derivative data which could increase the effect of noise (Delft University, 2002).

The most significant relationships involved the microbiological indicators E.coli and Total Coliform, which are positively correlated with reflectance at several wavelengths within the range:

❑ 301-360nm for E.coli

❑ 390-400nm, 442-446nm and 607-667nm (and 1341-1420nm which may be negatively correlated) for Coliforms

Other examples of indicated relationships are:

❑ 309-313nm, 332-338nm, 342-360nm for BOD

❑ 317-325nm, 303.35nm for dissolved oxygen

The values listed in Appendix 3A1 parts 2 and 3 (which contain full results and a summary Table for each parameter) were used to select appropriate ranges of wavelengths for further analysis of each water quality parameter. No correlation coefficients are high enough to be categorised as anything more than modest, the

highest for E.coli and Total coliform are listed in Table 6.1. However. it should be remembered that these correlation values were calculated using the full data set inclusive of data collected on all days irrespective of weather conditions. The full data set was used to ensure that no wavelengths of possible interest were omitted from the second phase of analysis due to a data filtering system.

Table 6. 1 Wavelengths (nm) with positive or negative correlation coefficients of > 0.35 or more with the water quality parameters.

nm	301.35	303.35	305.33	307.32	309.29	311.28	313.26	315.24
E.coli Correlation coeficient	0.547	0.557	0.522	0.509	0.523	0.515	0.494	0.47

nm	317.21	319.19	321.16	323.12	325.09	327.04	329.01	330.97
E.coli Correlation coeficient	0.451	0.448	0.466	0.473	0.452	0.447	0.436	0.431

nm	332.92	334.87	336.82	338.77	340.72	342.66	346.53	360.05
E.coli Correlation coeficient	0.451	0.396	0.429	0.43	0.361	0.366	0.353	0.35

nm	390.5	392.38	394.26	396.14	398.02	442.44	444.27	446.09
Coliform Correlation coeficient	0.351	0.365	0.363	0.359	0.35	0.353	0.356	0.354

nm	607.4	609.05	610.71	612.36	614.01	615.65	618.95	620.58
Coliform Correlation coeficient	0.35	0.36	0.363	0.358	0.355	0.352	0.35	0.35

nm	622.23	627.15	628.78	630.42	635.32	638.57	640.2	667.63
Coliform Correlation coeficient	0.352	0.352	0.355	0.355	0.351	0.352	0.357	0.374

6.3 Graphical Visual Analysis

As identified in the aims and objectives, this research aims to identify which wavelengths have the potential for a remote sensing flagging system for bathing water. It is therefore the ability of remote sensing to identify when levels of a water quality parameter are high or low that is important. It is not necessary for reflectance at a wavelength to have a relationship with a water parameter while the levels of that parameter are within the normal range. For example, if a massive influx of nutrient levels exceeding directive levels was introduced to the water mass this would act as a trigger to cause an abnormal temporary and unsustainable increase in biomass that would affect reflectance of the water body.

In order to identify prospective wavebands throughout the range recorded, a visual analysis was carried out. The data were separated into those with high and low levels of each water quality parameter based on the upper and lower quartile of each water quality parameter. This was highly representative of the high and low values as the water quality data collected showed an even distribution of different levels of each parameter throughout the ranges collected during the data collection period (Appendix 3A3). This resulted in 42 sets of water quality data and corresponding spectral data being categorised as extreme (i.e. high or low levels for each individual parameter). The levels categorised as high/low and the spectral data sets created from this process are listed in Appendix 3A2.

For each of the 42 water quality sample subsets there were a large number of spectral recordings (approximately 10, but numbers vary with field conditions). This meant that when all reflectance values were plotted, for each of the high/low level samples, each resultant graph contained over 1000 reflectance curves (or 846720 separate points) and such graphs were impossible to interpret. This was compounded by the fact that some reflectance curves contain data collection errors (as discussed earlier) which simply disguise relationships that might exist. Despite this, dominant patterns could occasionally be seen, but it was usually impossible to identify relationships between reflectance curves of low and curves of high levels. Figure 6.1 clearly illustrates the confusion caused by including all reflectance curves for high and low levels of E.coli.

Figure 6.1 Reflectance curves when E.coli levels were in the upper or lower quartile of levels recordeds

red-low levelsblue-highlevels
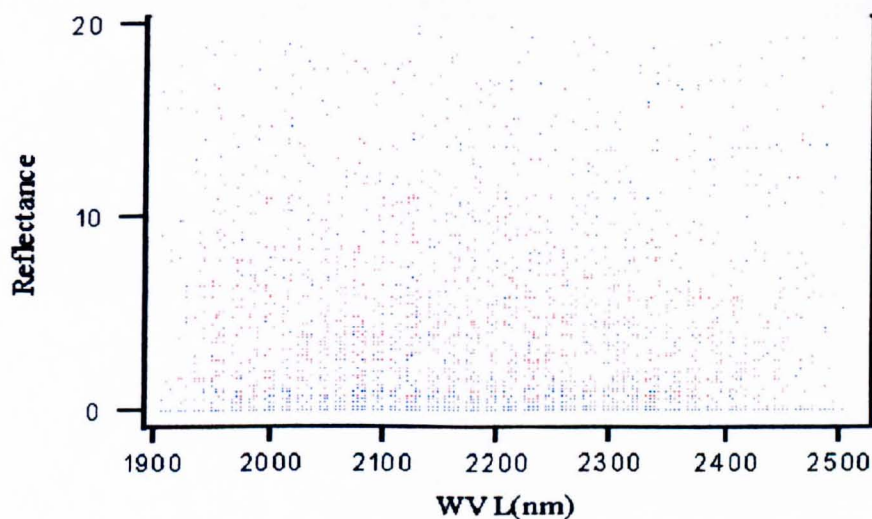
This exercise was repeated using only data collected on days with excellent field conditions (i.e. not obscured by any cloud) so that reflectance curves based on ideal data were produced. The inclusion of only cloud free days produced slightly clearer patterns

in the graphs (Figure 6.2) because fewer errors are included in the reflectance values. However, it was still impossible to identify any specific reflectance trends through visual analysis of the graphs. Animations of individual plots of reflectance curves were tried through animation software without success.

Figure 6.2 Reflectance curves (cloud free days) when E.coli levels were in the upper or lower quartile of levels recorded
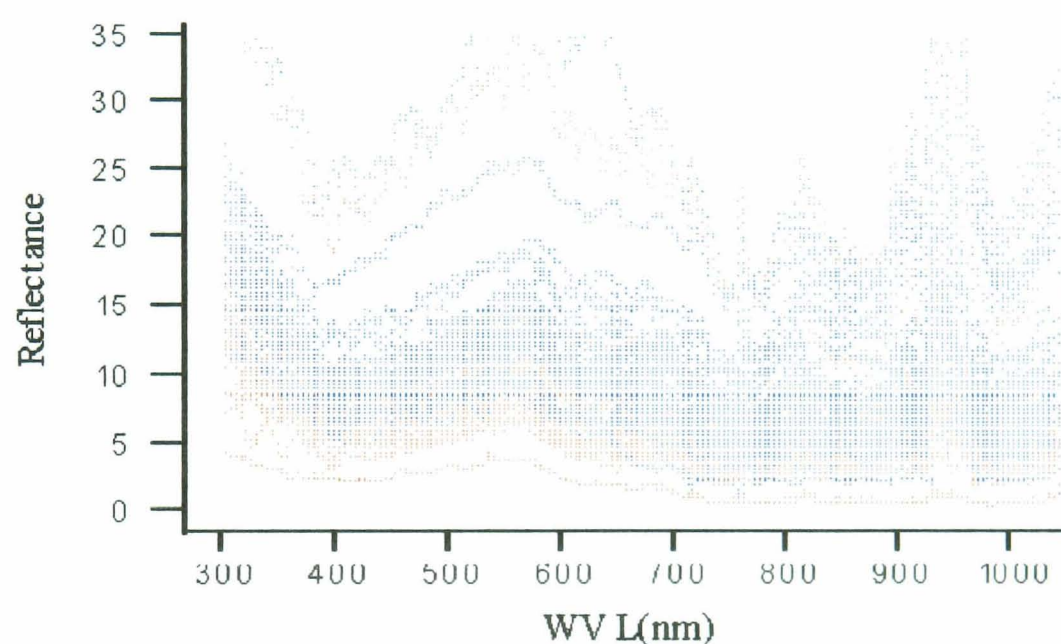
red-low levels blue-high levels

Therefore a clearer approach to identifying potentially useful spectral ranges or bandwidths had to be determined. The graphs were plotted using the mean of the reflectance of the estuary on all recordings when the level of the parameter was in the lower or upper quartile. These were intended to indicate any relationships between reflectance of the estuary and extreme values of each parameter.

In most cases the inclusion of wavelengths longer than 1043nm have little value because of the great variation of reflectance between recordings at longer wavelengths. The shorter wavelengths were far more consistent in reflectance. The graphs used for

the visual analysis, were constructed by calculating the mean of all spectral reflectance values (for all 840 wavelengths) when the estuary contained low or high levels of each parameter and plotting them on the same axis. The mean reflectance values when the water quality parameter was high were plotted in red and, when the water quality parameter was low, they were plotted in black.

This resulted in clear plots that allowed easy interpretation and are shown in Figures 6.3-6.20. It is important to note that these graphs include reflectance data gathered in all field conditions which means that relationships are visible despite field collection errors. This means that the results should be directly comparable with the preliminary statistical analysis of the full data set. A visual interpretation was undertaken for each of the water quality parameters to record the ranges of wavelengths that indicate a significant increase or decrease in reflectance when the parameter level was high and wavelength range where the level of reflectance remain constant despite the change in water quality parameter.

6.3.1 Ammonia

Ammonia had (illustrated in Figure 6.3) little effect on the reflectance of the estuary until the peak of reflectance at 800nm, when high levels induce a slightly increased height of the peak. This increase in reflectance remained through the range 800-880nm and for the next peak at around 900nm. This, therefore, suggests that an increase in the reflectance within these ranges can be expected when compared to reflectance between 400-550nm (high levels possibly even decrease reflectance). However, the overall changes were very small and are highly unlikely to be intelligible from raw spectral data due to the atmospheric and other physical errors discussed earlier. Therefore

reflectance between 800-880nm and 905-915nm (compared with a baseline reflectance between 400-550nm) offers the most potential of producing information.

Figure 6.3 Mean reflectance with high and low levels of Ammonia
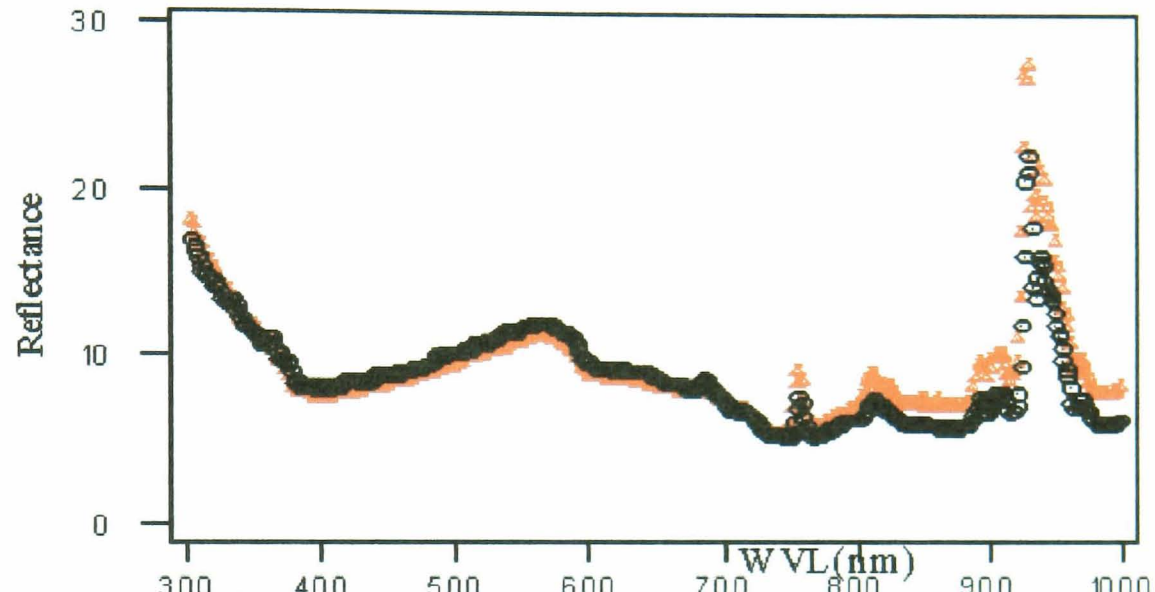
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995

6.3.2 BOD

Figure 6.4 Mean reflectance with high and low levels of BOD

Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995

Despite an unexpected lack of relationships with BOD and other water quality parameters (discussed in Chapter 7), Figure 6.4 revealed a noticeable increase in

reflectance, almost throughout the visible light range. This was all the more important because of the three reflectance peaks (750nm, 810nm, and 930nm) where reflectance were similar whether BOD was high or low. Future investigations would therefore be directed at the relationship between the mean of reflectance between 450-650nm where there was the greatest change (almost a 100% increase in mean reflectance) and the reflectance at the three peaks (750nm, 810nm, and 930nm), where there was a visible convergence of reflectance. When levels of BOD were low, there was a small peak of reflectance at 680nm (Chlorophyll absorption)(Dekker *et al.*, 1993). This peak was no longer pronounced when levels were high, which may be explained by higher chlorophyll levels.

Figure 6.5 Mean reflectance with high and low levels of BOD

Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

Figure 6.5 shows the full range 300-2500nm which displays the convergence of reflectance from these wavelengths (930nm) up to 2500nm with again one further exception at 1100-1300nm. This was one of the very few parameters that showed some relationship with reflectance above 1000nm. These longer wavelengths (above 1.0μm)

were highly erratic and therefore confidence in relationships above 1043nm had to be considered extremely weak and were therefore not included for further study.

6.3.3 Chlorophyll

Figure 6.6 Mean reflectance with high and low levels of Chlorophyll

Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

Chlorophyll was included as a secondary water quality parameter that can be remotely monitored and can be related to other water quality parameters. The number of samples actually collected were severely restricted to six days and so results must be viewed with less confidence. Figure 6.6 suggested a slight decrease in both the Infra Red and visible sectors with several exceptions. Logically, if chlorophyll levels were high, a slight change in reflectance in the green, absorption in the red and stronger reflectance in the NIR, should be expected but this was not immediately clear from Figure 6.6. However, if the overall increase in absorption of the estuary when chlorophyll levels were high is removed, then the expected relationships were present. i.e. the two curves converge at the end of the green sector (570-595nm) suggesting a proportional increase

in reflectance when levels were high. There was a divergence in the red (600-700nm) increasing at 680nm (the point at which chlorophyll-a strongly absorbs (Dekker *et al.*, 1993; Matthews *et al.*, 1994)). Finally there was a convergence coinciding with surface vegetation reflectance at 750nm and again in the NIR at approximately 815nm, 880nm and 910-960nm (Dekker *et al.*, 1993).

The estuary water, with high chlorophyll levels, was more absorbent throughout the electromagnetic spectrum from 0.3-2.5µm. However, when the data were standardised to remove the effect of this general increase in absorption, established (therefore expected) relationships were evident (see Chapter 8). The expected relationships from studies like van der Piepen *et al.* (1991) include an expected decrease in reflectance at 443nm, 680nm and 750nm (surface chlorophyll) and decrease in reflectance between 815 and 880nm.

6.3.4 Total Coliform

Figure 6.7 Mean reflectance with high and low levels of Total Coliform

M ean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

The average spectral reflectance of the estuary was significantly higher from 400nm to 700nm (as illustrated in Figure 6.7) and has a similar shape to that of BOD mean reflectance curves (Figure 6.5). However, there was little or no change in reflectance at 300nm, with a significant change in reflectance between 400-700nm with the maximum change in reflectance occurring between 520-580nm. When levels of total coliform were low, there was a small peak of reflectance at 680nm (Chlorophyll absorption). This peak was no longer pronounced when levels were high, possibly because of higher chlorophyll levels which could have occurred if more organic matter was present. There were further peaks with low levels of coliforms at around 720nm, 760nm and around 820nm. There was a convergence in reflectance, when coliform levels were low, with reflectance peaks at 760 and 820nm with high coliform levels.

6.3.5 Dissolved Oxygen

Figure 6.8 Mean reflectance with high and low levels of Dissolved Oxygen

Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995

Low levels of dissolved oxygen produced a lower average reflectance in the range 300-360nm, 800-810nm and 890-910nm (Figure 6.8). There was a significant increase in reflectance in the range 420-670nm (particularly 550-575nm) with the greatest change occurring between 440 and 575nm. Other evident relationships were the increase in height of the peak at 950nm. The mean value for 550 to 575nm reflectance, compared to reflectance at 380nm reflectance, could provide evidence that DO or associated water quality parameters are low e.g. DO could be indicated by:

$$RDO = (R_{550} + R_{575})/2 - R_{380}$$

Where: RDO   = suggested Dissolved oxygen reflectance value

R_{550}   = reflectance at 550nm

R_{575}   = reflectance at 575nm

R_{380}   = reflectance at 380nm

This implies a relationship that a high RDO reflectance value would indicate low dissolved oxygen.
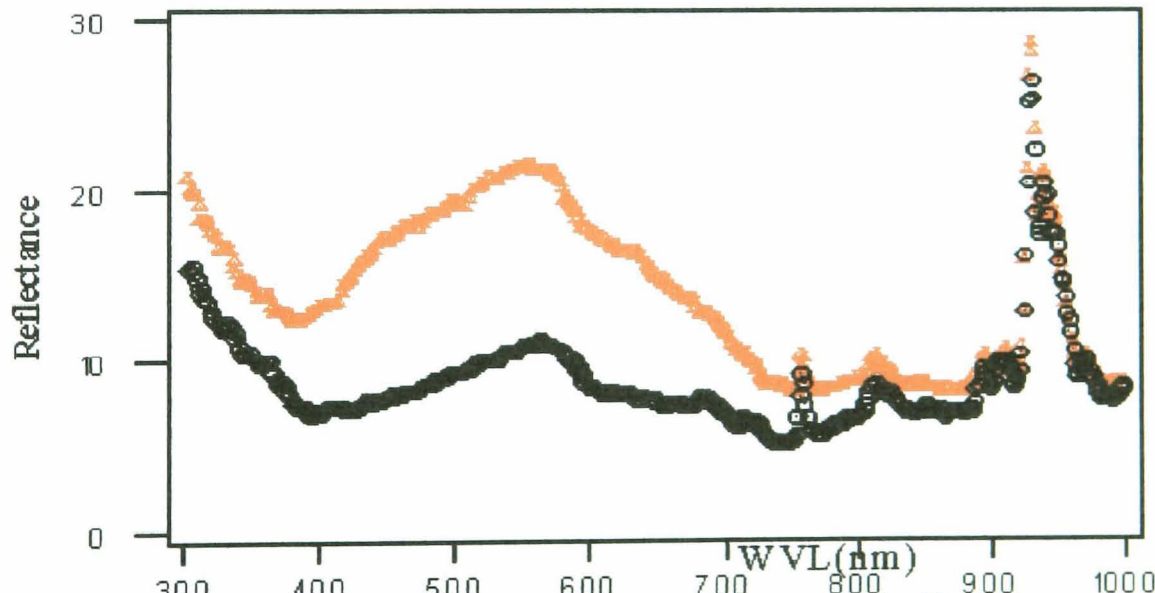
6.3.6 E.coli

Figure 6.9 Mean reflectance with high and low levels of E.coli
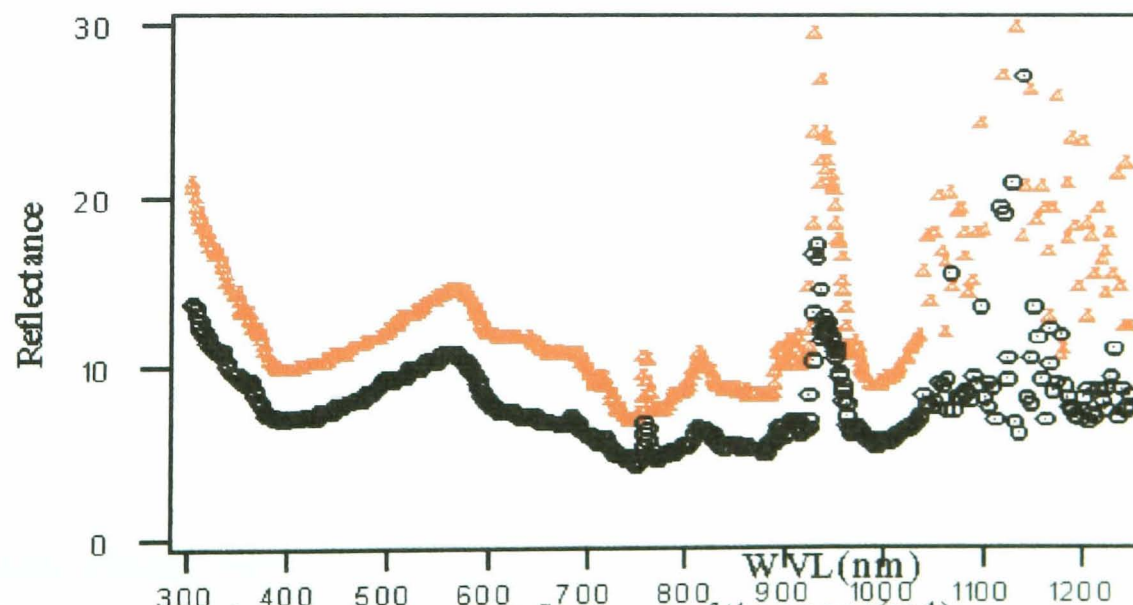
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

Figure 6.9 illustrates that high levels of E.coli generally produced a consistent increase in reflectance up to 1250nm with exceptions at around 300nm, 610nm-680nm (630nm cynobacteria absorption (Dekker *et al.*, 1993)), 810nm and at 940-950nm where the peaks diverge. The overall increase in reflectance could be explained by higher suspended content implicated in the release of primary effluent in periods of high rainfall or different tidal conditions.

6.3.7 Faecal Coliform

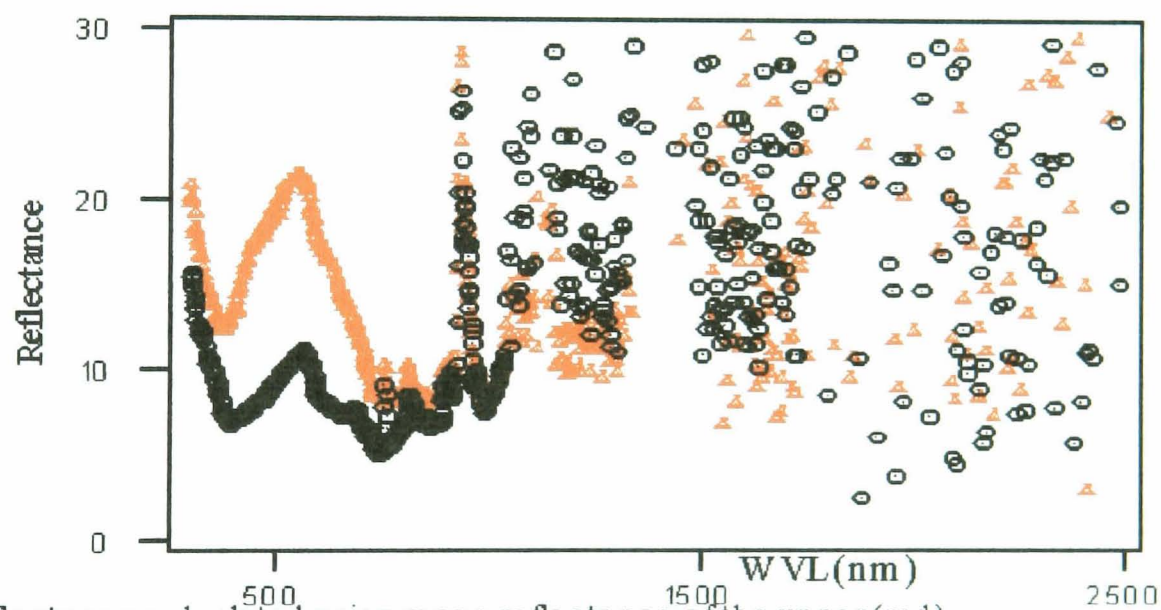**Figure 6.10 Mean reflectance with high and low levels of Faecal coliform**
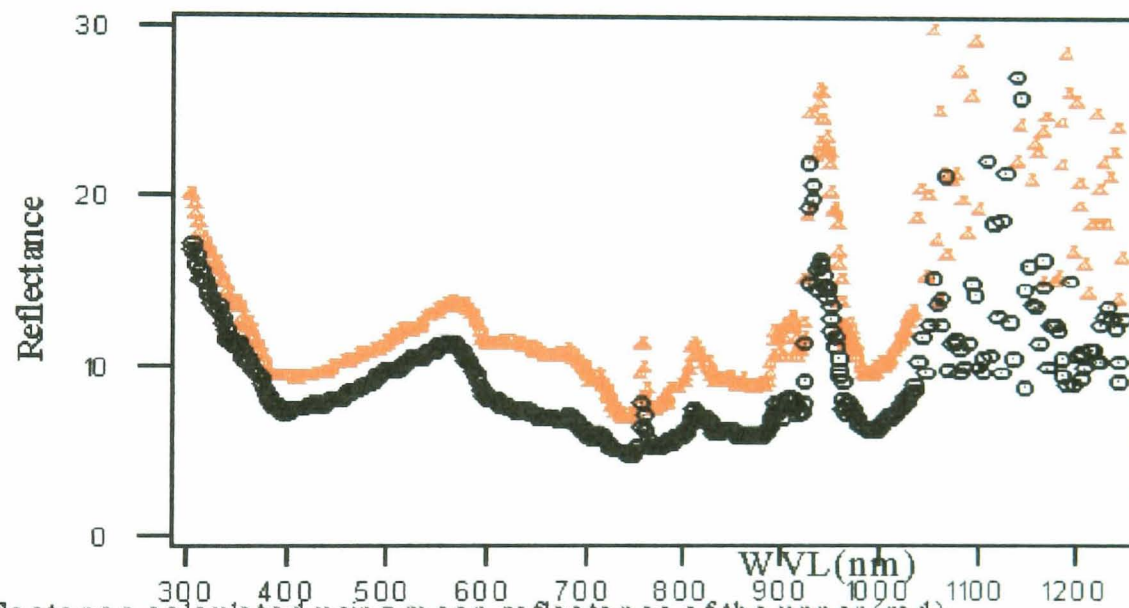
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

Figure 6.10 illustrates that there was only a very small physical change in reflectance at any point between 300-1250nm. There was a generally higher reflectance when faecal coliform levels were high except for mean reflectance from 300-370nm, and at approximately 940nm where reflectance was similar irrespective of faecal coliform levels. There was a distinct divergence from 600-700nm (particularly at around 630nm, as for E.coli), 820-870nm and 990-1010nm. There is a greater divergence in the NIR up

to 1250nm but this area of the spectrum in the field data has high levels of error and consequently there is a large deviation around the mean values in the NIR.

6.3.8 Nitrogen

Figure 6.11 Mean reflectance with high and low levels of Nitrogen
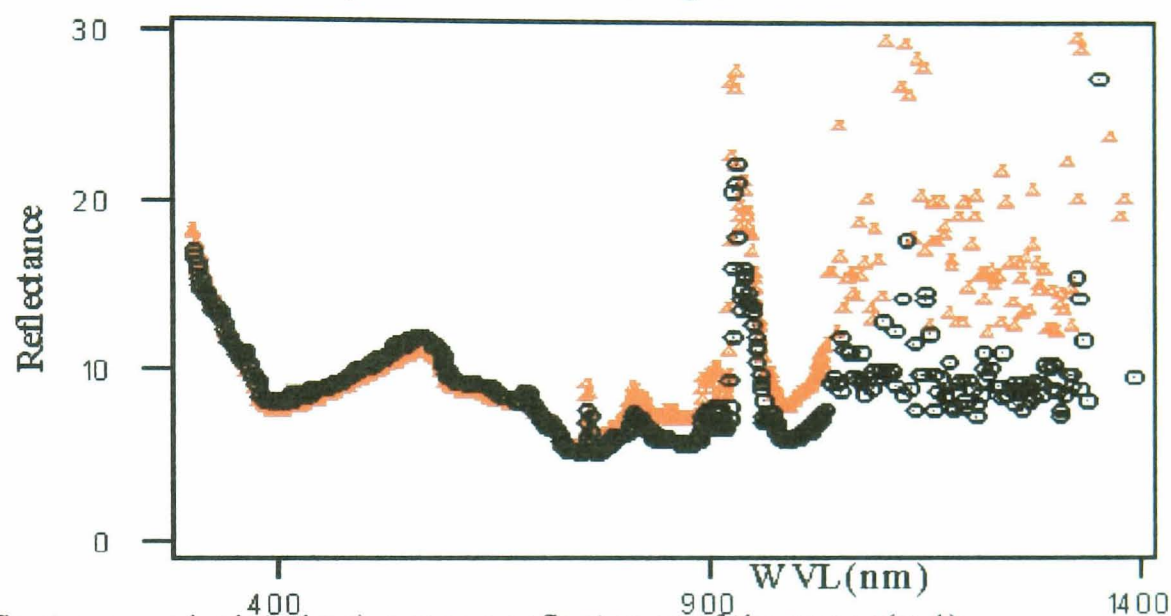
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

There were no obvious relationships between nitrogen and reflectance in the range 300-1000nm as illustrated in Figure 6.11. Despite this, there was a very slight divergence in reflectance the NIR from 1000nm to at least 1280nm. However, the longer wavelength range were (as expected) highly affected with calibration and atmospheric problems. Therefore, utilisation of any relationship found in the 1000-1280nm range is highly unlikely.

6.3.9 pH

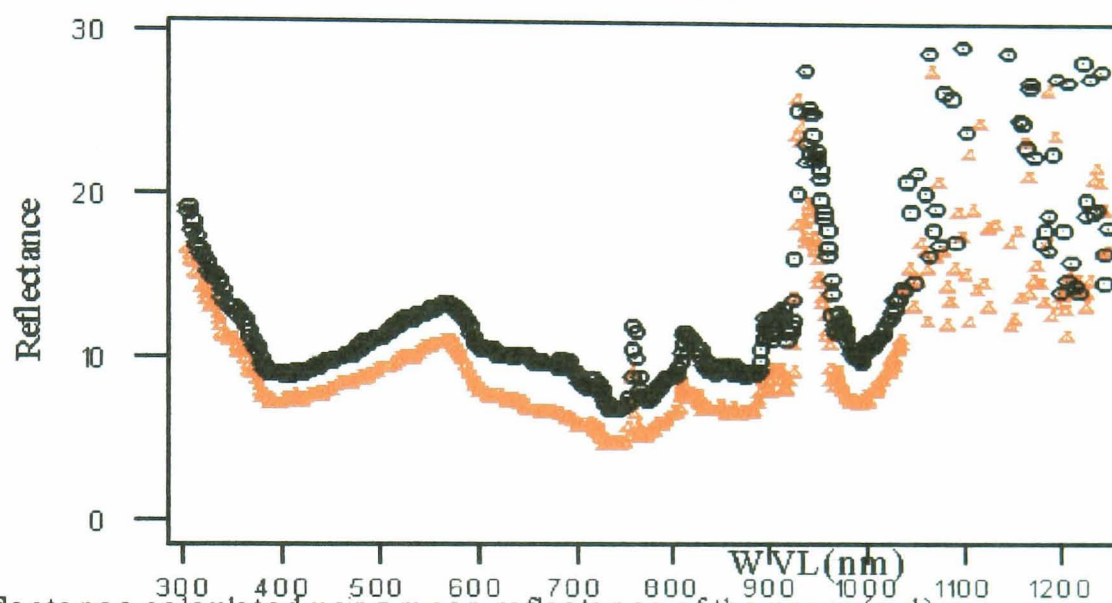**Figure 6.12 Mean reflectance with high and low levels of pH**
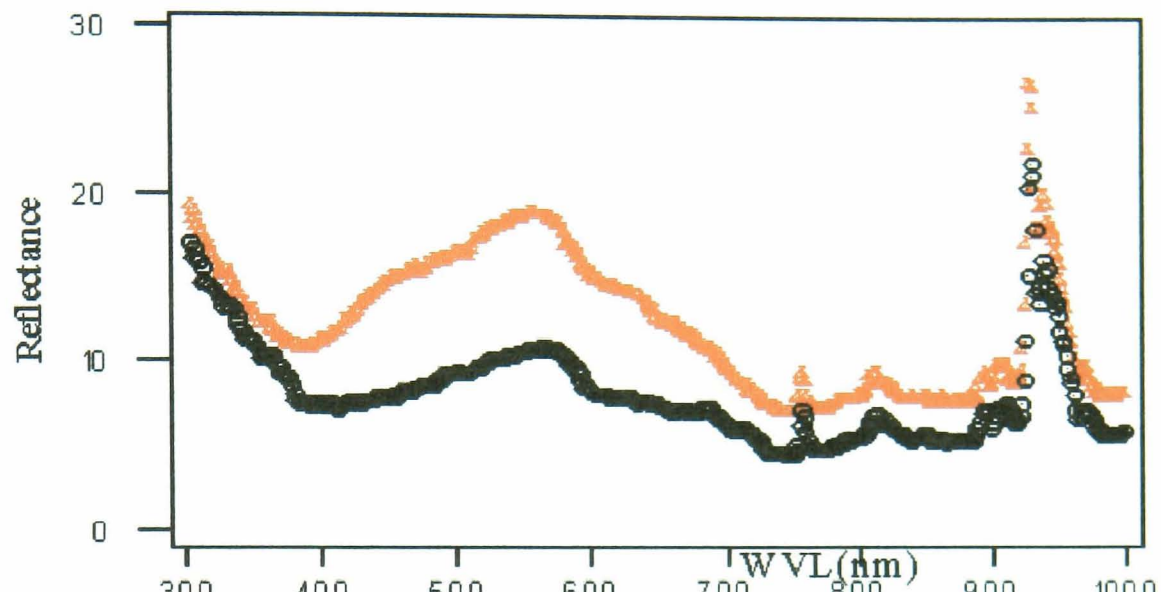
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

Levels of pH (Figure 6.12) had a marked affect on the overall reflectance of the estuary from 400nm to 700nm. pH did not change significantly with tidal flow and salinity as shown in Chapter 7. Thus the divergence in reflectance (with high pH) between 400 and 700nm was likely to be caused by the many interacting water quality factors that effect pH rather than simply a change in water type as a result of a change in tidal direction. Therefore factors related to pH do cause a reduction in reflectance in the range 400nm to 700nm compared to the normal reflectance when pH was lower, while mean reflectance in the range 300-350nm remains unchanged. The greatest increase in reflectance occurred at 450nm, 550nm and 600-630nm when pH was high.

6.3.10 Nitrates and Phosphates

Figure 6.13 Mean reflectance with high and low levels of Nitrates
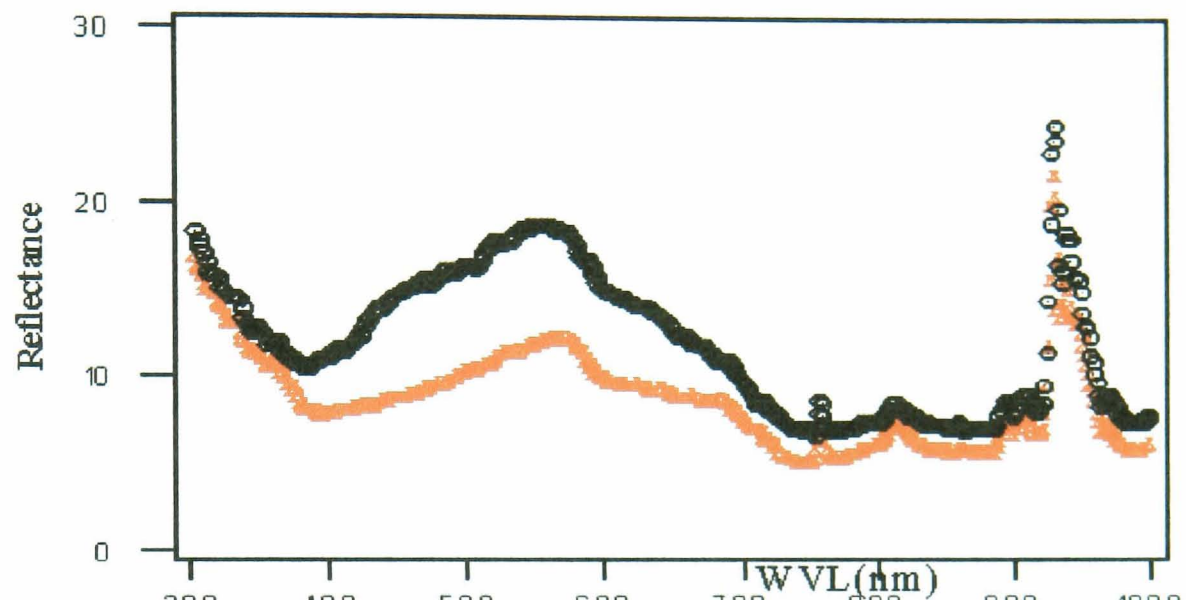
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995

Nitrates (Figure 6.13) and phosphates (Figure 6.14) had inversely very similar mean reflectance curves. High nitrate levels caused a decreased reflectance in the range 380-680nm, while high phosphate levels produced an increase in reflectance in the same range. Reflectance within the range 300-370nm remained unchanged irrespective of the levels of phosphates or nitrates. The strongest relationship suggested by the data was higher reflectance from the 450-580nm range when nitrates were low or when phosphates were high. This inverse similarity occurred again within the range 610-640nm, and to a lesser extent at 730nm where there was a reduction in reflectance when phosphates were low and nitrates were high.

Figure 6.14 Mean reflectance with high and low levels of Phosphates
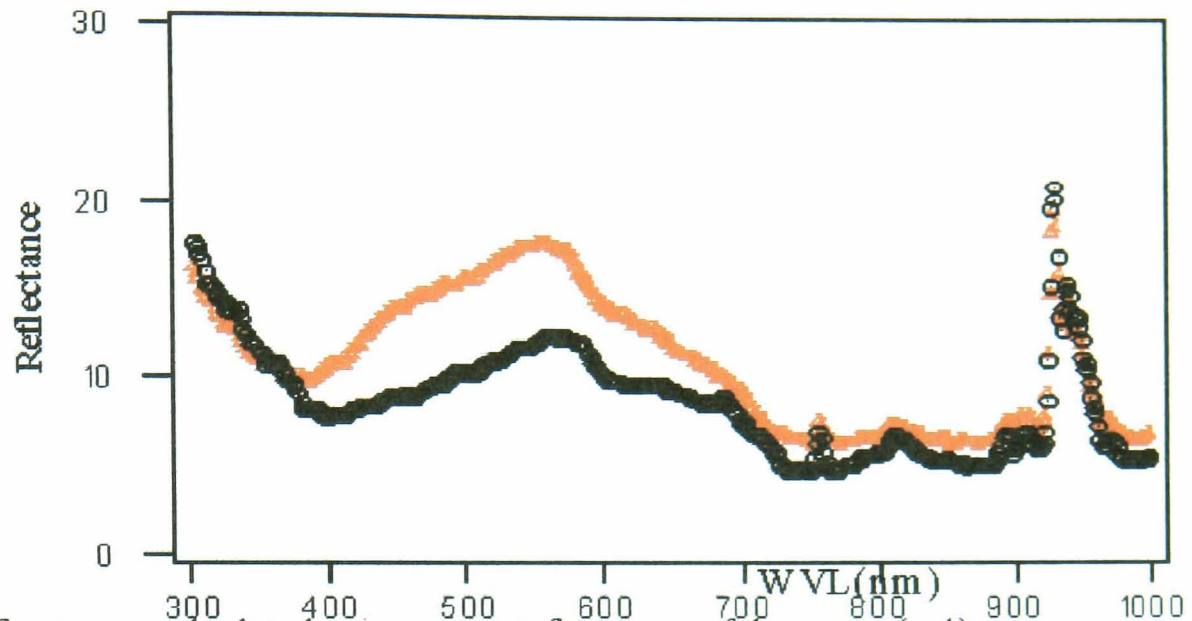
Mean reflectance calculated using mean reflectance of the upper (red)
and lower (blue) quartiles of levels recorded in August/September 1995
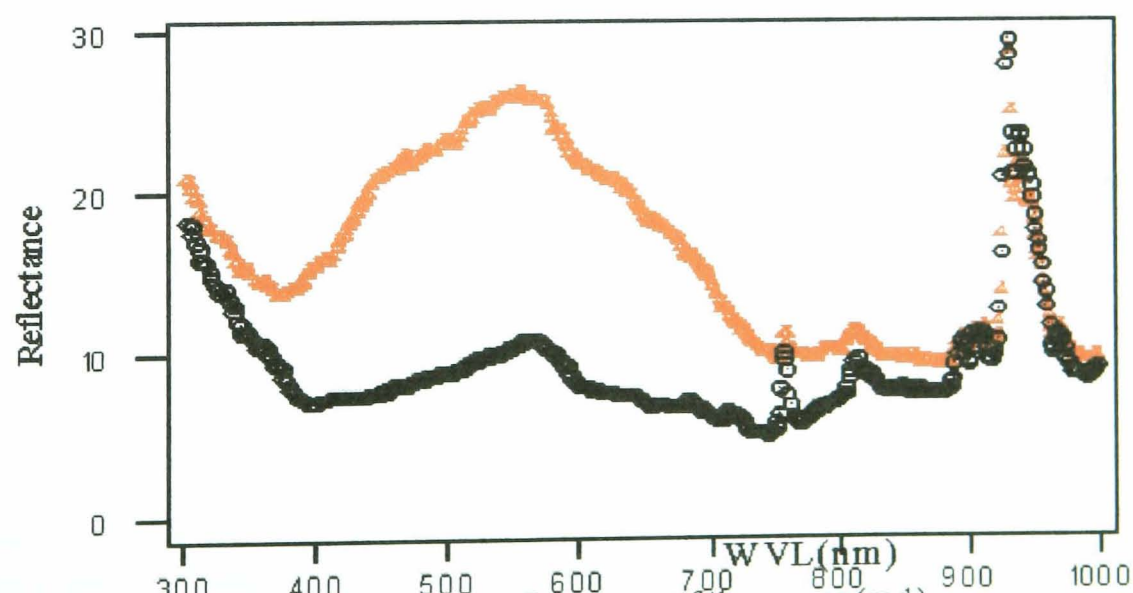at Southend on Sea Pier.

6.3.11 Salinity

Figure 6.15 Mean reflectance with high and low levels of Salinity
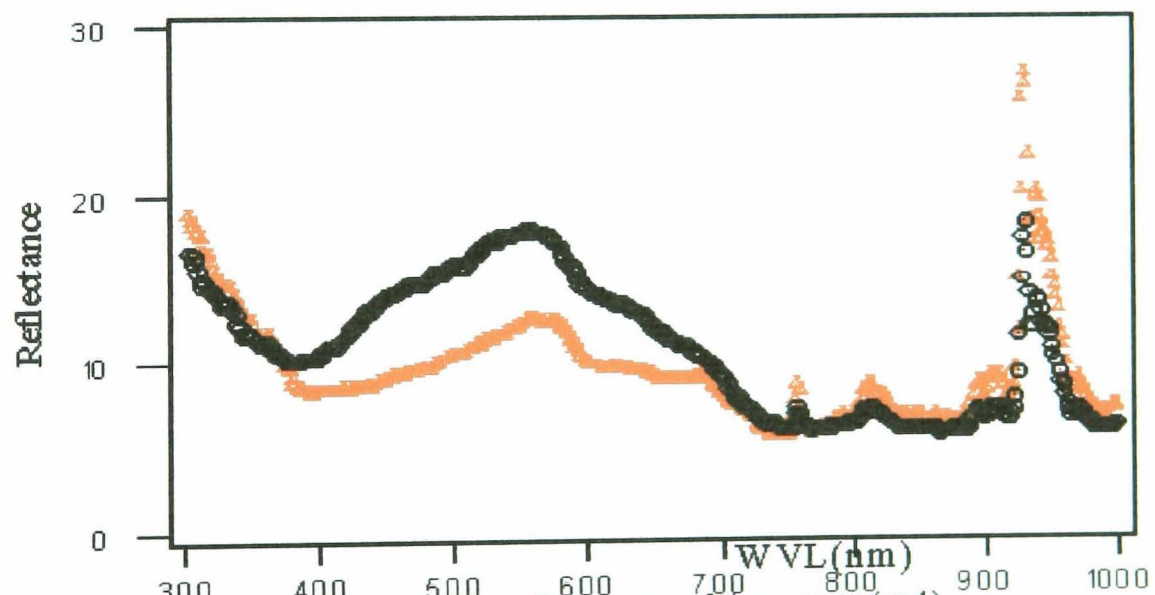
Mean reflectance calculated using mean reflectance of the upper (red)
and lower (blue) quartiles of levels recorded in August/September 1995
at Southend on Sea Pier.

The mean reflectance of the upper and lower quartiles of salinity levels (Figure 6.15)

showed a decrease in reflectance in the range from 380nm to 685nm when salinity was

high, particularly between 430nm-550nm and 600-640nm. The peak at 940-970nm was

highest when salinity was high, especially at 950nm. The curve showed a strong similarity with those for nitrates and phosphates. It is a false assumption that the decrease in salinity could be indicative of higher levels of river water or drainage water which might be expected to have higher levels of nitrates and overflow drainage water high levels of phosphates due to tidal flow. This is because the upper and lower quartiles involved different samples for nitrates, phosphates and salinity (listed in Appendix 3A2) and as the Figures 7.10,7.12,7.13 in Chapter 7 illustrate, tidal flow did not show any significant pattern between nitrates, phosphates and tidal flow.

6.3.12 Suspended Sediment

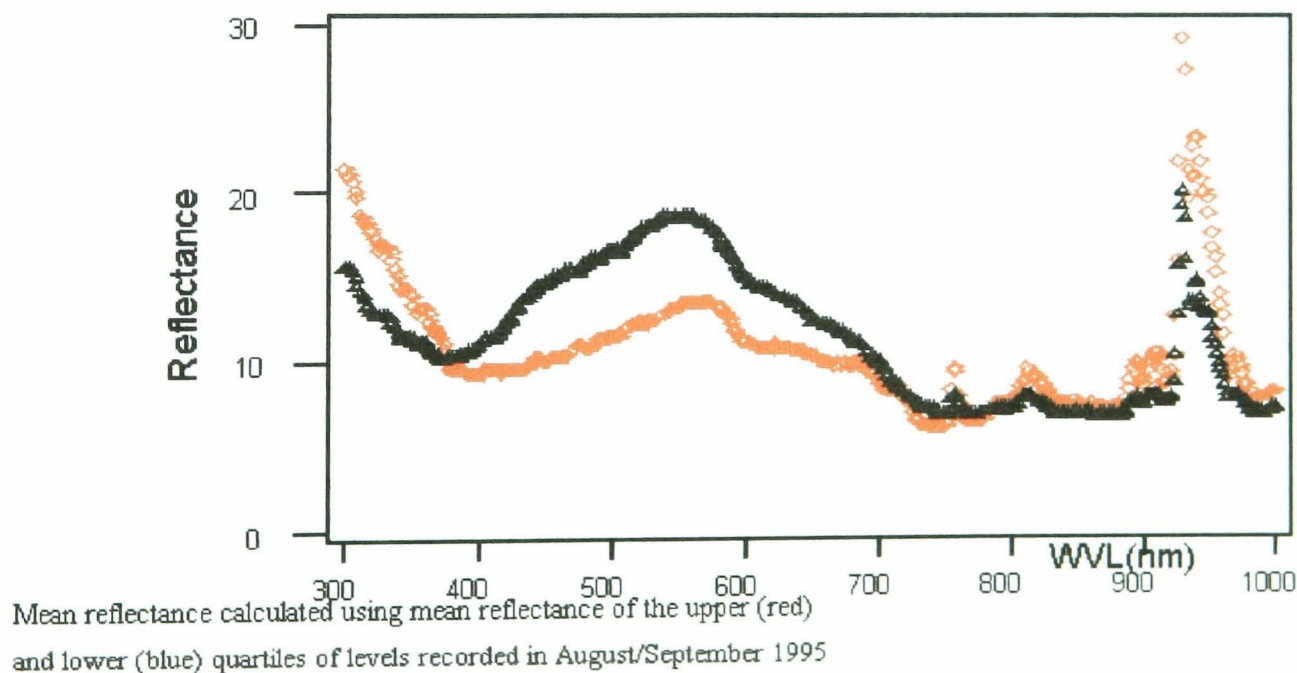**Figure 6.16 Mean reflectance with high and low levels of Suspended Sediment**

Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995
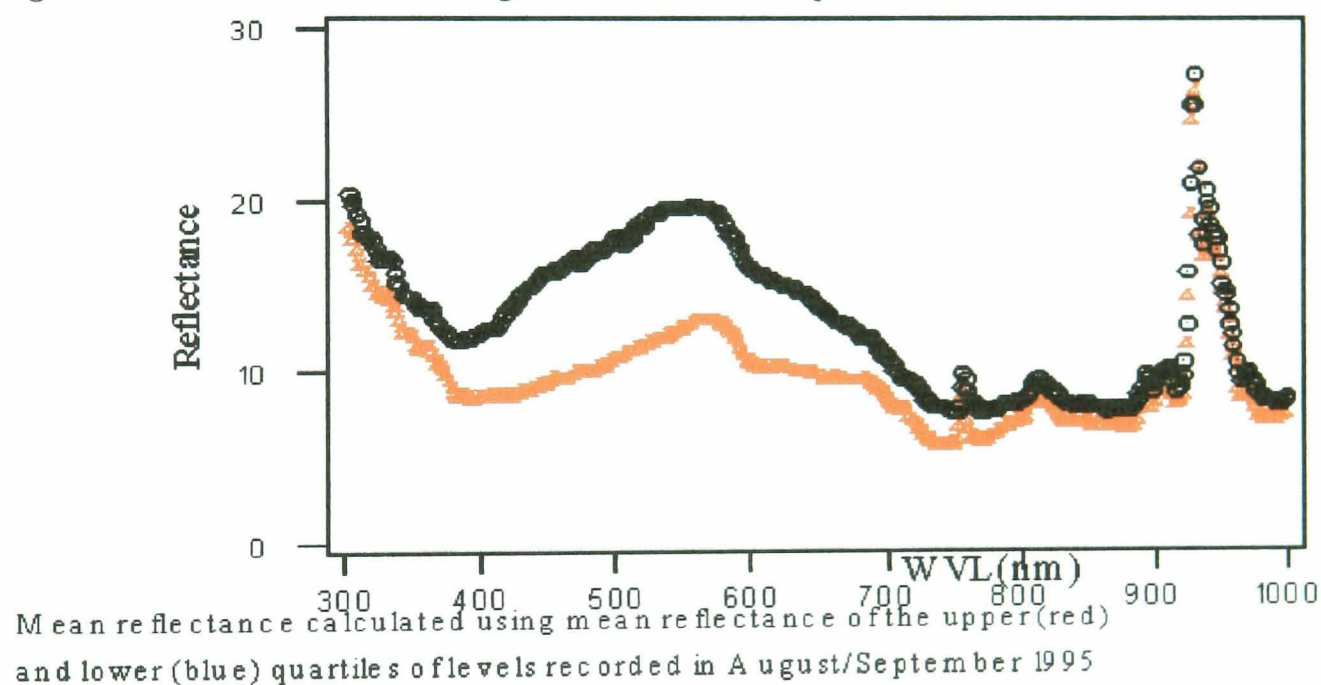
When sediment levels were high (>=54.550S.S.mgs), mean reflectance reduced through the range 400nm to 680nm and particularly at around 550nm as expected (Figure 6.16) from other studies (Dekker *et al.*, 1993; Doeffer *et al.*, 1999). When sediment levels were low, there was a significant peak, starting at 425nm, which was no longer present when levels were high. Therefore as sediment levels increased, the relationship

between reflectance at approximately 450nm and a baseline reflectance at 300-370nm and 800-1000nm suggested there would be a relative decrease in reflectance.

6.3.13 Turbidity

Figure 6.17 Mean reflectance with high and low levels of Turbidity
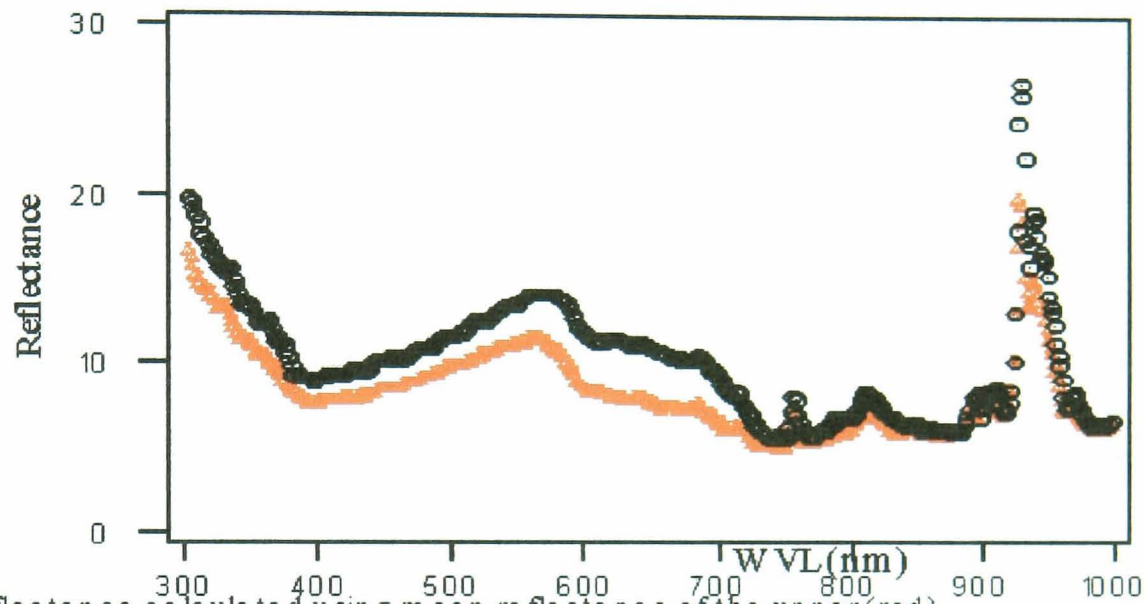
Mean reflectance calculated using mean reflectance of the upper (red) and lower (blue) quartiles of levels recorded in August/September 1995 at Southend on Sea Pier.

The range of recorded turbidity was extremely limited with little or no variation so that the difference between the upper and lower quartile was just 0.6m. Inevitably the changes in reflectance for turbidity were small (see Figure 6.17) and therefore cannot be taken as particularly significant. The high mineral content (largely clay) may well be expected to absorb visible light and this is perhaps evident with lower reflectance from 600nm-700nm. With that one exception, the reflectance curves for high and low turbidity levels are of very similar shape with no distinct peaks or troughs.

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6.4 Summary of preliminary analysis

The two processes of correlation and visual analysis have identified a number of wavelengths that show potential for further investigation. The erratic distribution of longer wavelengths in comparison to wavelengths shorter than 1100nm and repeated failure of wavelengths above 1100nm to show a worthwhile relationship to any of the water quality parameters led to their exclusion from further analysis. This allowed the next stage of spectral analysis to concentrate on the shorter wavelengths from 300-1100nm. The results from the preliminary analyses (statistical and graphical) allows targeted statistical analysis for each parameter. The results for the statistical and graphical analysis are summarised in Tables 6.2 and the full results of the preliminary statistical analysis are listed in Appendix 3A1.

Table 6. 2 Results of visual analysis of mean reflectance

Parameter	When at level	Suggested relationship to area of spectrum with change in reflectance	Control area of spectrum (for comparison in reflectance)
Ammonia	>=1.5	>800-880nm & >905-915nm	400- 550nm or mean
BOD	>=5.958	>450-650nm & >1100-1300	peaks at 750, 810 and 930nm
Chlorophyll	>=17	<600-700nm(esp680) >750-760nm (surface vegetation)	570-595nm,815,880,910- 960nm(especially 950) or mean
Coliforms	>=435	>400-700nm(esp520-580) >770-880 (less significant)	300nm, 760nm and 820nm
DO	<=3.7692	>440-575,<940, <300-320nm Peaks at 550nm but moves to 575nm when DO high	Compare peak at 550nm to 380nm & 575nm to 380nm (if change at 550nm is greater than the change at 575 then DO may be low
E. Coli	>=288	>300nm,>610-680nm(esp630), >810nm, >940-950nm	mean or median reflectance level
Faecal Coliforms	>=103	>600-700nm (esp630), >820-870nm, >990-1010nm	300-350nm or mean
Nitrogen	>=1.95	>1000-1280 (very weak)	300-800nm
pH	>=8.07	<400-700nm	300-350nm
Nitrates	>=2.635	<450-580nm, <610-640nm, <730nm (to lesser extent)	300-370nm
Phosphates	>=1.355	>450-580nm, >610-640nm, >730nm	300-370nm
Salinity	>=1.023	<380-685nm (esp430-550& 600-640nm), >peak at 950nm	300-370nm, 700-870nm
Suspended Sediment	>=54.55 ssmgs	<400-680nm(esp 425-480nm)	300-350nm, 800-900nm
	<=42.425	peak at 425nm not present with high levels of sediment	
Turbidity	>=1.3m	<600-700nm(very small change)	mean or median or 750-900nm

6.5 General Chapter Summary

Two approaches were taken in the preliminary analysis. A correlation analysis of the full data set comparing the correlation between individual wavelengths and each of the water quality parameters. This analysis allowed the identification of ranges between 300-2500nm that showed potential for inclusion for further study. The correlation analysis found that there were low but significant relationships evident between reflectance and several water quality parameters. The wavelengths that showed the highest correlation and relationships through the visual analysis of mean reflectance were then used in the second stage analysis (see Table 6.2 and the individual tables in Chapter 8 or Appendix 3A1). The visual analysis of the data showed that inclusion of wavelengths beyond 1043nm were not of interest to this study as well as highlighting wavelength ranges that showed a relationship to high or low levels of water quality parameters.

CHAPTER 7

Water Quality Analysis

7.1 Overview

Our understanding of coastal water and estuary water quality is complicated due to multiple inputs from the surrounding land and tributaries; and tidal effects with variations in the freshwater, effluent and surface run off content. To analysis the data it is necessary to understand the variability in water quality of the study area and the relationships between the selected water quality parameters. An aim of this study is to investigate the ability of remote sensing to detect excessive levels of water quality parameters directly whilst recognising that it may not be possible to detect all parameters directly. Therefore these will depend on the use of 'secondary' water quality parameters that can be used as indicators of the likely presence of parameters of interest. Chlorophyll and BOD were included for their potential as secondary indicator parameters. Salinity was included to provide some evidence of the impact of tidal activity upon the estuary water quality.

7.2 Interpretation of water quality data

The figures in Appendix 3A3 show the distribution of water quality that was recorded during data collection in 1995 and illustrate that a range of concentrations were recorded for all water parameters with the following exceptions:

1. Turbidity. Values only varied between 0.3-2m which was in keeping with the normal local values (based on previous years EA data) but offers a limited range on which to build any relationships with either water parameters or reflectance;

2. Temperature. Values did vary widely between 15.5-23.5 degrees c but most values were within the range 17-18 degrees c resulting in a limited number of samples within the higher and lower temperatures ranges;

3. Phosphates. Most samples were low in the range $0.2-1.2mgl^{-1}$ with just 3 samples with significantly higher values of $4-6mgl^{-1}$.

The variations in water quality throughout the tidal cycles showed that concentrations were related to the water quality of that day irrespective of the tidal flow direction at the time of data collection. This reduced the likelihood of water samples being related to time rather than the environmental conditions of the day i.e. wind level, sewage discharge, very recent precipitation were the dominant factors in controlling water quality. Figures 7.1-7.14 show the distribution of water parameter levels collected in this study in 1995 coded by the point in the tidal cycle rather than by time.

Figure 7.1 Distribution of Ammonia sample (1995) concentrations through tidal cycle
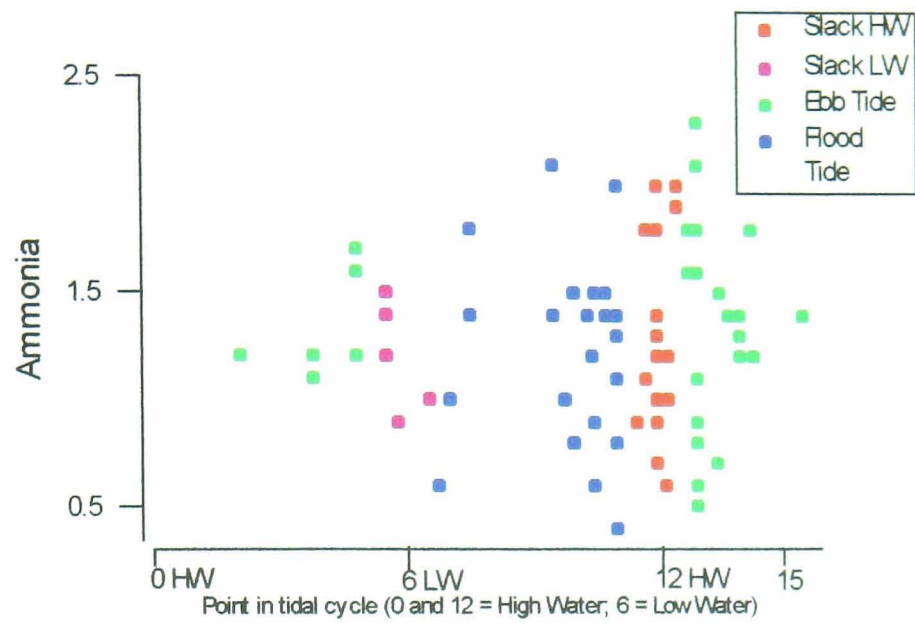
Figure 7.2 Distribution of Biological Oxygen Demand sample (1995) concentrations through tidal cycle
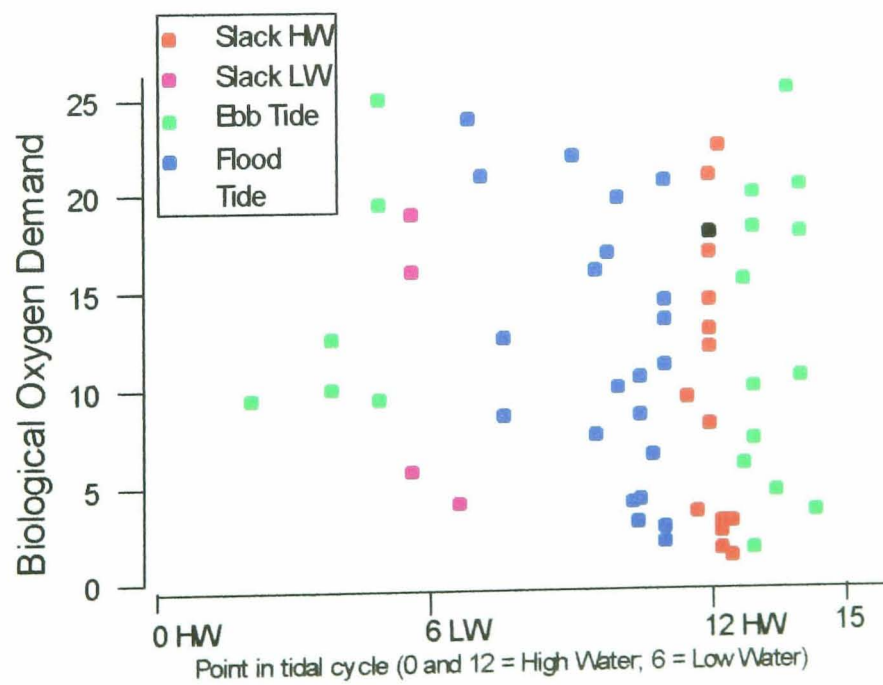
Figure 7.3 Distribution of Chlorophyll sample (1995) concentrations through tidal cycle
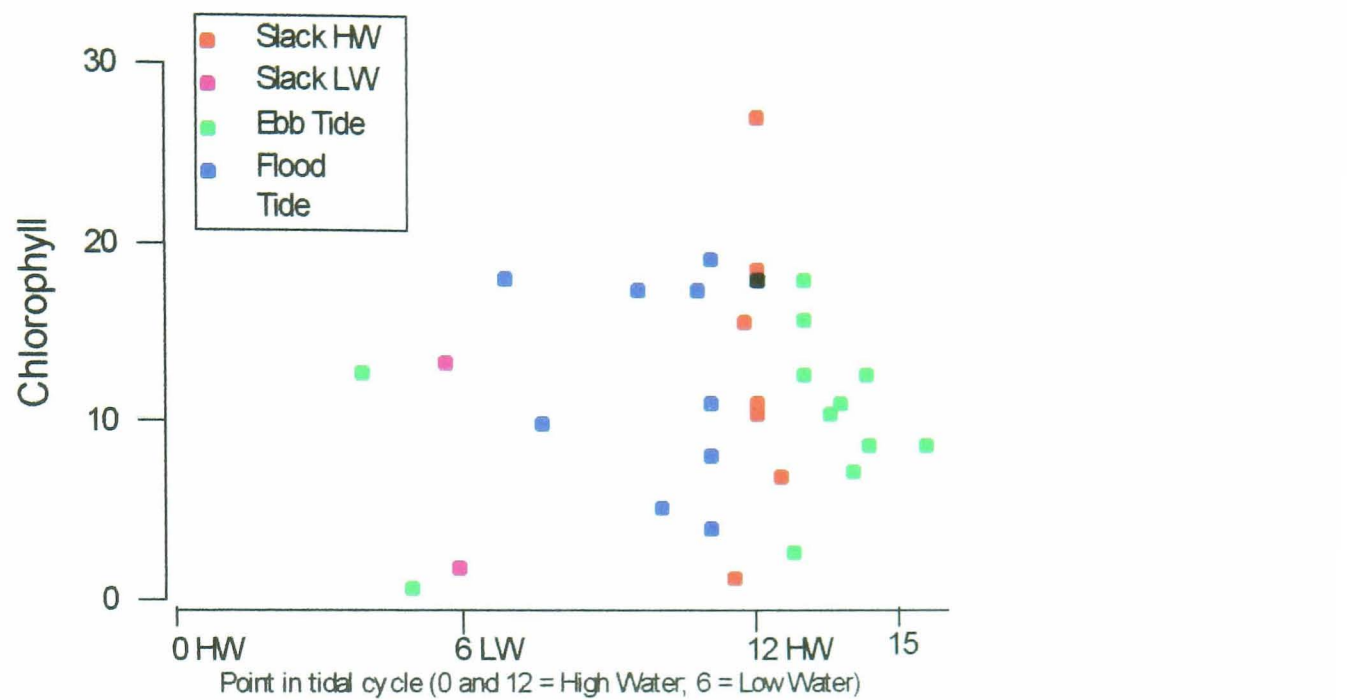
Figure 7.4 Distribution of Dissolved Oxygen sample (1995) concentrations through tidal cycle
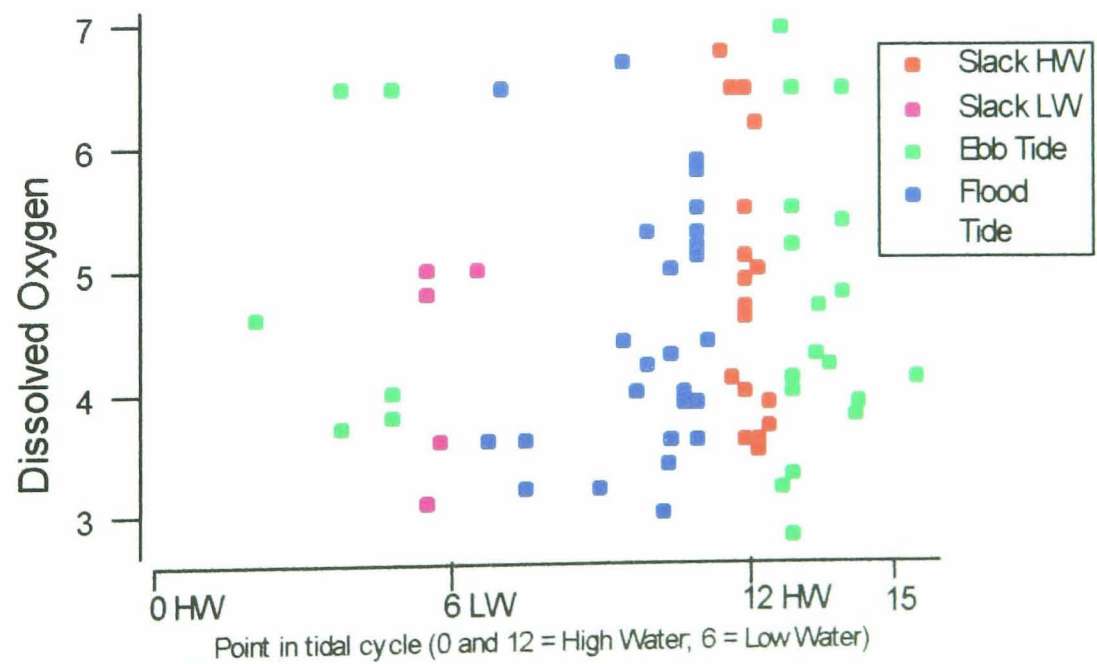
Figure 7.5 Distribution of Echeria Coliform sample (1995) concentrations through tidal cycle
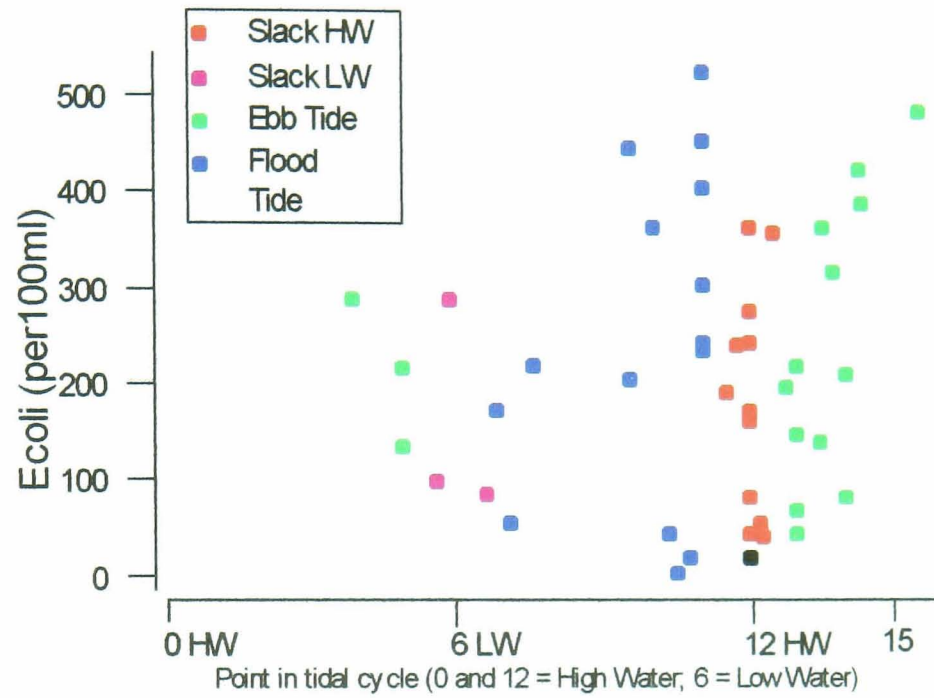
Figure 7.6 Distribution of Faecal Coliform sample (1995) concentrations through tidal cycle
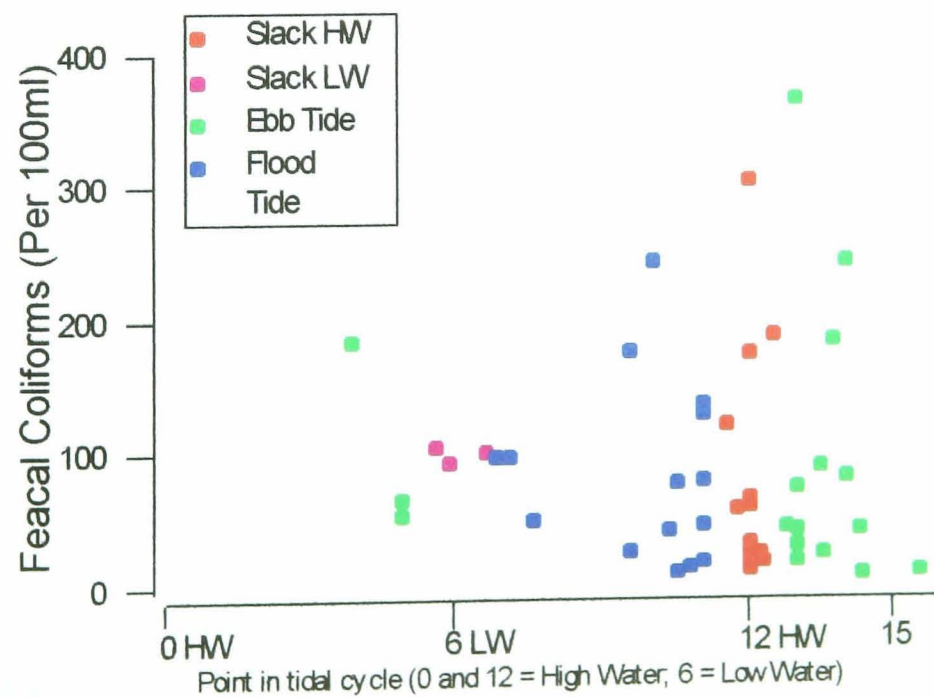
Figure 7.7 Distribution of Nitrate sample (1995) concentrations through tidal cycle
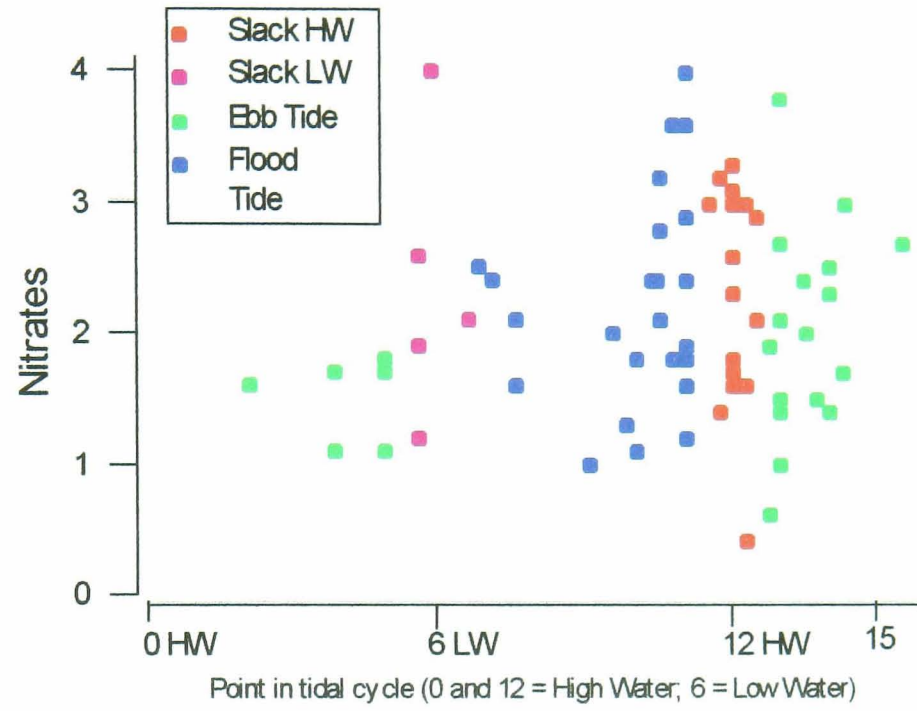
Figure 7.8 Distribution of pH sample (1995) concentrations through tidal cycle
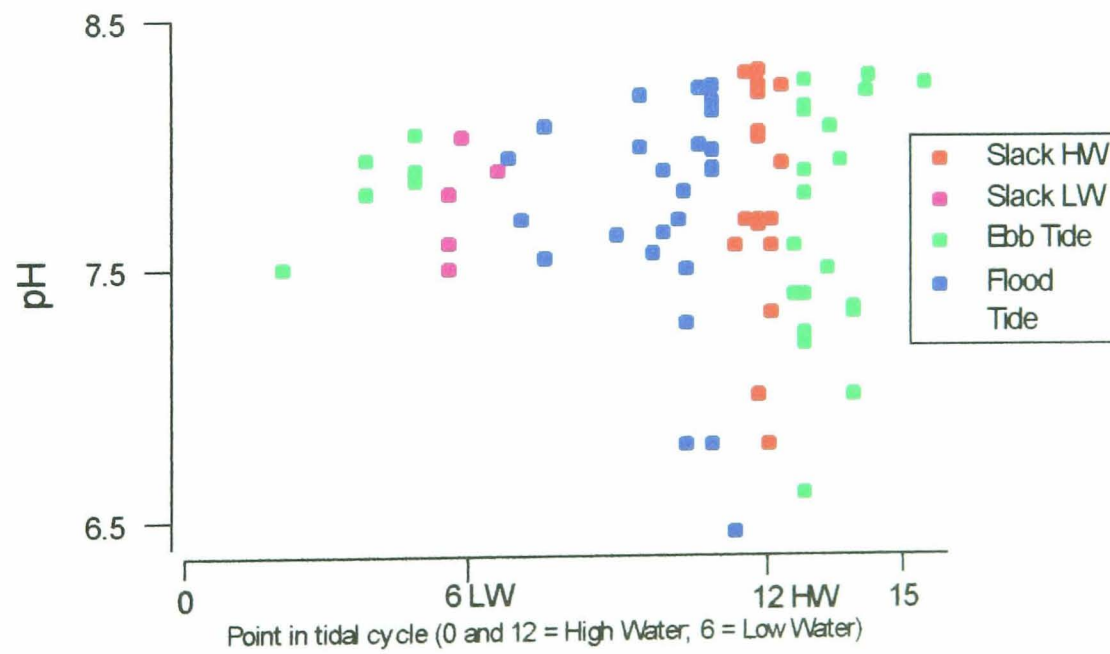
Figure 7.9 Distribution of Phosphate sample (1995) concentrations through tidal cycle
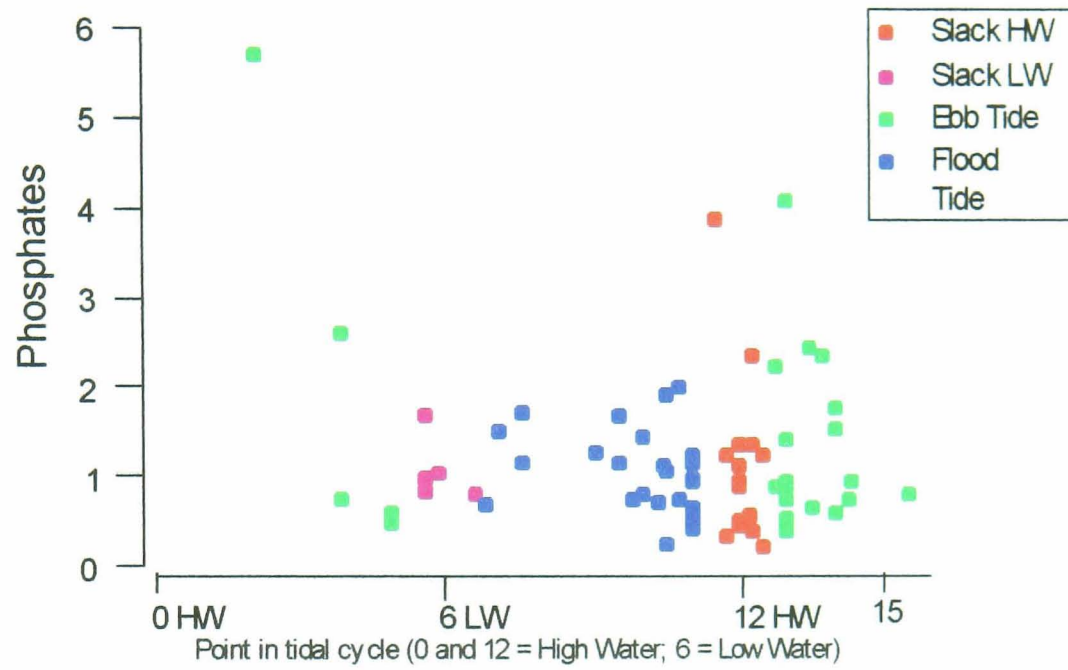
Figure 7.10 Distribution of Salinity sample (1995) concentrations through tidal cycle
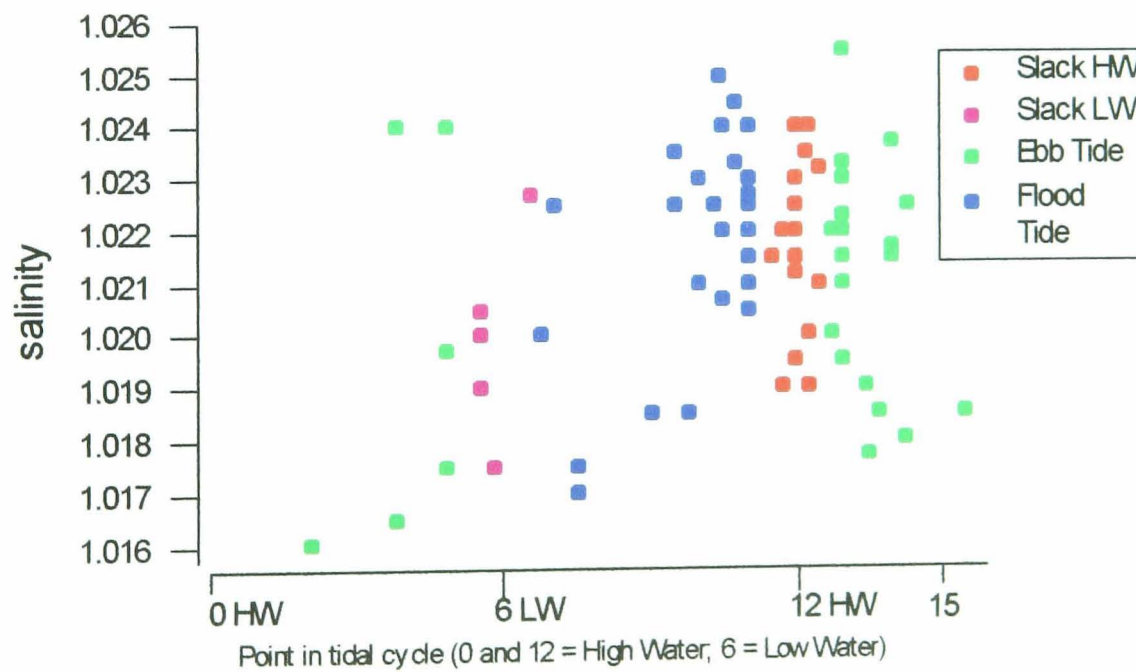
Figure 7.11 Distribution of Suspended Sediment sample (1995) concentrations through tidal cycle
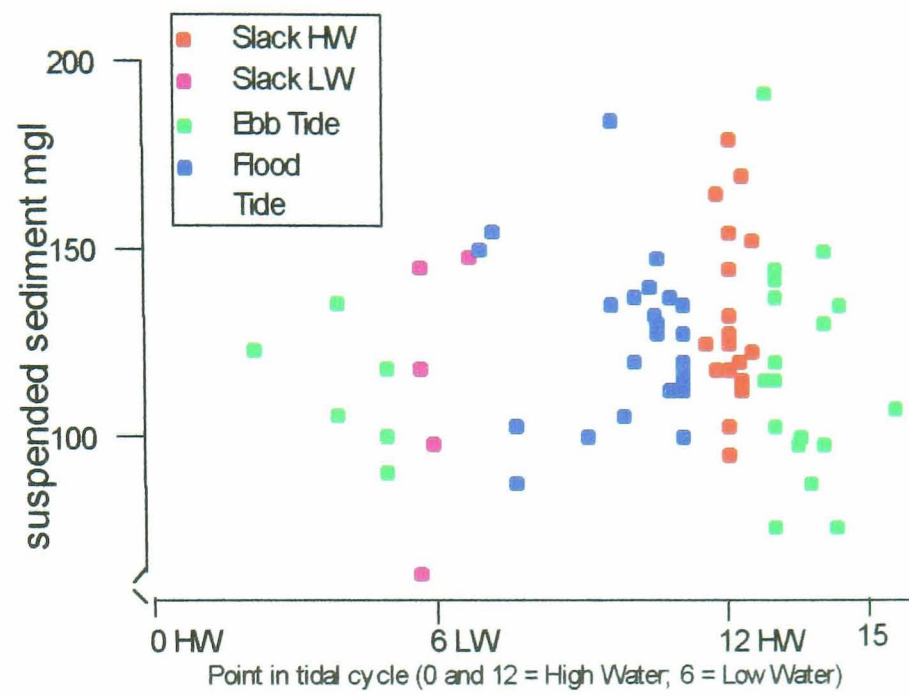
Figure 7.12 Distribution of Total Coliform sample (1995) concentrations through tidal cycle
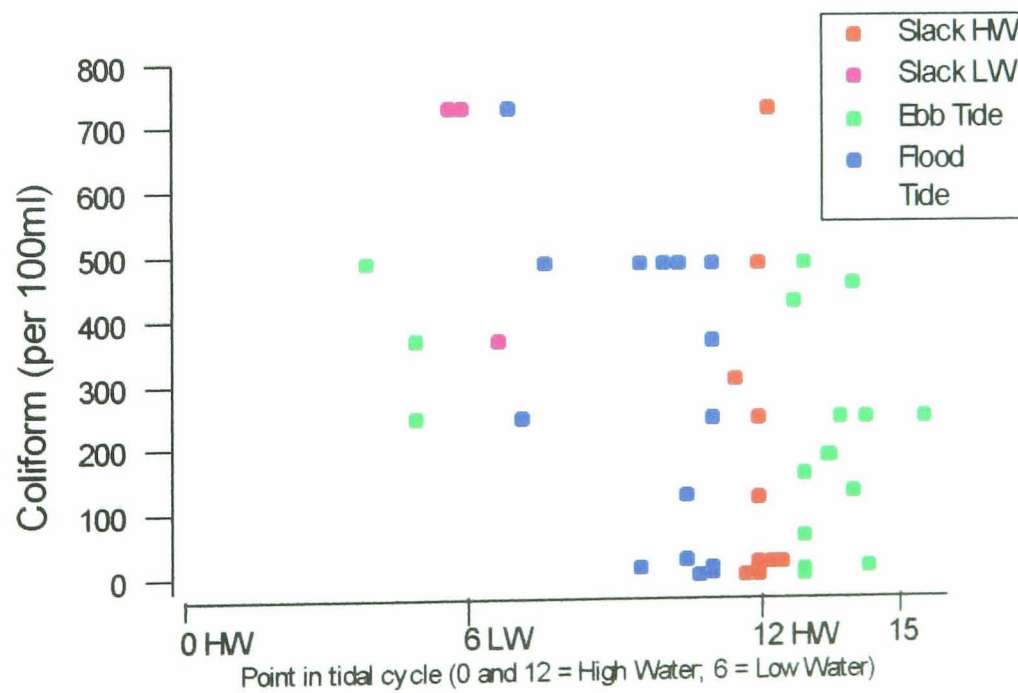
Figure 7.13 Distribution of Temperature sample (1995) concentrations through tidal cycle
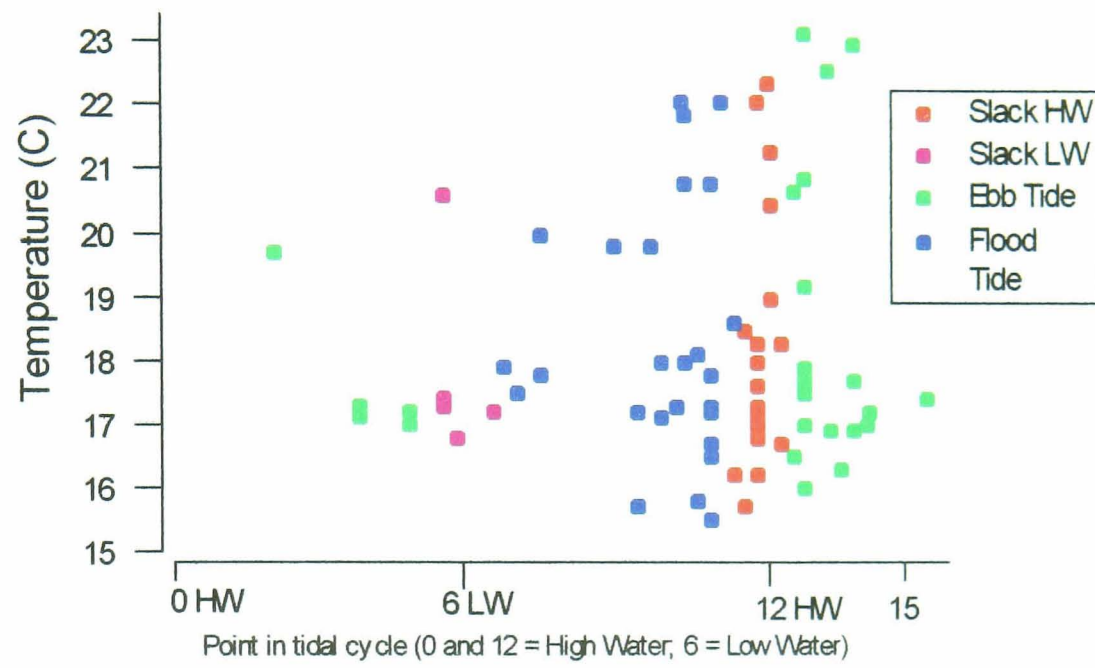
Figure 7.14 Distribution of Turbidity sample (1995) concentrations through tidal cycle
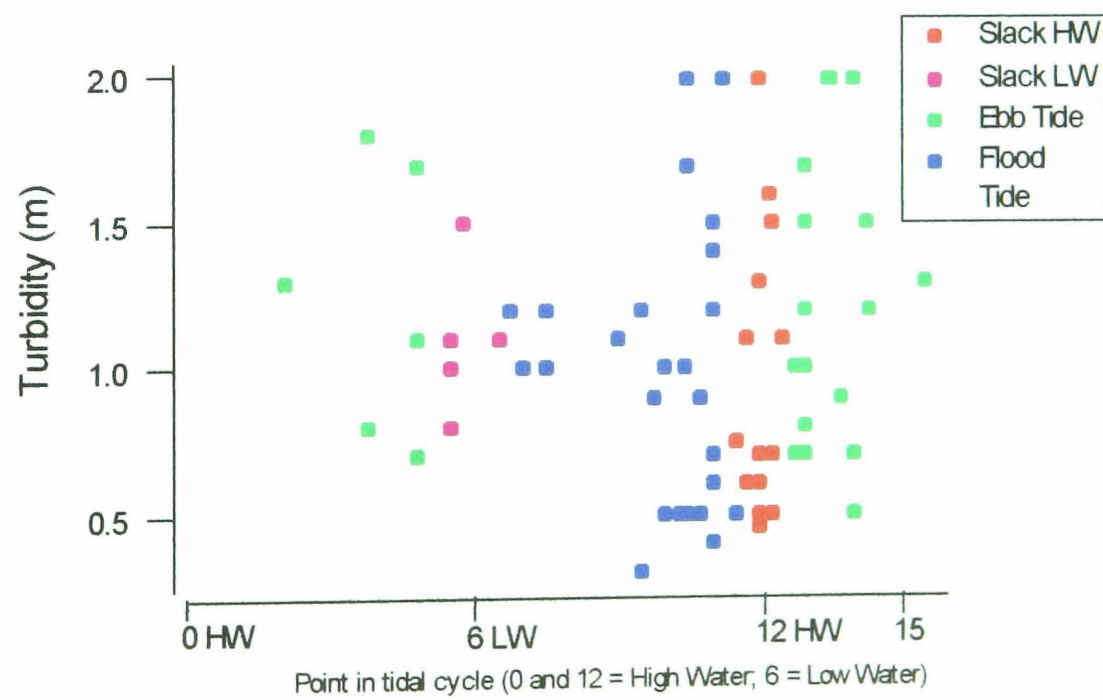
7.3 Secondary parameter identification and understanding

The water body around the Southend-on-Sea bathing water area (like other coastal bathing areas) is complex and multi-dimensional with constantly changing inputs (many of which are unknown). As discussed in the methodology, the use of field data meant that these complex water quality relationships were incorporated into this study's data. This allowed the inclusion of the effects of change in secondary water quality parameters on reflectance. This required secondary water quality parameters to be related to the water quality parameters of direct interest. The use of known water quality relationships from other environments is strongly supported by research over the last 75 years into lake, river and ocean water quality such as models proposed by Biswas (1981) (illustrated in Figure 4.1), Street-Phelps(1925), Chapra (1997) and Thomann (1987). The relationships inferred by these models will remain true for coastal or estuarine waters i.e. nutrient levels will be related to algal growth, but the complexity of the coastal region means that quantifying these changes may vary from area to area. Harris *et al.*'s (1993) work with their simulation model (discussed in Chapter3) provides a possible means to achieving this in the longer term. This research required the production of a water quality model for the Southend bathing water area and this was based utilising the data collected in 1995 and checked against the relationships inferred by the water quality models referred to above that were developed for closed systems (Biswas (1981) etc.). This model could then be used to allow the inclusion of secondary parameters related to reflectance (in particular chlorophyll).

The models could not be applied directly because of the influence and complexity of the local environment. While Alexander Marcet in 1819 showed that the relationship between

the percentage of some of the major parameters and the salinity of the sea water is a constant (Open University, 1978). When a parameter remains constant, varying only with salinity, it is termed conservative. The theory put forward by Marcet was further tested in other experiments in the 19th Century by Forchhammer (1843-1863), Dittmar (1872-1876) and in the 1960s at the University of Liverpool and the Institute of Oceanographic Sciences (Open University, 1978). However, estuary areas have a "substantial inflow of river water which not only contains less total dissolved salts than sea water, but also has very different ionic ratios" (Open University, 1978 p13). The Thames estuary is relatively shallow and termed 'well mixed' due to a large tidal flux (Harris *et al.*, 1993; Laws *et al.*, 1993) which means that the saline input is widely dispersed throughout the water body and therefore allows normal relationships between parameters to operate. This means that the interpretation of the inter-relationships identified in models such as Biswas' general mass equation (Figure 4.1) will remain the same but the size of effect on secondary parameters may be different. Water quality parameters stabilise after any input to a new or previous equilibrium (depending on whether the input is constant). This relationship is summarised in the general mass conservation equation for an element (Biswas, 1987). Established water quality models for harbours and estuaries maintain the same relationships as models for rivers and lakes (Thomann, 1987). Therefore, although seawater varies from area to area, relationships between parameters can be understood because relationships between parameters remain constant in any given environment.

In nearly all waters BOD can sometimes be as high as $5mgl^{-1}$ but where there has been discharge of industrial or domestic waste into inadequately diluted receiving waters, levels can be several hundred mgl^{-1} (Warren, 1971). Heterotrophic organisms, particularly

bacteria are responsible for the oxidative breakdown of organic material. They flourish

with the increased input of consumable organic substances and Southend-on-Sea's sewer

outfalls at Thorpe Bay discharged primary sewage in 1995. Now the levels of treatment

are higher than in 1995, but even effluent that has secondary treatment will be enriched

with nitrates and phosphates and other inorganic plant nutrients made through the

decomposition of organic material.(Warren, 1971). This increase in nutrient levels can

lead to increased production of micro-organisms, especially algae which are autotrophic,

and use them along with carbon dioxide to form protoplasm (Warren, 1971). Thus in

estuarine areas, and inshore coastal areas, they can lead to the development of nuisance

blooms of algae (Thomann, 1987). Hence chlorophyll-a and any of the microbiological

parameters (total coliform, faecal coliform, E.coli and BOD (BOD is the oxygen necessary

for the oxidative decomposition of material by micro-organisms)) collected can operate as

secondary parameters to organic material and nutrient levels (phosphates and nitrates).

Similarly inputs of suspended sediment and dissolved solids can have effect the

equilibrium of the water quality as shown in Biswas's (1981) interpretation of the general

mass equation illustrated in Figure 4.1. A rise in suspended sediments causes a water body

to become increasingly turbid, with the result that the rate of photosynthetic activity will

reduce (Open University, 1978; Thomann, 1987).

7.4 Creating a water parameter model

Due to the complexity of the Southend-on-Sea bathing water area with large numbers of separate and unknown sources of contamination, a model had to be created using the actual data collected in 1995. This water quality model was constructed on the basis of the statistical relationships found when the 1995 water quality data were correlated (see Table 7.1) whose level of significance was 0.01 when the correlation coefficient > 0.27.

Table 7. 1 Correlation of 1995 water quality data collected at Southend-on-Sea (Pearson product moment correlation coefficients)

	salinity	pH	temp	DO	Ammonia	Turbidity	Coliform	Ecoli
pH	0.009							
temp	-0.004	-0.651						
DO	0.288	-0.141	-0.17					
Ammonia	0.054	0.451	-0.367	-0.27				
Turbidity	-0.141	-0.043	0.428	-0.273	-0.039			
Total Coliform	-0.25	-0.183	0.036	0.16	-0.367	-0.285		
Ecoli	-0.335	0.346	-0.392	0.188	0.041	-0.261	0.105	
faecal coliform	-0.099	-0.096	-0.022	0.077	0.077	-0.287	0.303	0.09
Nitrates	0.127	-0.067	0.061	0.138	-0.203	-0.031	0.051	0
sus.sed.	0.557	0.102	-0.192	0.236	0.2	-0.158	-0.056	-0.227
phosphates	-0.199	-0.04	0.132	-0.047	0.019	0.226	-0.093	-0.116
chlorophyll	0.322	0.422	-0.248	-0.163	0.145	-0.065	-0.312	-0.389
BOD	-0.152	0.026	-0.266	0.323	-0.082	-0.143	0.478	0.014

	faecal coliform	Nitrates	suspend. sediment	phosphates	chlorophyll
Nitrates	-0.093				
sus.sediment	0.104	0.006			
phosphates	0.156	-0.137	0.071		
chlorophyll	-0.34	-0.284	0.155	-0.12	
BOD	0.038	-0.051	-0.14	-0.106	0.171

The strength of the relationships were measured on the basis of correlation coefficient values greater than 0.27 (level of significance 0.01) between the water quality parameters. This produced a water quality model for the Southend-on-Sea study area that is shown in Figure 7.15.

Figure 7.15 Statistical model of water quality in the Thames Estuary
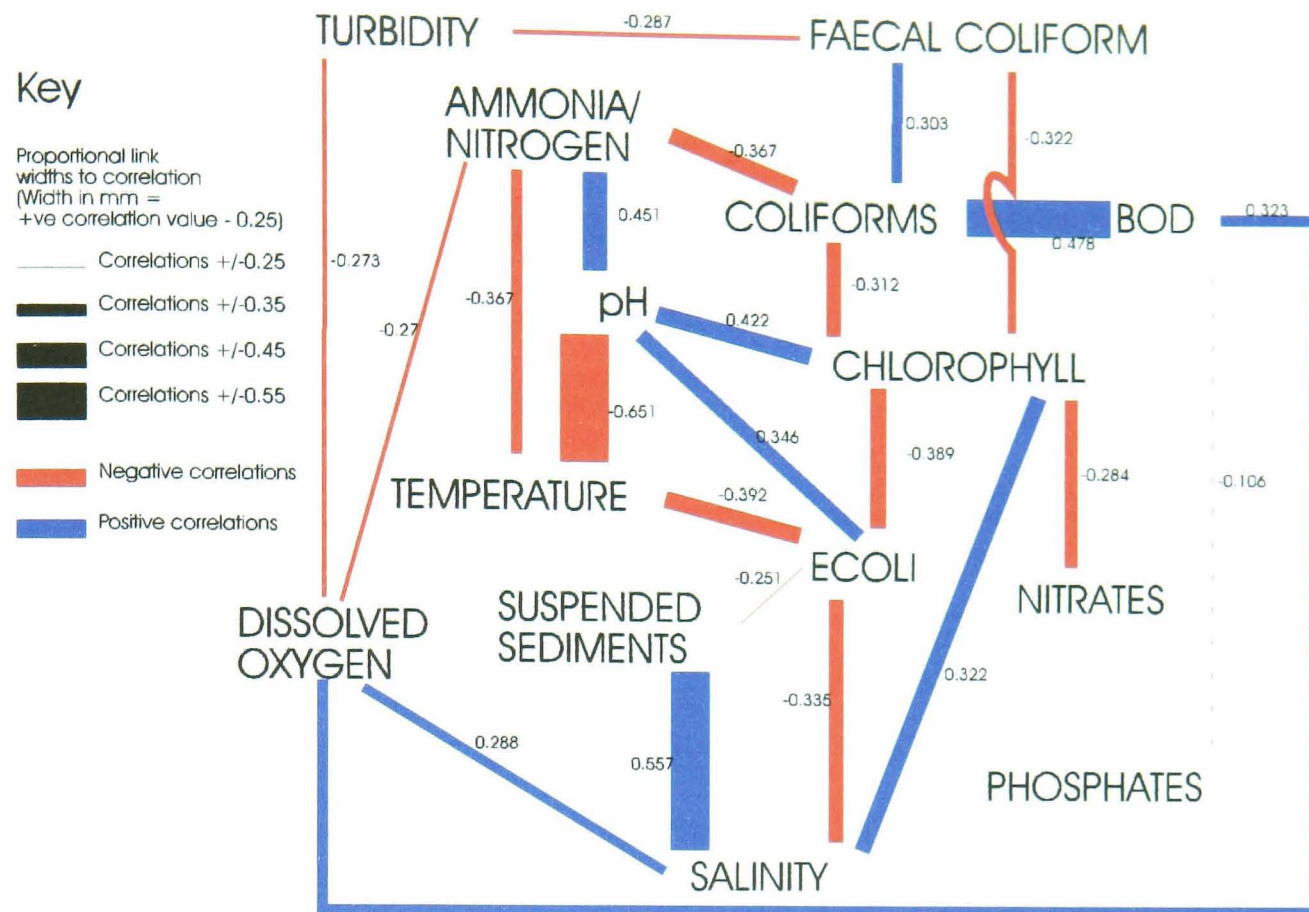
Nitrates, phosphates and chlorophyll had been expected to be strongly positively related but phosphates showed little evidence of any relationship and nitrates showed a negative correlation with chlorophyll. It is likely that phosphate the relationship is strongly influenced by inputs from the local area such as from the land fill site at Two Tree Island. The nitrate levels did not vary significantly during data collection and so they were not a major input into the area and therefore would not act as a trigger to algal bloom growth as indicated by chlorophyll-a. Algal growth use nutrients and so the nitrate level would decrease. The microbiological parameters (E.coli, faecal coliform, total coliform) had also been expected to be closely correlated and illustrate the reason why E.coli is suggested as a replacement for total coliform as an indicator by the EU. However the model created and illustrated in Figure 7.15 fits expected relationships, especially between those parameters with stronger correlation coefficients.

Finally, a water quality model (Figure 7.16) was constructed from the 1995 data, that excluded weakly correlated and misleading (based on existing understanding of water quality) relationships from the model. In constructing this model, phosphates were removed as they showed little evidence of any relationship potentially due to the lack of variation in concentration during the data collection period. Turbidity was also excluded because the variation in levels of turbidity over the data collection period was narrow from 0.3m to 2m (normal for the area). This variation is unlikely to change water quality i.e. changing from highly turbid to very highly turbid and appeared to show no relationship with suspended solids. The relationship between BOD and DO was expected to be negative and so the inclusion of that relationship was likely to be misleading possibly due to a local anomaly and was therefore omitted from the model.

Figure 7.16 Water quality model for Thames Estuary
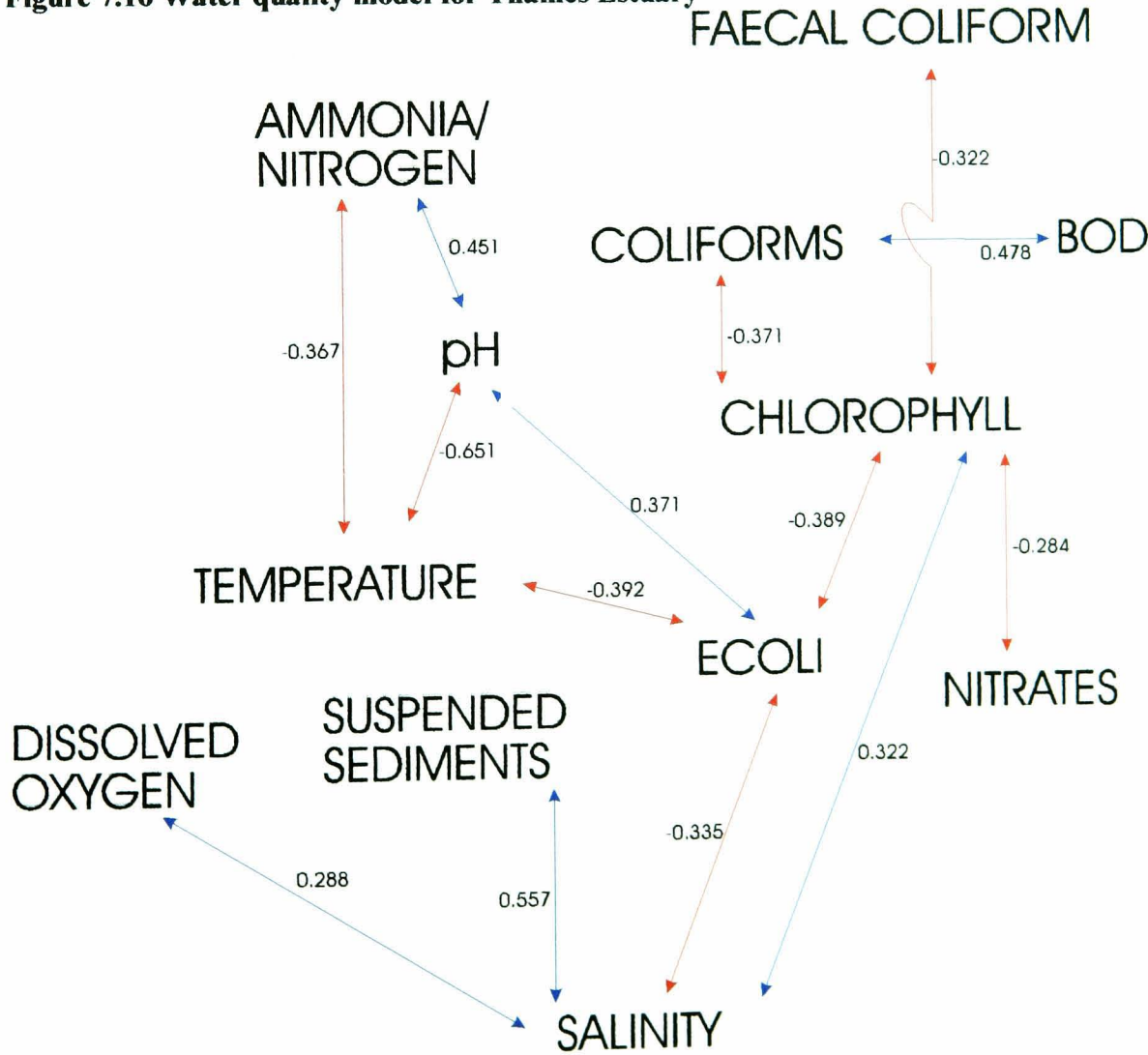
7.3 General Chapter Summary

A water quality model was produced to allow the integration of secondary parameters in subsequent analysis. The variations in water quality throughout the tidal cycles showed that concentrations were related to the water quality of that day irrespective of the tidal flow direction at the time of data collection. Figures 7.1-7.14 show the distribution of water parameter levels collected in this study in 1995 coded by the point in the tidal cycle rather than by time except in the case of the microbiological samples which showed few low concentrations. The majority of water quality data collected showed a normal distribution (using an Anderson normality test) which allowed the production of a statistical water quality model. This meant that any complex (possibly localised) factors would be included in the water quality model and the relationships found were cross referenced to either established, existing understanding from water quality models and relationships or through known local relationships. This results in the production of a water quality model for the Thames Estuary at Southend-on-Sea illustrated in figure 7.16.

CHAPTER 8

Second-Stage Analysis

8.1 Overview

The preliminary data analysis (Chapter 6) identified bands of wavelengths that show potential relationships with each of the water quality parameters either through visual interpretation (using mean reflectance when high or low levels of the water quality parameter were present) or through statistical correlation. These results guided the second-stage analysis by suggesting in-depth study of identified wavelengths within the range 300-1100nm. The second-stage analysis involved the identification and evaluation of the wavelengths of interest and involved four operations (listed below) for each water quality parameter. The whole process is illustrated in Figure 8.1.

1. The data were standardised using an established standardisation method (Bryman and Cramer, 1996). Both the reflectance data and water quality parameter concentration data were standardised so that a visual comparison of the data could be performed at 10nm intervals.

2. The ranges and/or wavelengths resulting from the preliminary analysis were integrated into this stage of the analysis. Where ranges of wavelengths had been highlighted in the preliminary analysis, comparisons were made every 2nm (i.e. on every recorded wavelength within that range) to allow further study using the standardised data analysis.

3. If a comparison of the standardised curves (described in more detail later) showed a significant relationship the strength of the relationship was tested through regression analysis. If several wavelengths were identified then the wavelength with the strongest relationship found through regression analysis was selected as the optimum wavelength.

4. If a possible optimum wavelength(s) was identified, this wavelength was used to predict high levels of the water quality parameter from the data and test the accuracy of prediction.

Figure 8.1 Flow chart of analysis
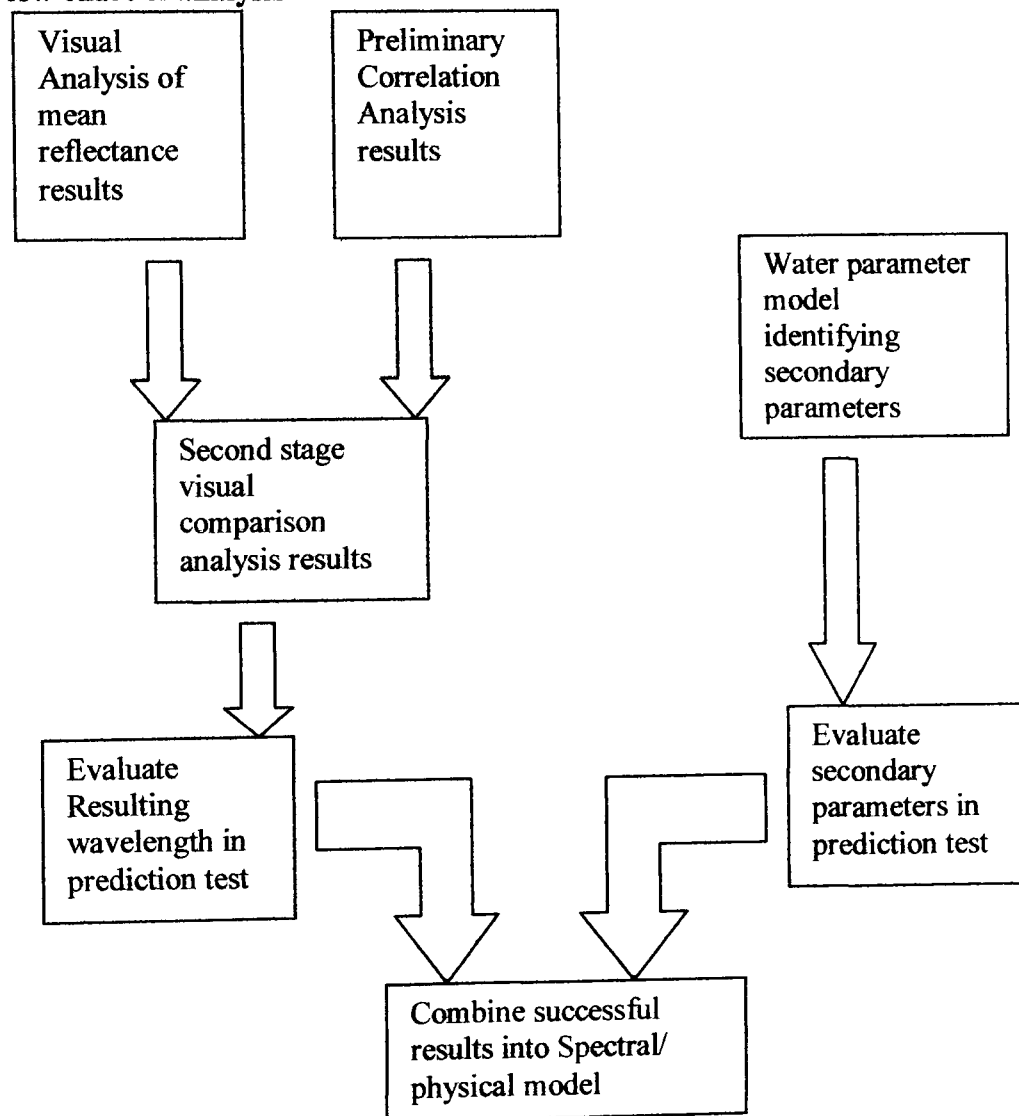
The data for each water quality parameter and its corresponding spectral data were standardised using an established standardisation method (Bryman and Cramer, 1996) by subtracting the mean and dividing by the standard deviation for each parameters' data

excluding missing values. In order to standardise the data rows of data with missing values had to be removed. This led to the creation of separate data sets for each water quality parameter. Both the reflectance data and water quality parameter concentration data were standardised so that a visual comparison of the data could be performed at 10nm intervals. A visual comparison of the standardised reflectance curve and standardised concentrations of each water quality parameter were undertaken at every 10nm with every 50nm illustrated in the following sections or appropriate appendices (Appendix 4).

The results from the preliminary analysis were incorporated into the analysis as follows:

- The wavelengths selected with the highest correlation value from the preliminary analysis were selected for visual comparison.

- The wavebands identified in the preliminary visual analysis of mean reflectance were visually compared at 2nm intervals (i.e. at every spectral recording)

Visual analysis was undertaken using the Scan Chemometric Software (Minitab,1995) graph analysis tools, which permit detailed visual study of the standardised curves of each wavelength plotted against the concentration of the water quality parameter. The software allowed a detailed comparison of the patterns of distribution of the standardised water quality parameter data and the standardised reflectance data. To assist in this process, the software tools allowed the selection and display of related data which included weather, data values recorded, standardised values, values either side of the point selected to be displayed in simultaneous but separate window so that curves could be compared at sample by sample level. This ability to cross reference to see if a value appeared different to preceding and following values, or to see if any

record had been made of passing surface foam/debris or other factors enabled an evaluation of the importance of outliers to be considered. The comparison of the curves involved comparing peaks and troughs of the reflectance with those of the parameter concentration curves peak and troughs i.e. comparing the pattern of the graphed water quality and reflectance data. The wavelength curves that had similar shape and peaked and troughed at the same time were selected as the optimum wavelengths. Where patterns appeared similar at more than one wavelengths, measurements were made between the two curves to determine the wavelength which has the best fit to the pattern of distribution of the water quality parameter. In order for this process to yield the best possible results, the data were reduced to a new subset that included only data collected on the 'best' days i.e. those classified as cloud cover 1-4 on the EPFS cloud coverage coding system as discussed in Chapter 4. These data will be referred to from herein as the "best data set". The visual analysis was repeated at least three times (approximately 1-2 months apart) for each parameter to ensure the results found were not subject to human error. Limitations of the Scan software graphical analysis tools meant that this process had to be carried out using a subset of the data that excluded any rows of data with missing values. This meant that separate data sets were created, one for the laboratory analysed data (nitrates, phosphates, suspended sediment, E.coli faecal coliform and total coliform), individual ones for BOD and chlorophyll (whose number of samples were lower due to the laboratory processes involved), and one for the remaining parameters collected in the field. Due to the software limitations, a further reduction in the number of samples was required. This was achieved by taking the Scan *random % data subset routine* to reduce the sample down to 99 within the maximum 100 samples allowed.

The wavelengths showing the best fit (as defined above) from the visual analysis of the standardised wavelengths and parameter concentrations from this selection were then compared through regression analysis. The wavelength that showed the strongest relationship through regression analysis was selected as the optimum wavelength if a reasonably strong relationship was indicated. The optimum wavelength was then used to try to predict the number of instances when the parameter either exceeded the legal or guideline limit or, if no guideline limit is set such as nitrates, the upper quartile of the data was used as the threshold value. This allowed an evaluation of the monitoring potential of each wavelength/water quality parameter relationship.

8.2 Microbiological Water Quality Parameters

8.2.1 Faecal Coliforms

The preliminary visual analysis of the curves (mean reflectance compared against high count levels of faecal coliform, as described in Chapter 6.2) showed that there were no strong relationships, but that there were possible relationships within the range 600-700nm, especially around 630nm, and within the ranges 820-870nm, 990-1010nm.

Correlation analysis showed that the wavelengths over 669nm were statistically unrelated, with very low positive correlation coefficient values of below 0.1. The range 600-670nm does show a peak in correlation with reflectance at wavelengths around 630.42nm, 632.05, 646.69, 656.38 with low (but significant to level 0.01) correlation coefficient values as illustrated in Table 8.1. Because of this, the wavelengths shown in

Table 8.1 were included for individual inspection in the visual analysis of the standardised data.

Table 8. 1 Correlation of wavelength and Faecal coliform

Wavelength (nm)	Correlation Coefficient from Preliminary Analysis
338.77	0.242
342.66	0.236
630.42	0.262
632.05	0.264
633.69	0.253
646.69	0.268
651.53	0.268
656.38	0.267

Careful visual analysis (described earlier in this chapter) was undertaken using the available graph analysis tools. This involved every wavelength at 2nm intervals around the wavelengths in Table 8.1 and every 10nm throughout the rest of the range 300-1100nm. This analysis showed that the ranges around 633.69nm and 338.77nm did show a similarity in pattern to that of Faecal coliforms, except for around the 80th sample of the subset of data (subset of data described in section 8.1). The 80th sample did not possess any obvious difference in field conditions and was therefore considered to be significant and unable to be discounted. The similarity in patterns were strongest at 633.69nm and 338.77nm and are illustrated in Figures 8.2 and 8.3 (others are shown in Appendix 4). The relationship at 338.77nm was similar to that shown by E.coli and is supported by the laboratory spectroscopy studies of sewage plumes by the Ocean

Physics Laboratory, California (OPL, 1997) and by Pinnick *et al.*'s(2002) highly specialised microbiological studies in the USA on airborne particles. Pinnick *et al.* (2002) also highlighted a peak in fluorescence spectra of bacteria in vegetative cells at around 640nm.

Figure 8.2 Standardised reflectance against standardised levels of faecal coliform
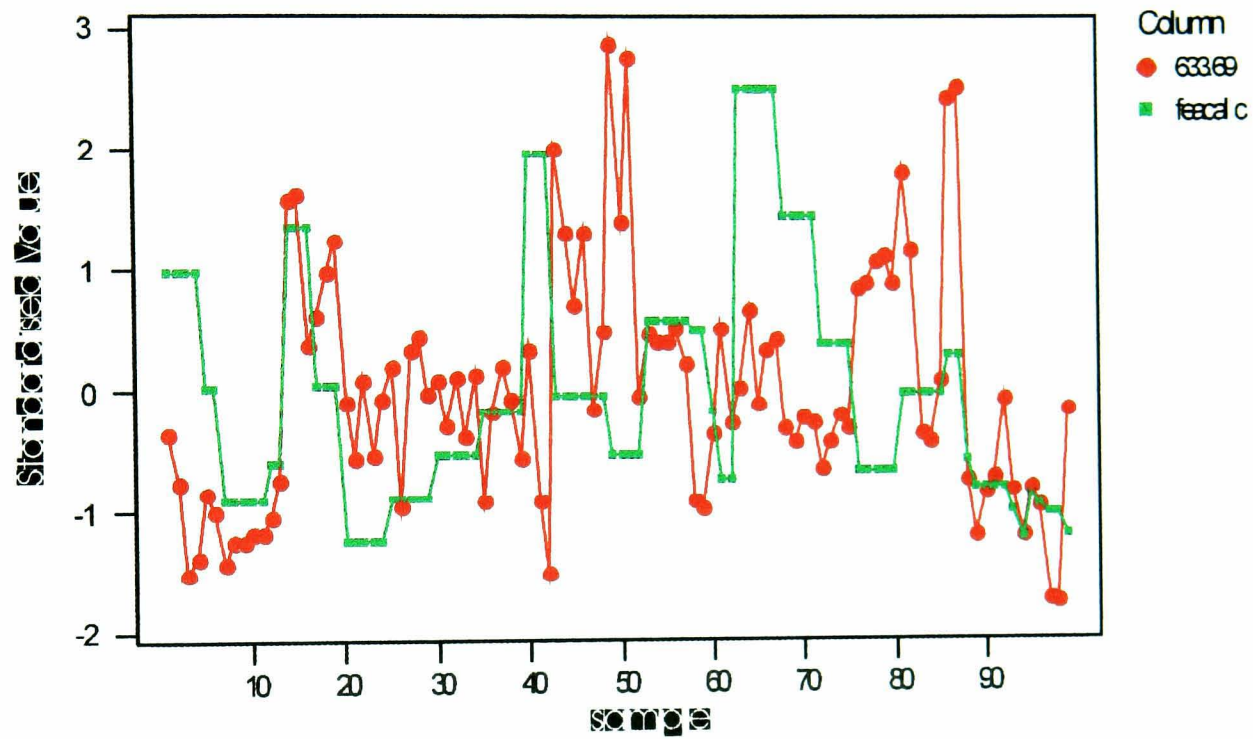
Figure 8.3 Standardised reflectance against standardised levels of faecal coliform
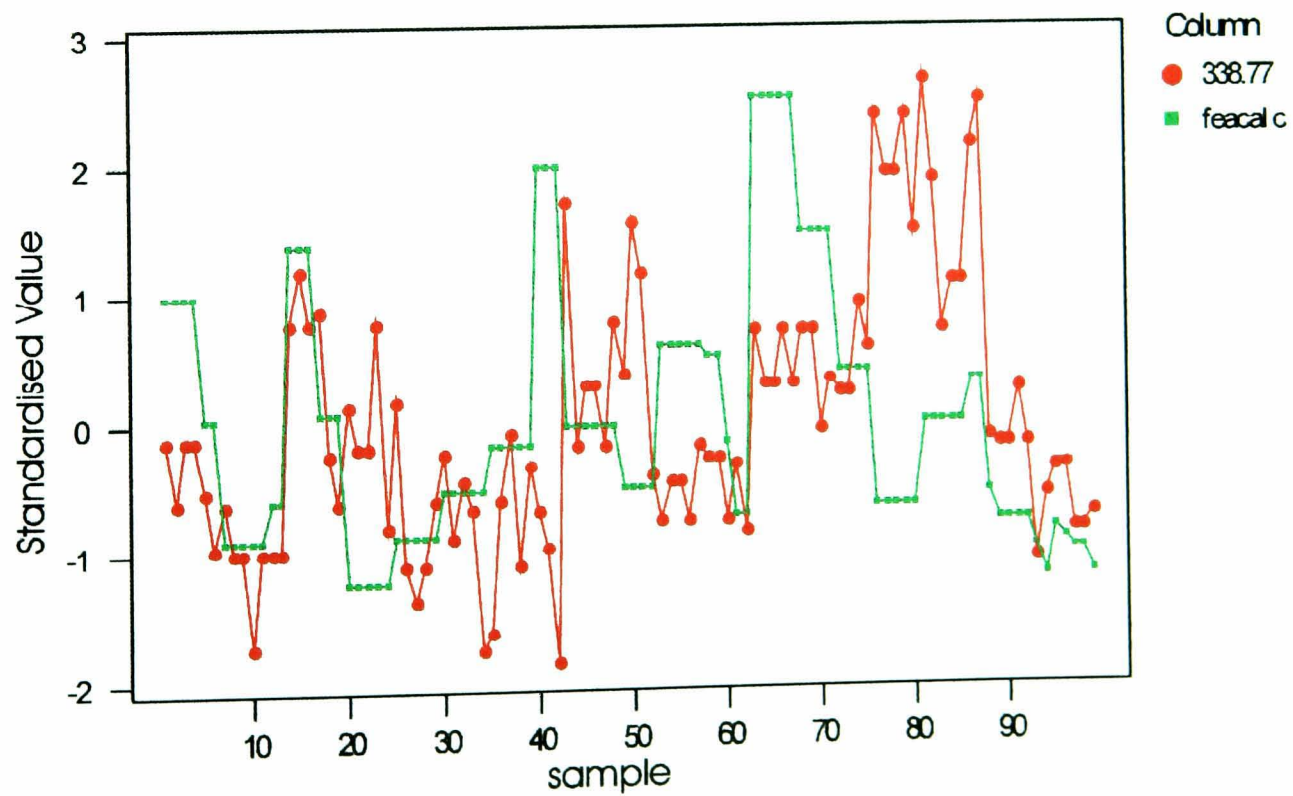
Regression analysis was carried out on each of these wavelengths using the full data subset (i.e. all data recorded excluding obvious anomalies and missing values as defined in Chapter 5). Regression analysis using the full data subset did not produce any meaningful results (R-sq=5.9% for 338.77nm and 6.4% for 633.69nm). Further details on the regression analysis are contained within Appendix 4A2. The regression analyse were therefore repeated using the best data subset which excluded all data collected in poor cloud cover conditions for spectral data collection as defined by the NERC EPFS (see Chapter 6). The best data sub-set regression analysis results (shown in Figures 8.4 and 8.5) showed low but statistically significant relationships of R-sq=23.5% for 633.69nm and 25.3% for 338.77nm, as shown in Table 8.3. While the p values indicated in Table 8.3 do show the results as statistically significant, it must be noted that the best data subset only included 82 original samples so these results should be considered in the light of the earlier regression analysis of the full data set.

Figure 8.4 Regression plot of faecal coliform against 338.77nm using the best sub set data

$Y = -78.1657 + 13.3598X$

R-Squared = 0.253

————— Regression

· · · · · 95% CI

— · — 95% PI
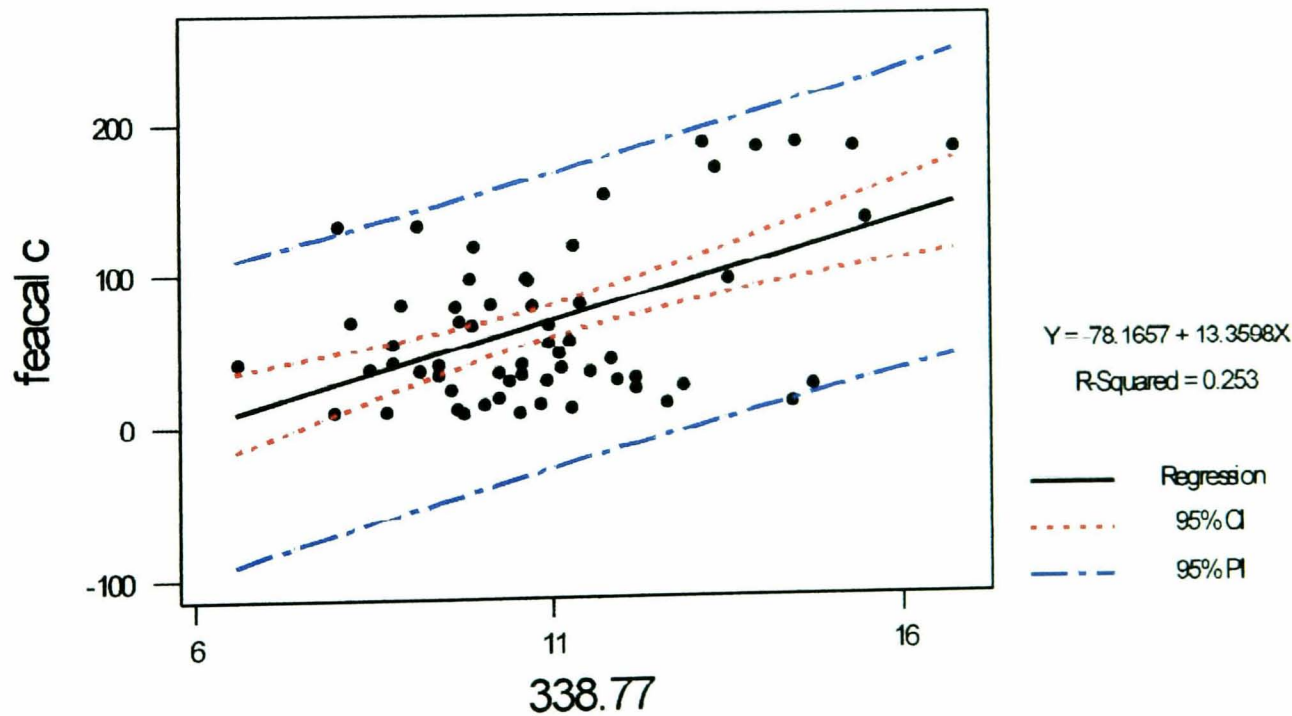
Figure 8.5 Regression plot of faecal coliform against 633.69nm using the best sub set data
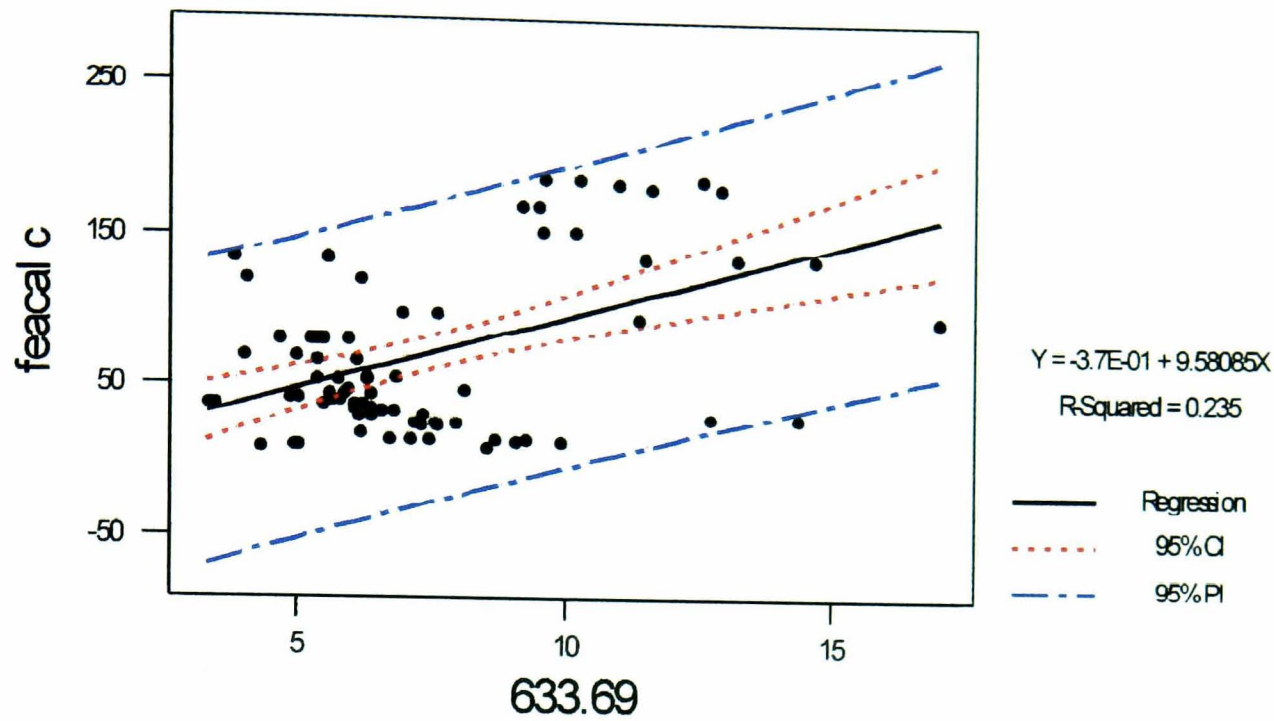
As indicated by the weak correlation values and visual analysis, no relationships could be described as statistically strong particularly as the best subset reduces the micro-bacterial sample numbers. However, the regression analysis highlighted 338.77nm and 633.69nm as being possible predictor wavelengths from their corresponding parts of the spectrum because of the higher r-sq value and steeper regression curve. The best subset regression equation for 338,77nm and 633.69nm are shown in Table 8.3).

Table 8. 2 Regression analysis results

338.77

faecal coliform = - 78.2 + 13.4 338.77 (s = 49.00   R-sq = 25.3%   R-sq(adj) = 24.4%)

Predictor	Coef	Stdev	t-ratio	p
Constant	-78.17	29.29	-2.67	0.009
338.77	13.360	2.564	5.21	0.000

s = 49.00   R-sq = 25.3%   R-sq(adj) = 24.4%

Table 8. 3 Regression analysis results

633.69nm

faecal coliform = - 0.4 + 9.58 633.69 (s = 49.60 R-sq = 23.5% R-sq(adj) = 22.5%)

Predictor	Coef	Stdev	t-ratio	p
Constant	-0.37	15.57	-0.02	0.981
633.69	9.581	1.933	4.96	0.000

s = 49.60   R-sq = 23.5%   R-sq(adj) = 22.5%

Figure 8.6 Plot of standardised faecal coliform data and standardised reflectance at 338.77nm and 633.69nm
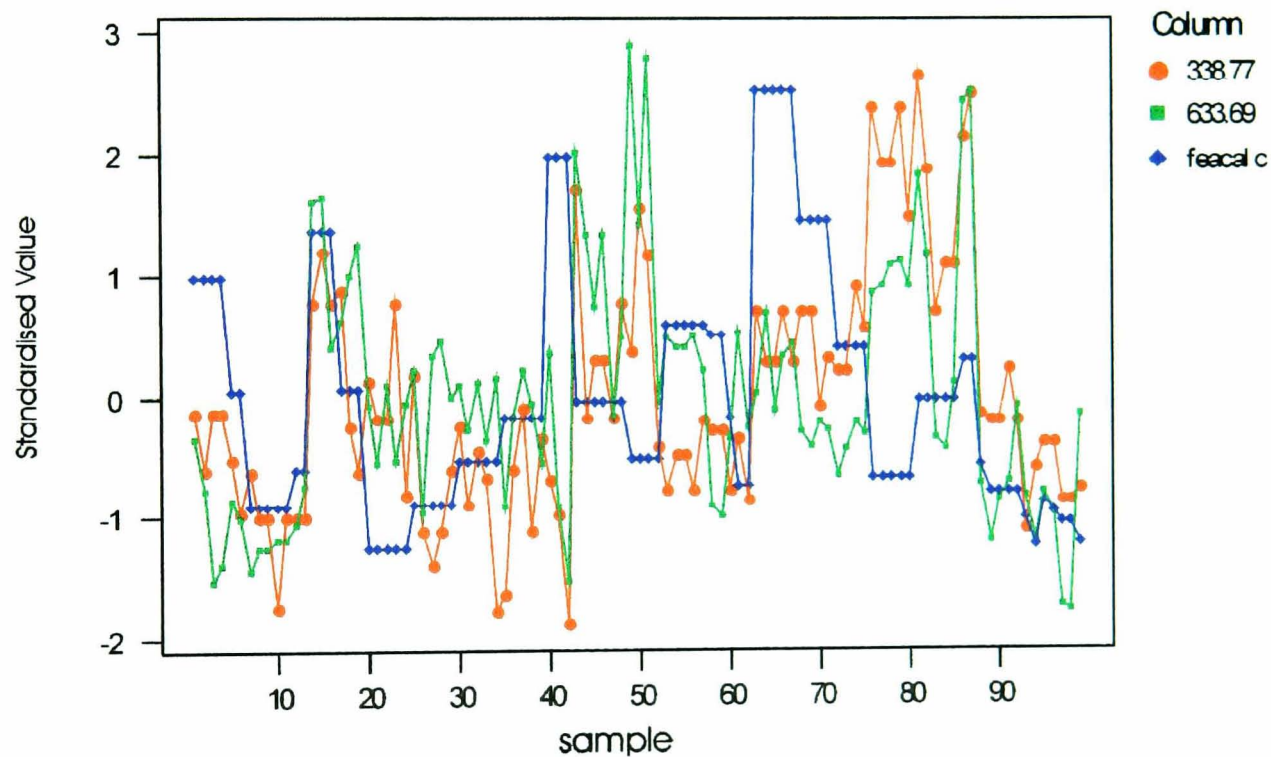
Neither 338.77nm nor 633.69nm wavelengths had statistically or visually strong relationships with faecal coliform (Figure 8.6) and neither was particularly stronger than the other. Therefore both wavelengths were used to assess the level of accuracy that could be achieved in predicting high levels of faecal coliform. The level of faecal coliforms specified by the EU Bathing Water Directives (EU 76/160/EEC) are guide levels of 100 counts per 100ml and failure at over 2000 counts per 100ml. The study area only failed on 2 samples in the year 1995 at just two of the EA sample locations. It

was therefore not surprising that no samples were recorded during the fieldwork period that actually exceeded the failure rate. However, the guide limit of 100 counts per 100ml was exceeded on numerous occasions, as shown in Figure 8.7, and this value was therefore used as the threshold level to test the wavelengths as predictors of high faecal coliform.

Figure 8.7 Faecal coliform levels recorded with EU guide and fail levels
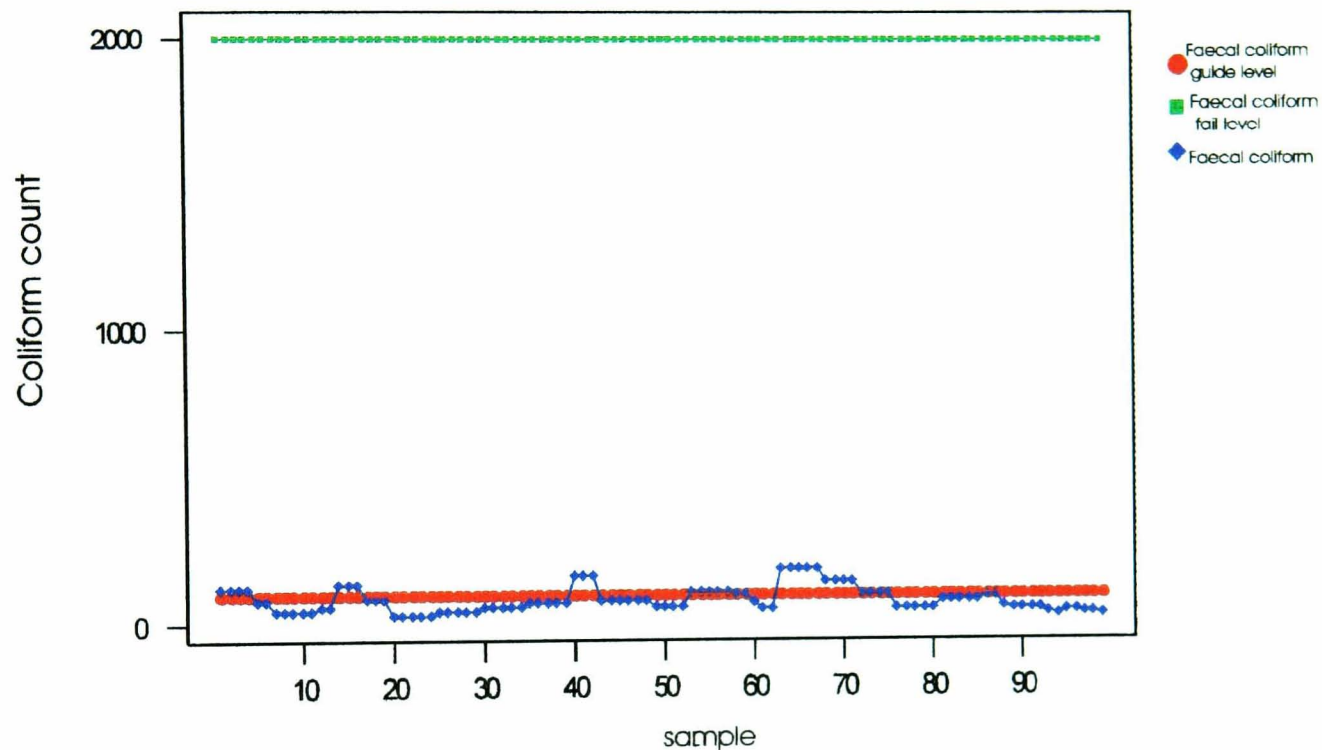
The values of guide and field measurements for faecal coliforms were standardised (by subtracting the mean and dividing by the standard deviation) along with the reflectance values at 338.77 and 633.69nm and plotted alongside each other. The reflectance level used to identify high levels of faecal coliform was selected through trial and error based on variations around the upper quartile of reflectance using the best data subset. This process established the threshold value of reflectance at 338.77nm and 633,69nm that corresponded to the EU guide threshold level for Faecal coliforms. For 338.77nm the reflectance level for prediction at 100 counts per 100ml was 14.034 and 9.691 for 633.69nm (Figures 8.8, 8.9,8.10). This threshold was then applied to the whole data set

as a predictor for EU guide levels of faecal coliform with the following results for each wavelength.

Figure 8.8 Standardised data: EU faecal coliform guide level (100counts per 100ml) against faecal coliform data collected and reflectance at 633.69nm, 338.77nm.
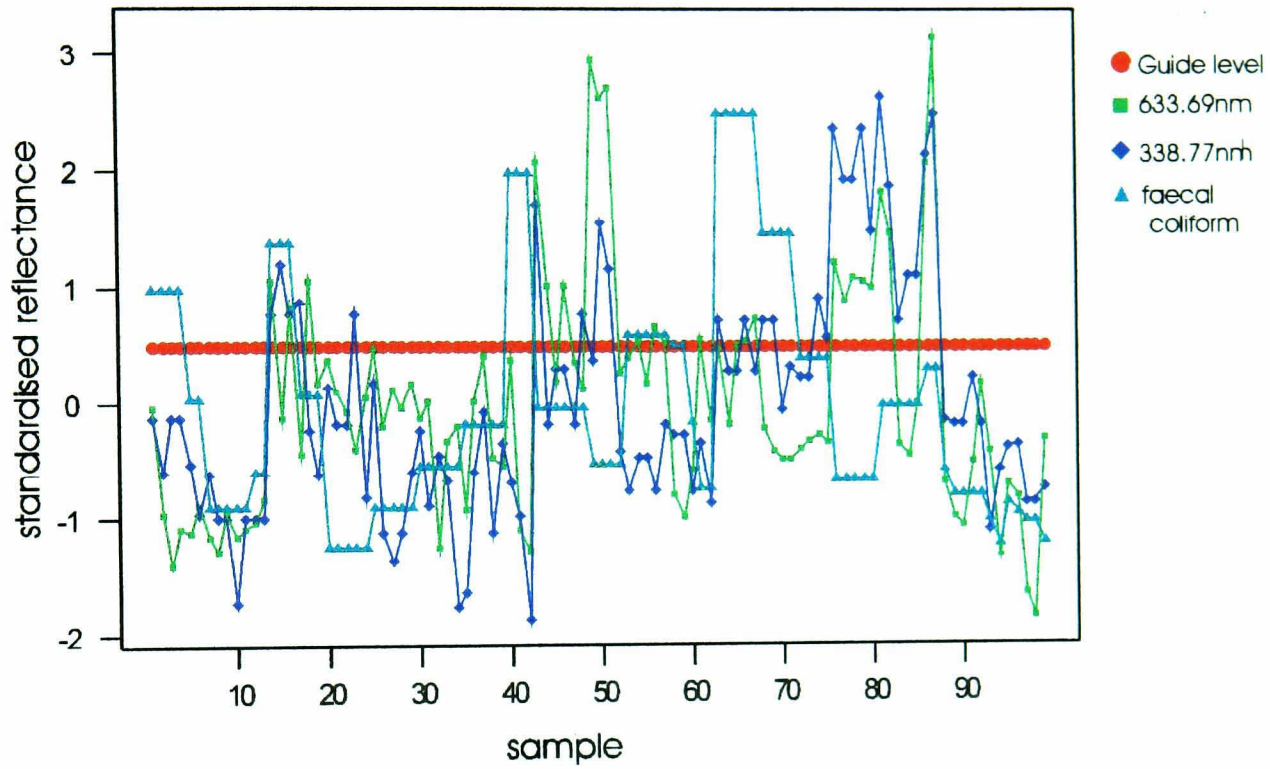
Figure 8.9 Standardised data: EU faecal coliform guide level (100counts per 100ml) against faecal coliform data collected and reflectance at 338.77nm and reflectance level for prediction identified as 14.034.
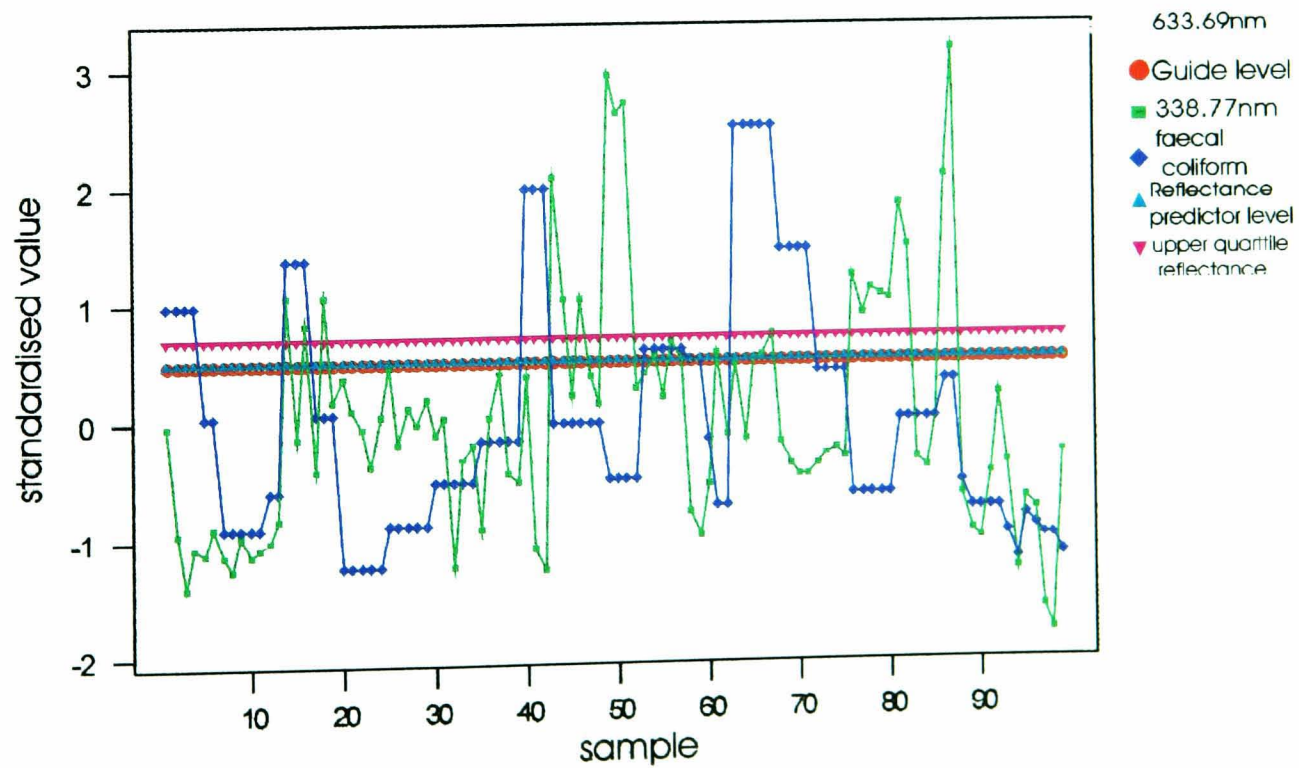
Figure 8.10 Standardised data: EU faecal coliform guide level (100counts per 100ml) against faecal coliform data collected and reflectance at 633.69nm and reflectance level for prediction identified as 9.691.
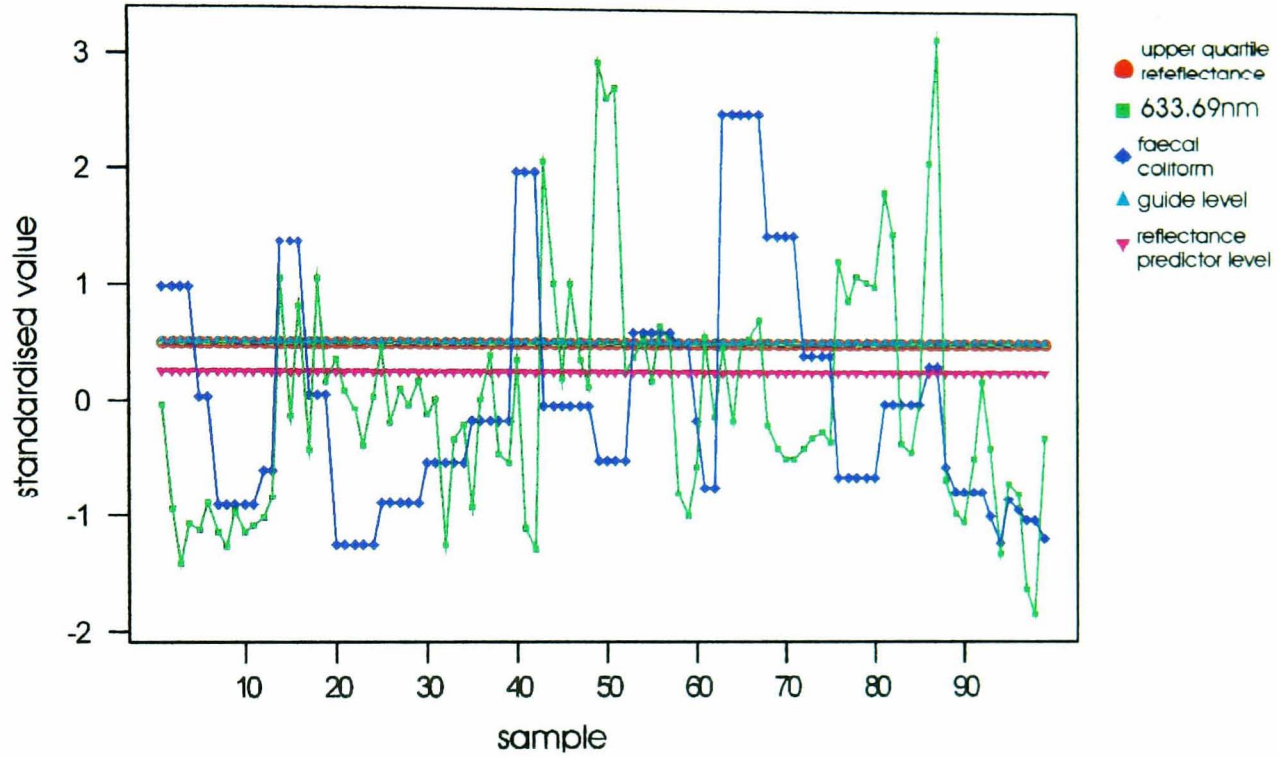
The use of 338.77nm as the predictor wavelength to identify samples over 100counts per 100ml of faecal coliform resulted in 69% (296 samples out of 427 samples) correct identifications, 30% (130) incorrect of which 8% were underestimated, and 22% overestimated, as shown in Table 8.4.

Table 8. 3 Results of 338.77nm as predictor for >100counts /100ml Faecal coliform

338.77nm CORRECT	%
296 correct	69.2
130 incorrect	30.4
of which	
34 underestimated	7.9
96 over-estimated	22.4

The use of 633.69nm as the predictor wavelength to identify samples over 100counts per 100ml of faecal coliform resulted in 64% (273 samples out of 427 samples) correct identifications, 36% (153) incorrect of which 5% were underestimated, and 31% overestimated as shown in Table 8.5.

Table 8. 4 Results of 338.77nm as predictor for >100counts /100ml Faecal coliform

633.69nm CORRECT	%
273 correct	63.8
153 incorrect	35.7
of which	
20 underestimated	4.7
133 over-estimated	31.1

8.2.2 Total Coliforms

The preliminary analysis showed a low/modest positive correlation between reflectance and total coliform count (significant at the 0.01 level) peaking at 654.77nm (correlation of 0.392) and 392.38nm (correlation of 0.365). A threshold correlation coefficient value of 0.35 (significant at the 0.01 level) was used to select the best potential predictor wavelengths from the preliminary analysis the wavelengths ranges 390.5-399.9nm, 440.61-447.91nm, 607.4-667.63nm were selected as the ranges of potential interest (see Table 8.6. The preliminary visual analysis highlighted the ranges 400-700nm and possibly 770-880nm. These values were used as before (section 8.21) to target wavelengths in the second-stage visual analysis. However, visual analysis of the standardised reflectance and standardised total coliform count showed there were no discernable relationships between reflectance and levels of total coliform (see the figures in Appendix 2A1).

Table 8. 5 Selected examples of correlation of wavelength and Total Coliform

Wavelength(nm)	Correlation Coefficient from Preliminary Analysis
390.5	0.351
394.26	0.363
442.44	0.353
610.71	0.363
649.69	0.393

The lack of a positive result from the second stage visual analysis meant that a regression analysis was carried out for each of these potential predictor wavelengths to select the wavelengths that showed the strongest relationship to total coliform using the full data set. None of the wavelengths showed a strong relationship with total coliform. However the strongest of these relationships are shown in Table 8.7, 8.8 and Figures 8.11 and 8.12. Further details of the results of this analysis are contained within Appendix 4A4.

Table 8. 6 The results of regression analysis of reflectance (442.44nm) against total coliform

Regression Analysis

The regression equation is

Coliform = 80.2 + 22.9 442.44

Predictor	Coef	Stdev	t-ratio	p
Constant	80.23	26.37	3.04	0.002
442.44	22.899	2.825	8.11	0.000

s = 206.3   R-sq = 13.4%   R-sq(adj) = 13.2%

Figure 8.11 Regression analysis of total coliform with 442.44nm

$Y = 80.2265 + 22.8985X$

$R\text{-}Squared = 0.134$

—— Regression

⋯⋯ 95% CI

— · — 95% PI
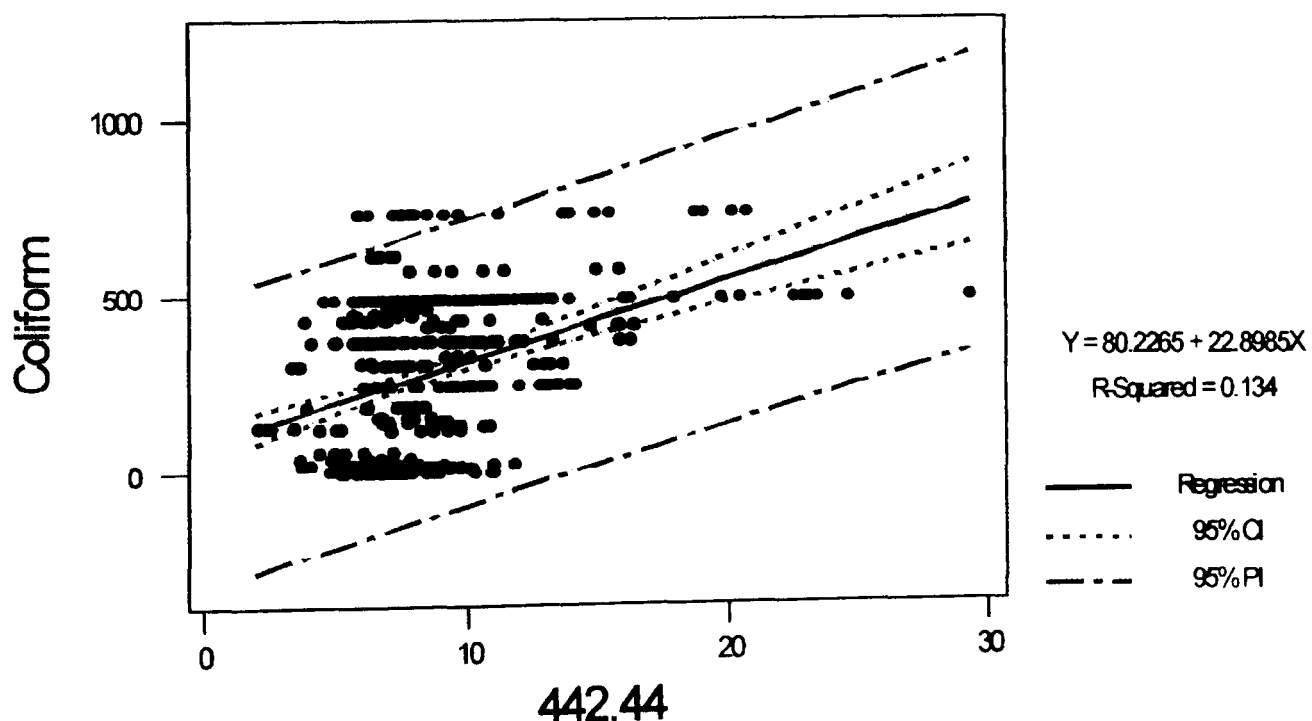
Table 8. 7 The results of regression analysis of reflectance (649.93nm) against total coliform

Regression Analysis

The regression equation is

Coliform = 104 + 20.5 649.93

Predictor	Coef	Stdev	t-ratio	p
Constant	103.76	23.05	4.50	0.000
649.93	20.451	2.440	8.38	0.000

s = 205.4   R-sq = 14.2%   R-sq(adj) = 14.0%

Figure 8.12 Regression analysis of Total Coliform with 649.93nm

$Y = 103.758 + 20.4507X$

R-Squared = 0.142

Regression
95% CI
95% PI
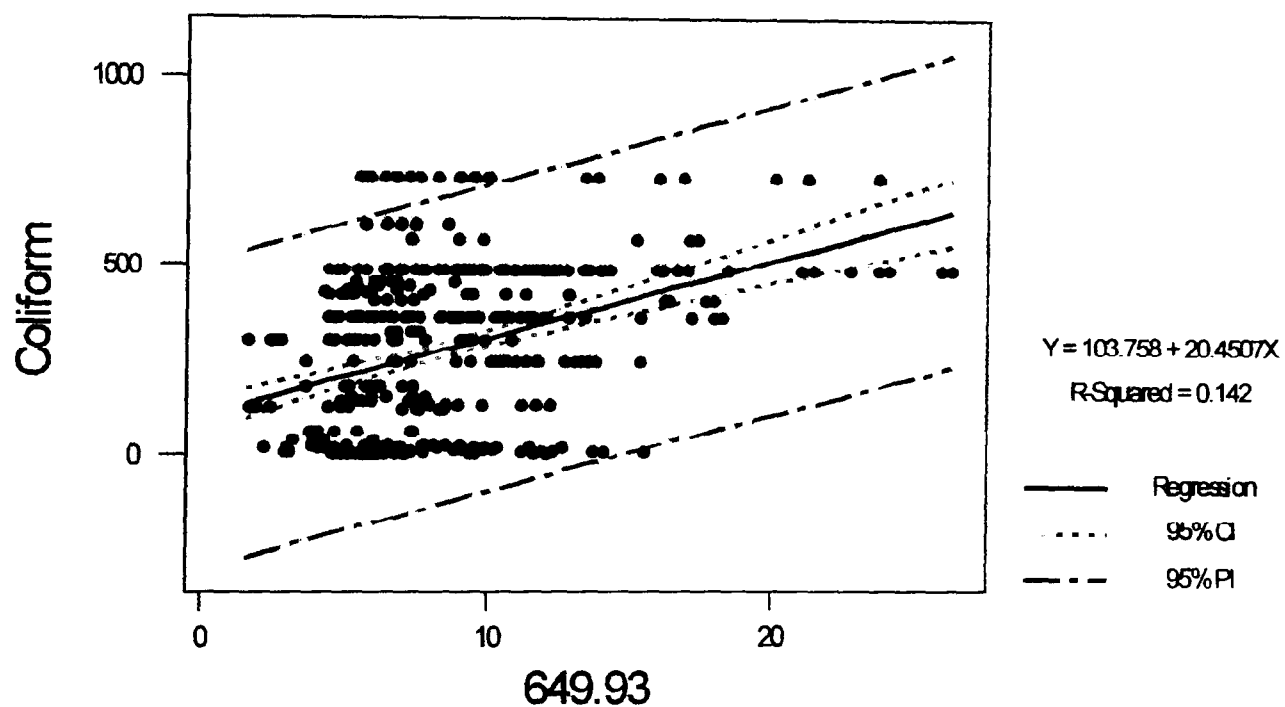
Regression analysis showed that there were no strong relationships present between total coliform and reflectance at any wavelength. However, weak relationships were suggested (as shown in Figure 8.11-8.12) on the basis of the regression analysis using the full dataset. The best wavelengths were selected for analysis using the best subset

data i.e. the data collected in optimum conditions as described at the beginning of this chapter.

The selected wavelengths were:

- 442.44nm R-Sq 13.4% , regression equation coliform = 80.2+22.9 442.44nm

- 649.93nm R-Sq 14.2%, regression equation coliform = 104+20.5 649.93nm

and Table 8.9 contains the results from the regression analysis.

Table 8. 8 Regression analysis using the best subset data for total coliform

Regression Analysis				
The regression equation is				
Coliform = 151 + 20.7 442.44				
Predictor	Coef	Stdev	t-ratio	p
Constant	150.95	75.63	2.00	0.049
442.44	20.745	8.201	2.53	0.013
s = 205.6	R-sq = 6.2%	R-sq(adj) = 5.2%		
Regression Analysis				
The regression equation is				
Coliform = 83.8 + 31.7 649.93				
Predictor	Coef	Stdev	t-ratio	p
Constant	83.78	55.43	1.51	0.134
649.93	31.743	6.573	4.83	0.000
s = 190.6	R-sq = 19.4%	R-sq(adj) = 18.6%		

Figure 8.13 Regression analysis of best data sub set of Total Coliform with 649.93nm

$Y = 83.7846 + 31.7427X$

R-Squared = 0.194

—— Regression

...... 95% CI

— — 95% PI
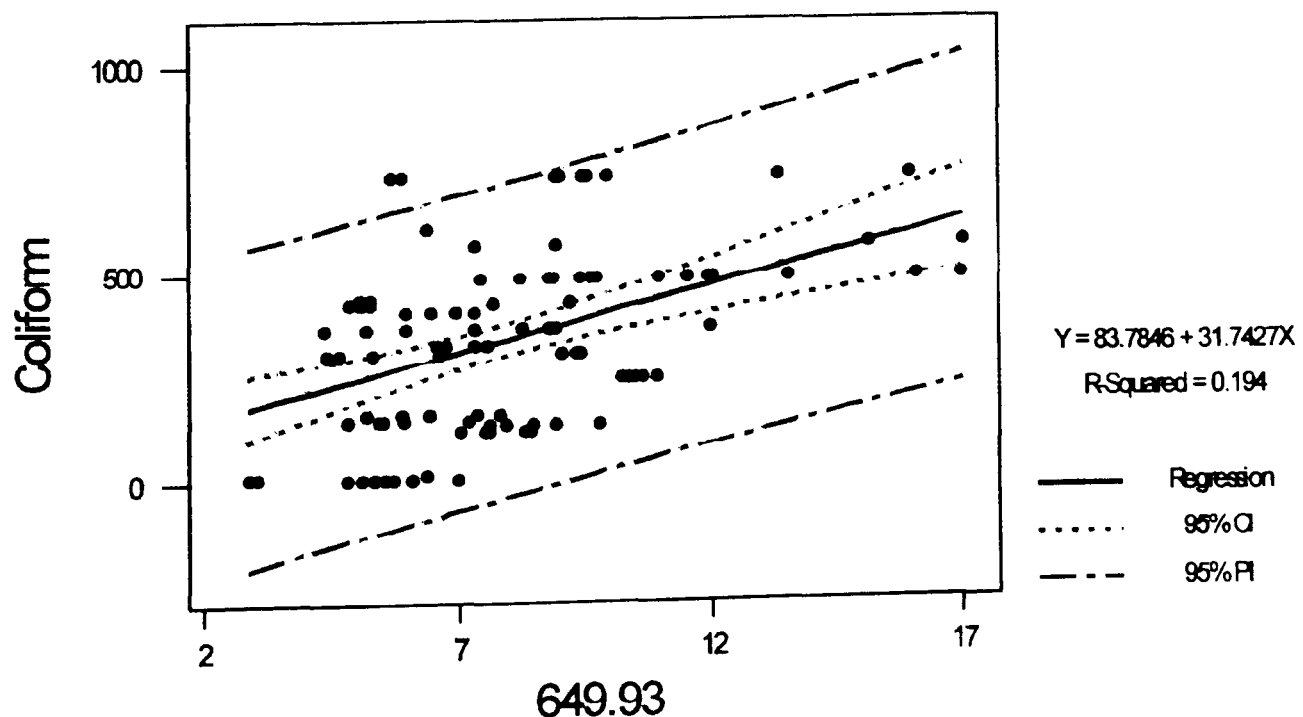
The regression of the best data subset shows 649.93nm to have a stronger and much steeper regression curve than that shown by the other parts of the spectrum and on this basis was selected as the potential predictor wavelength for total coliform.

Figure 8.14 Standardised data: EU guide level for total coliform with recorded levels of total coliform and reflectance at 649.93nm with the upper quartile of 649.93nm as a threshold predictor level
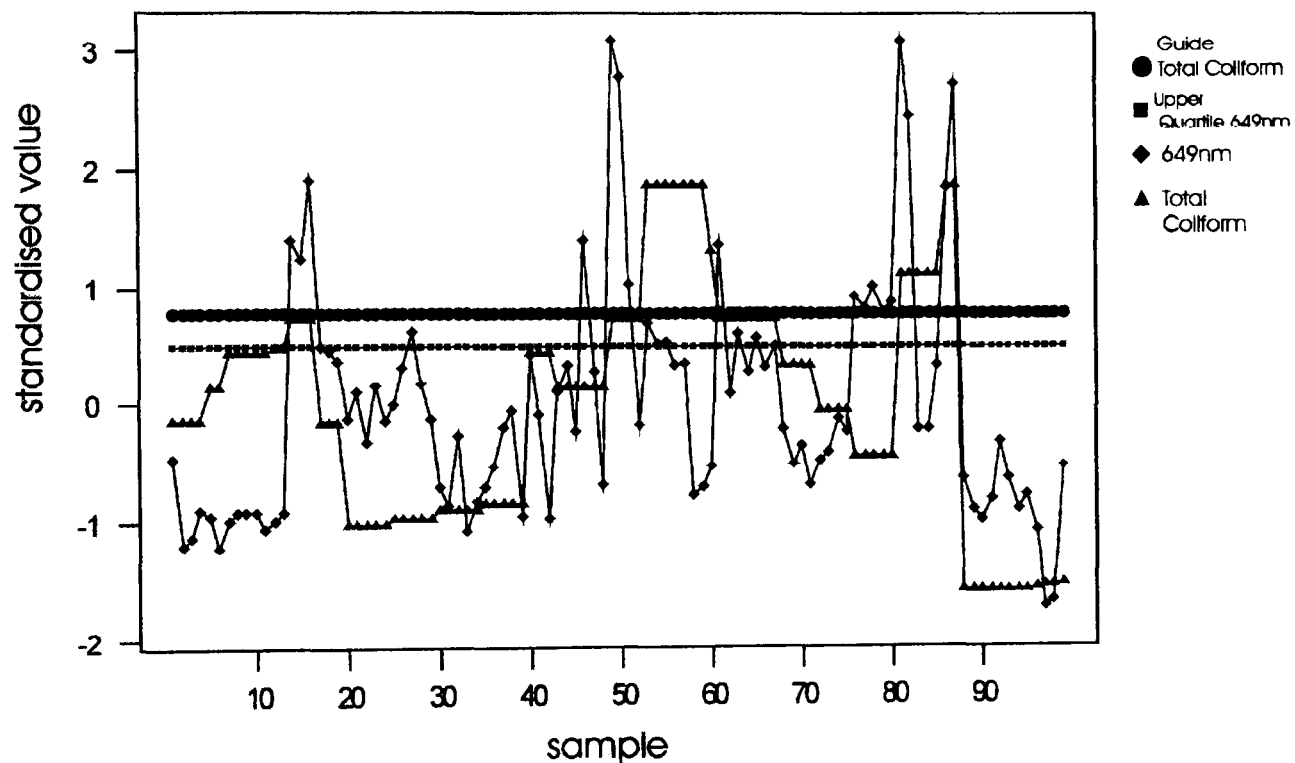
The E.U. Directive for Bathing Water Directive has a guide level of 500 counts of total coliforms per 100ml and a limit of 10000 counts per 100ml. The highest level recorded in the field was 732 and therefore did not exceed 10000 counts per 100ml. Data from the Environment Agency for the last 5 years showed that this level had only been exceeded four times at the four sample points in the surrounding area. Figure 8.14 illustrates that while the reflectance curve and total coliform curve do show some weak similarities in pattern, the guide level of 500 counts, which is just above the upper

quartile of 488 counts per 100ml will produce a poor prediction of levels of total coliform.

This reflectance level threshold was applied to the full data set to predict when the count level exceeded the minimum guideline. The results are summarised in Table 8.10.

Table 8. 9 Results of 649.93nm as a predictor for >500 counts of Total Coliform per 100ml

649.93nm CORRECT	%
239correct	55.8
187incorrect	43.7
of which	
17 underestimated	4.0
170 over-estimated	39.7

Little more than 55% of the samples were predicted correctly, and 43% were incorrectly determined as being over (4%) or under (39%) the guide level. From this, the conclusion was drawn that direct reflectance cannot be used to predict specific levels of total coliform. This was not surprising as the levels of total coliform can be affected by many other water quality parameters. This result showed that the relationship between total coliform with reflectance could only ever be expected to be identified through secondary relationships i.e. related to changes in the load of chlorophyll, or suspended sediment using the development of a water quality model for the area.

8.2.3 E.coli

Correlation analysis (Chapter 6) of E.coli with reflectance showed that there was a modest (Bryman *et al.*,1996) positive relationship present. This was significantly stronger than any other shown by any water quality parameter and reflectance in this research thesis with the strongest relationships being in the shorter wavelengths 300-322nm. These are shown in Table 8.11 (full listings in Appendix 3A1).

Table 8. 10 Selected examples of correlation of wavelength and E.coli where correlation coefficients >0.45

Wavelength(nm)	Correlation Coefficient from Preliminary Analysis
301.35	0.547
303.35	0.557
305.33	0.522
307.32	0.509
309.29	0.523
311.28	0.515
313.26	0.494
315.24	0.470
317.21	0.451
321.16	0.466
323.12	0.473
325.09	0.452
332.92	0.451

Visual analysis of the standardised curves illustrated in Figures 8.15-8.21 (standardised reflectance against the standardised count of E.coli) showed that while there were no strong positive relationships, there was a visibly strong relationship between reflectance and E.coli in the shorter wavelengths, particularly 301-311nm. This range was highlighted in the initial visual analysis and correlation analysis and was a similar trend

to that shown by Faecal coliform although in the case of E.coli the similarity in pattern was much stronger. The range 610-680nm and especially 630nm had also been identified as a potential predictor wavelength by the initial visual analysis using mean reflectance values and there was some similarity in the trends when analysing the standardised data in the second visual analysis. However, as Figures 8.22-8.23 illustrate, the relationship was not as strong as those with the reflectance around 301-310nm range. Statistically, the 630nm reflectance was also shown to a have a weak positive relationship correlation coefficient value of only +0.295 instead of 0.547 for 301.35nm and 0.557 for 303.35nm. On this basis the shorter wavelength range between 301-332.92nm were selected for detailed examination.

Figure 8.15 Standardised reflectance 300-501nm against E.coli
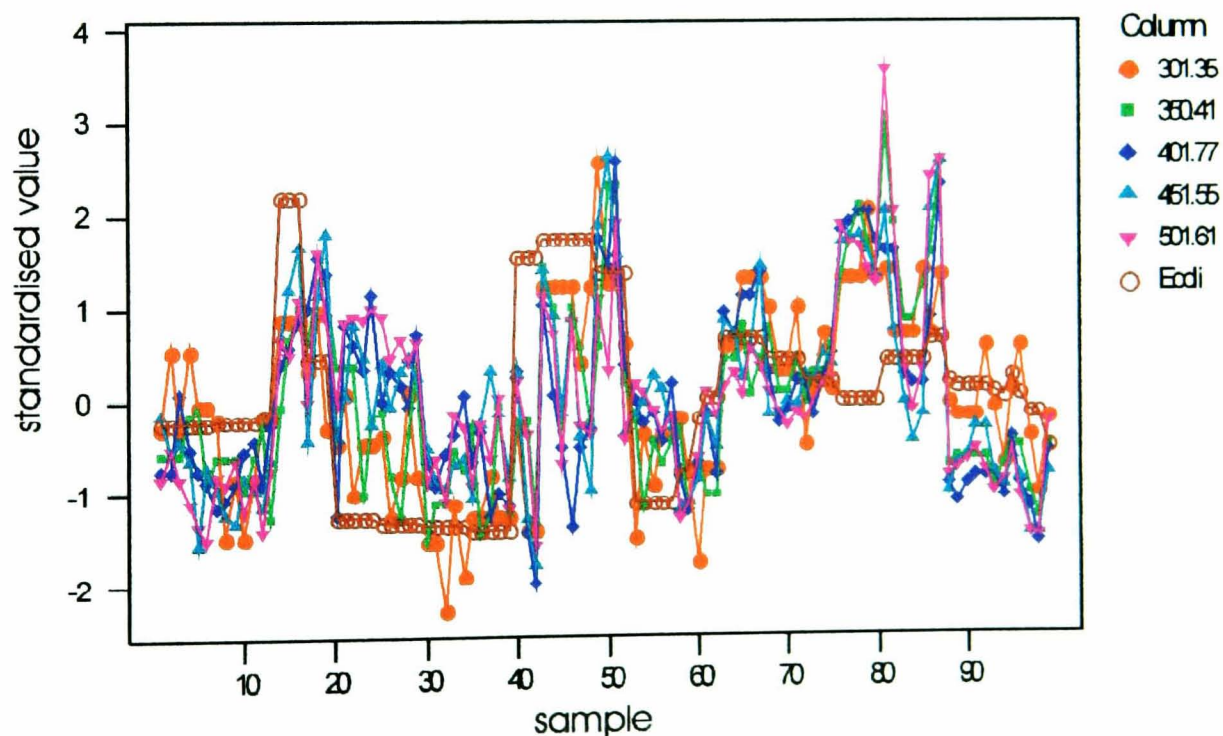
Figure 8.16 Standardised reflectance in shorter wavelengths 300-330nm against E.coli
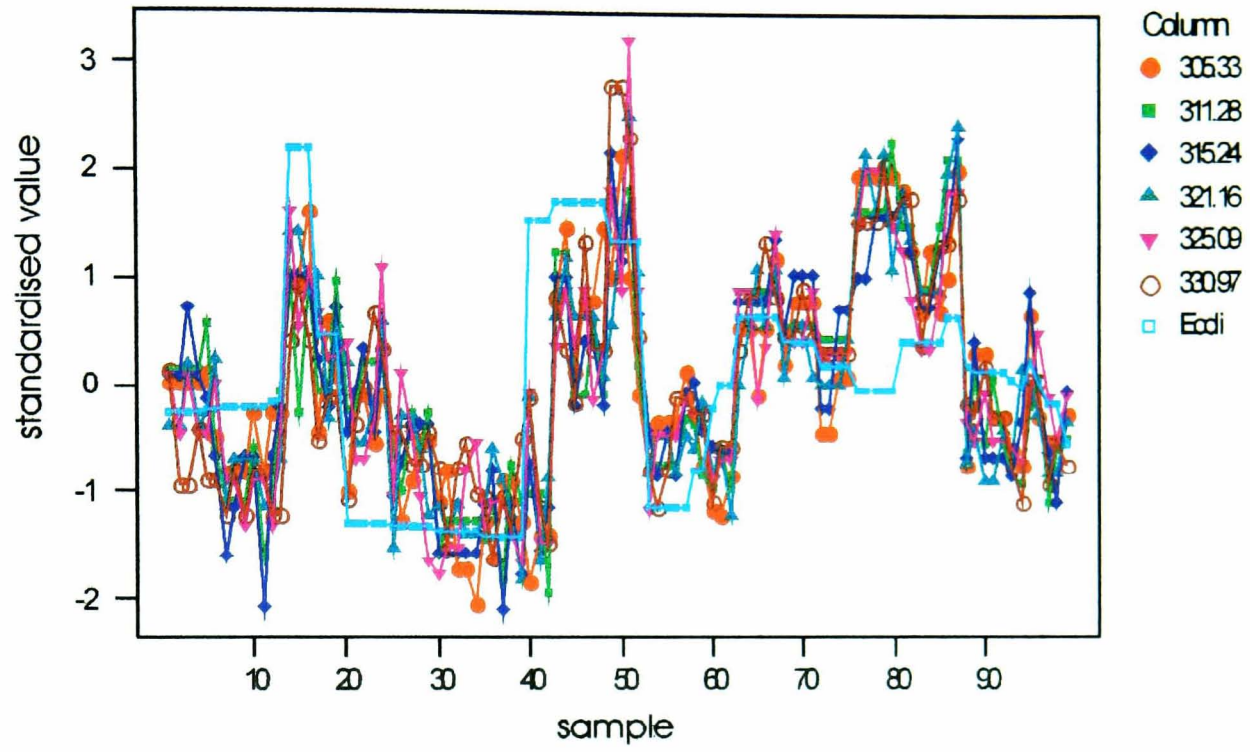
Figure 8.17 Standardised reflectance 336-360nm against E.coli
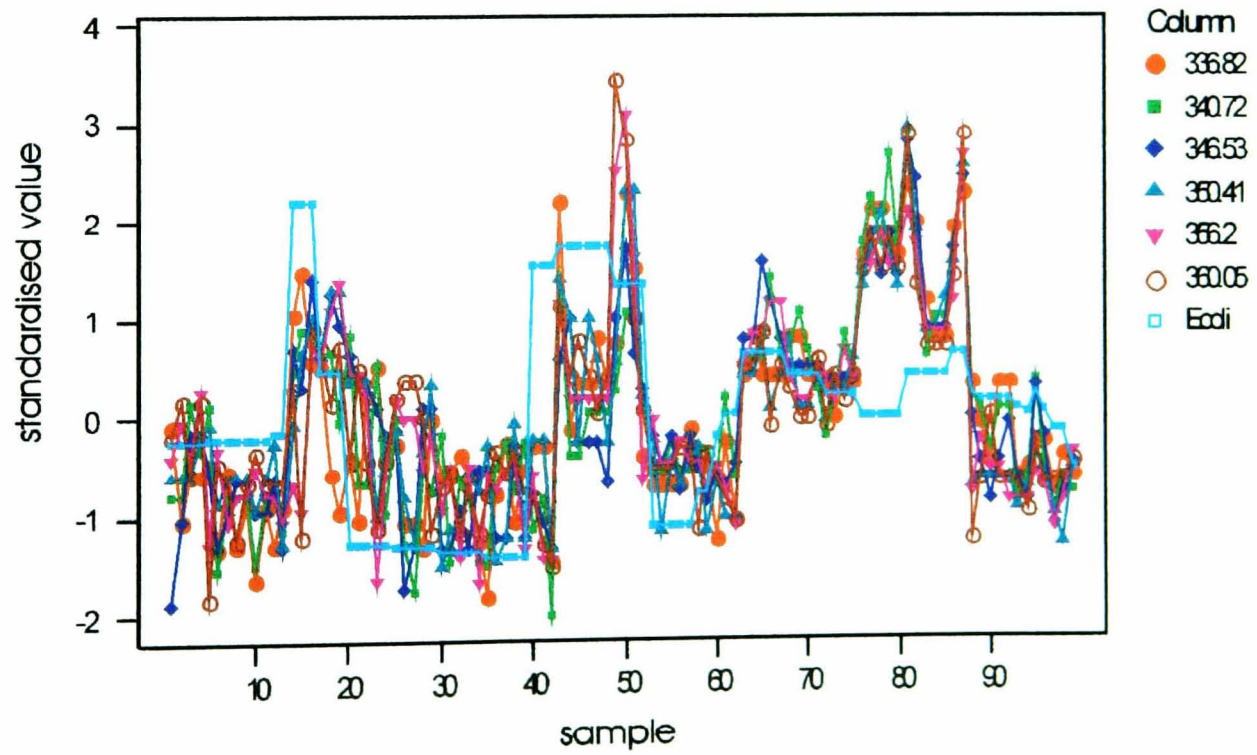
Figure 8.18 Standardised reflectance 365-401nm against E.coli
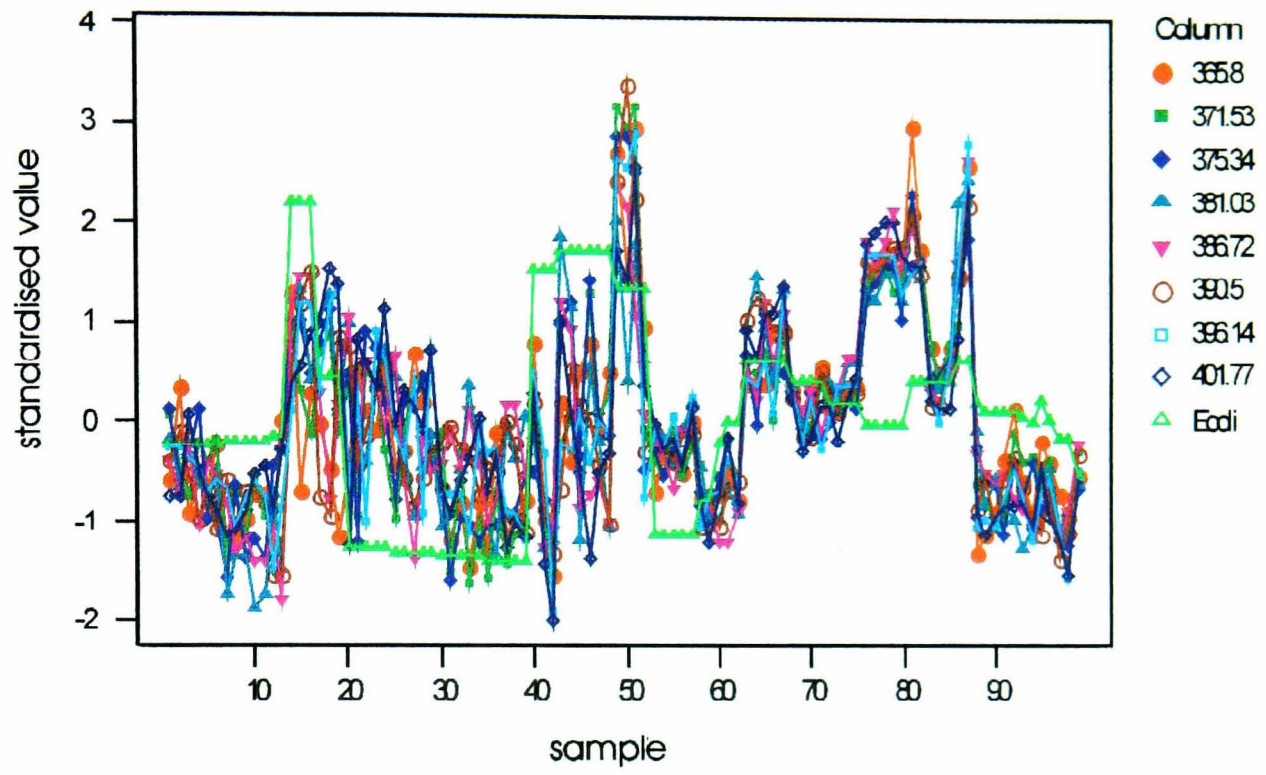
Figure 8.19 Standardised reflectance 451-600nm against E.coli
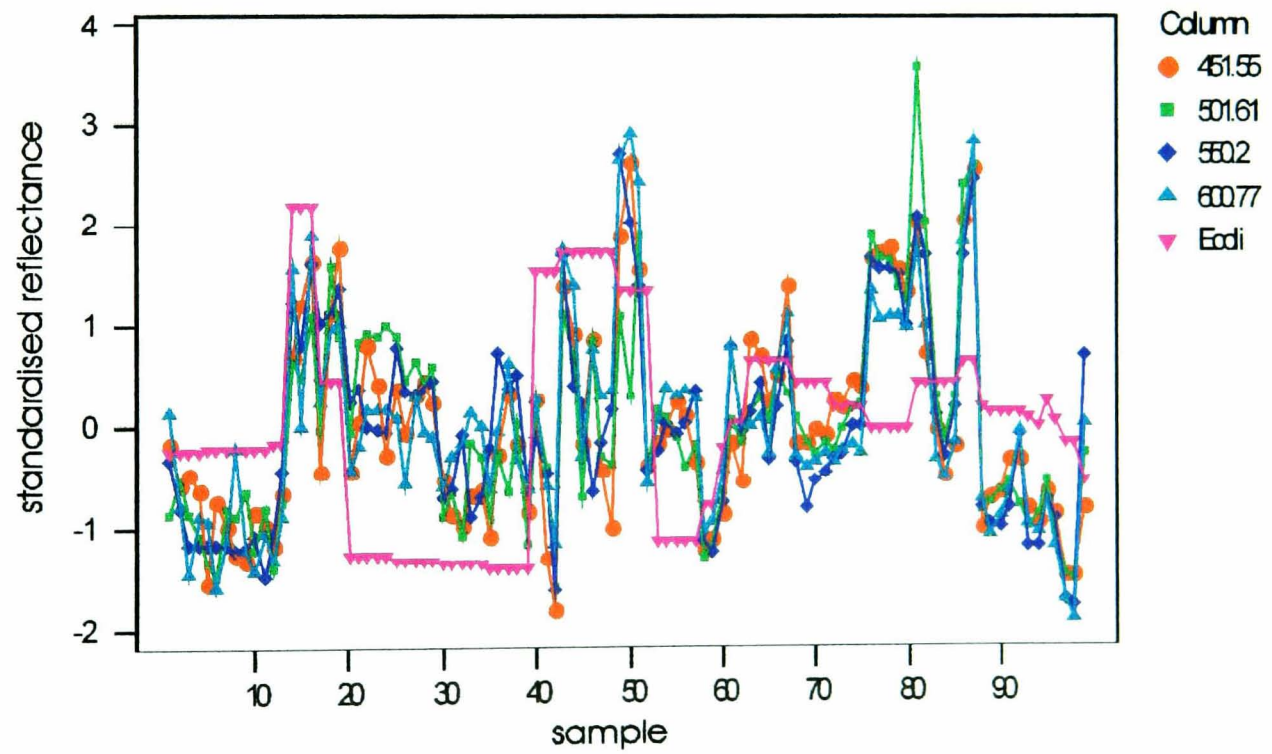
Figure 8.20 Standardised reflectance 650-850nm against E.coli
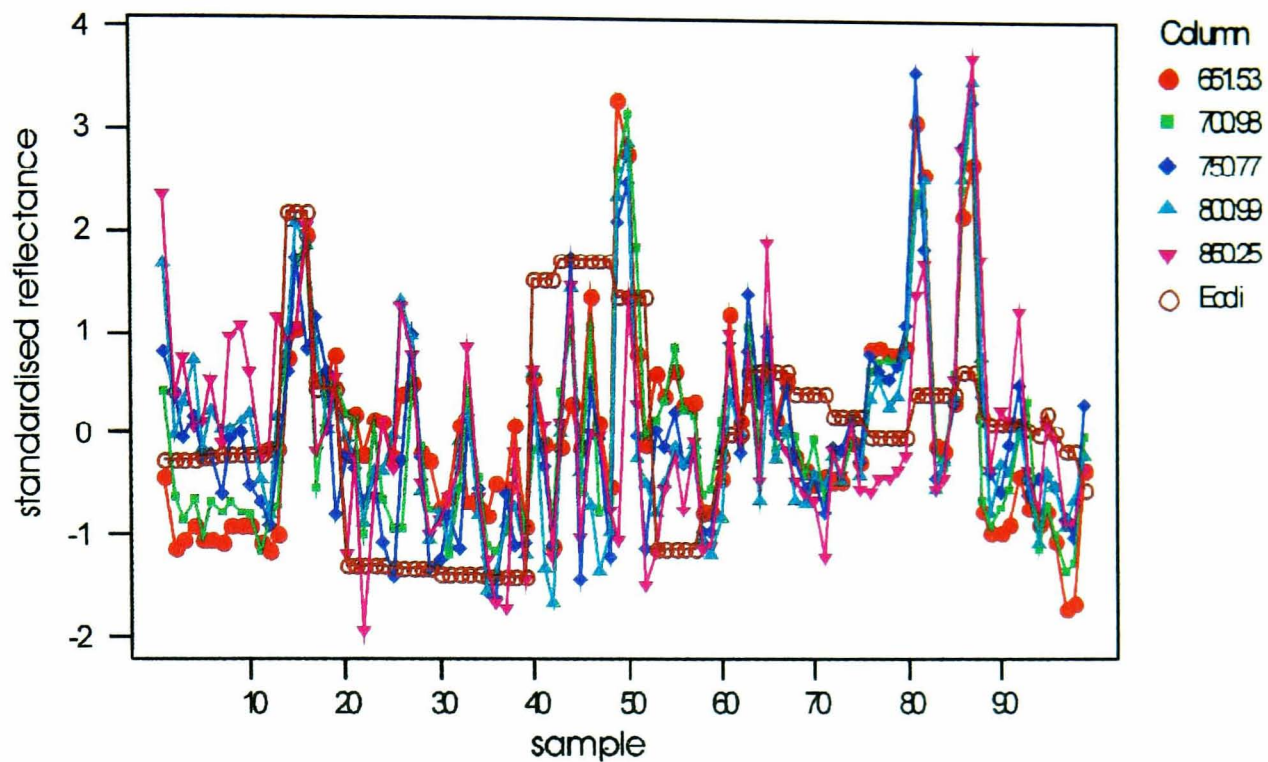
Figure 8.21 Standardised reflectance 900-1100nm against E.coli
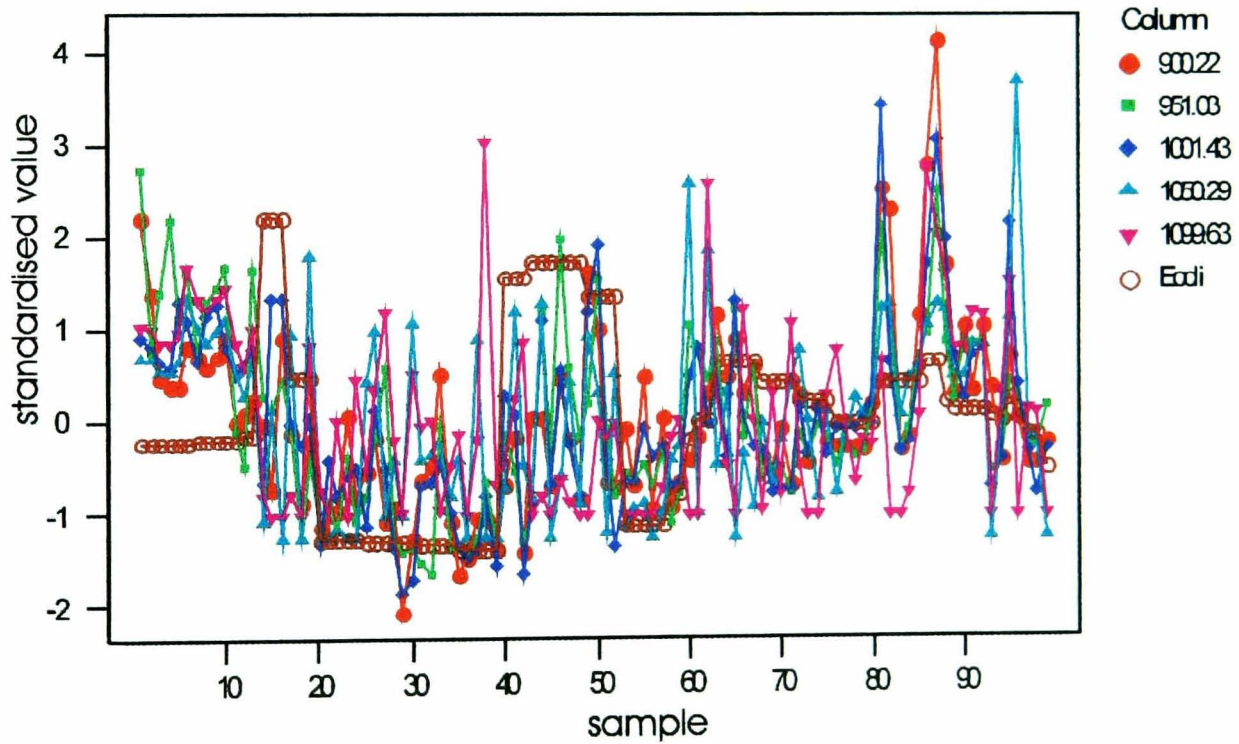
Figure 8.22 Standardised reflectance at 630.42nm against E.coli
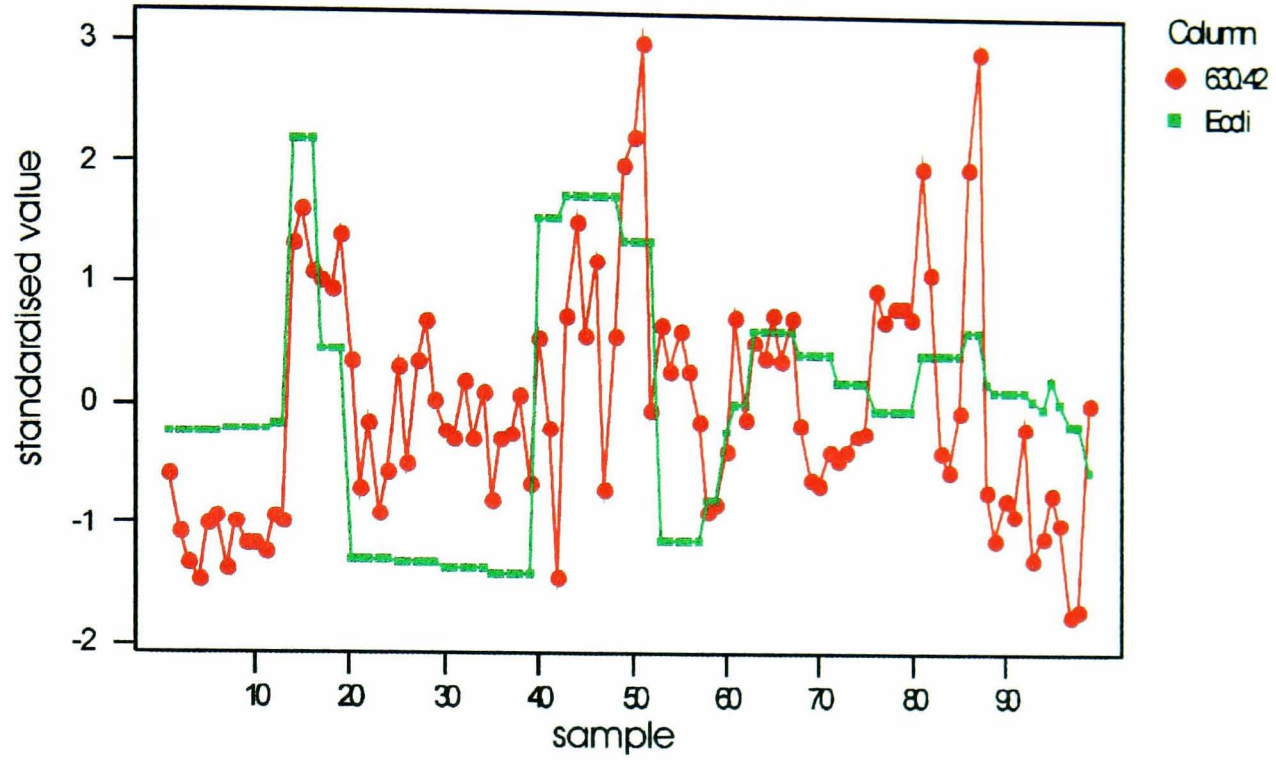
Figure 8.23 Standardised reflectance at 301.35nm against E.coli
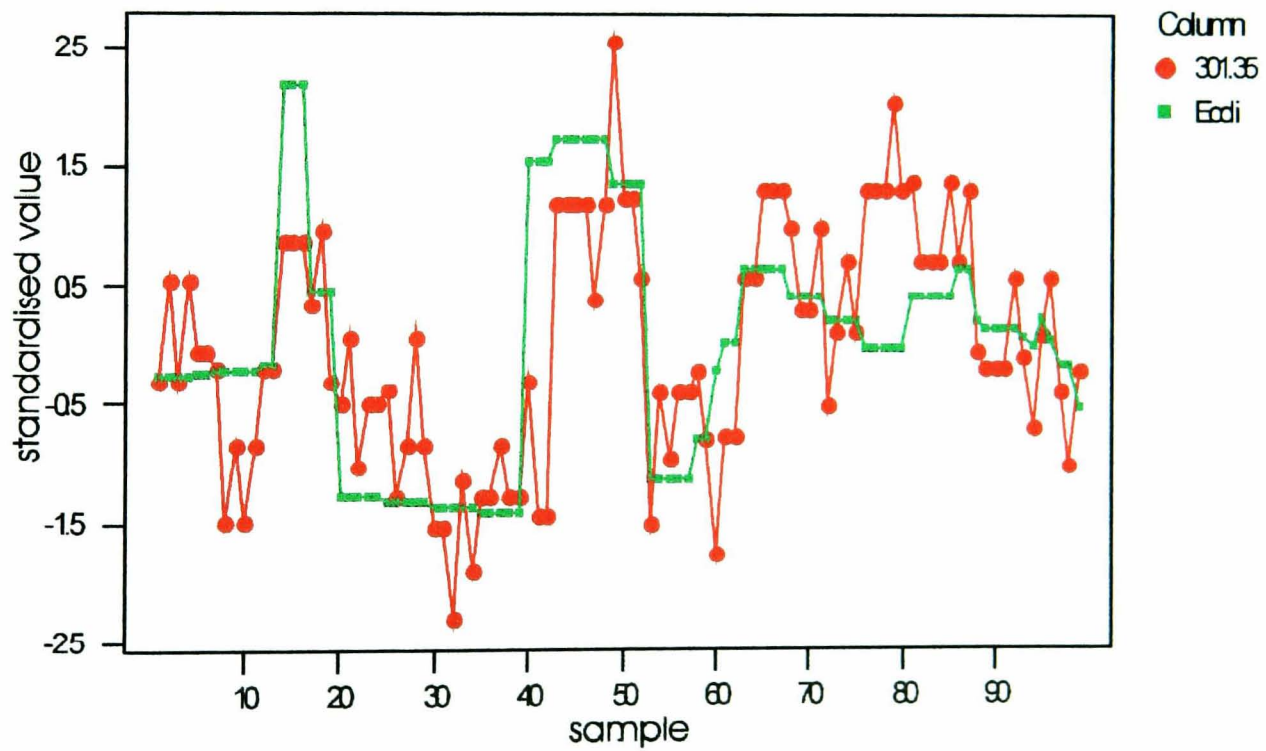
Regression analysis using the standardised subset data was performed on the 301.35nm

wavelength data as this was identified as having the strongest relationship with E.coli.

Figure 8.24 Regression of E.coli and 301.35nm

$Y = 7.32E-07 + 0.63186X$

R-Squared = 0.399

Regression

95% CI

95% PI
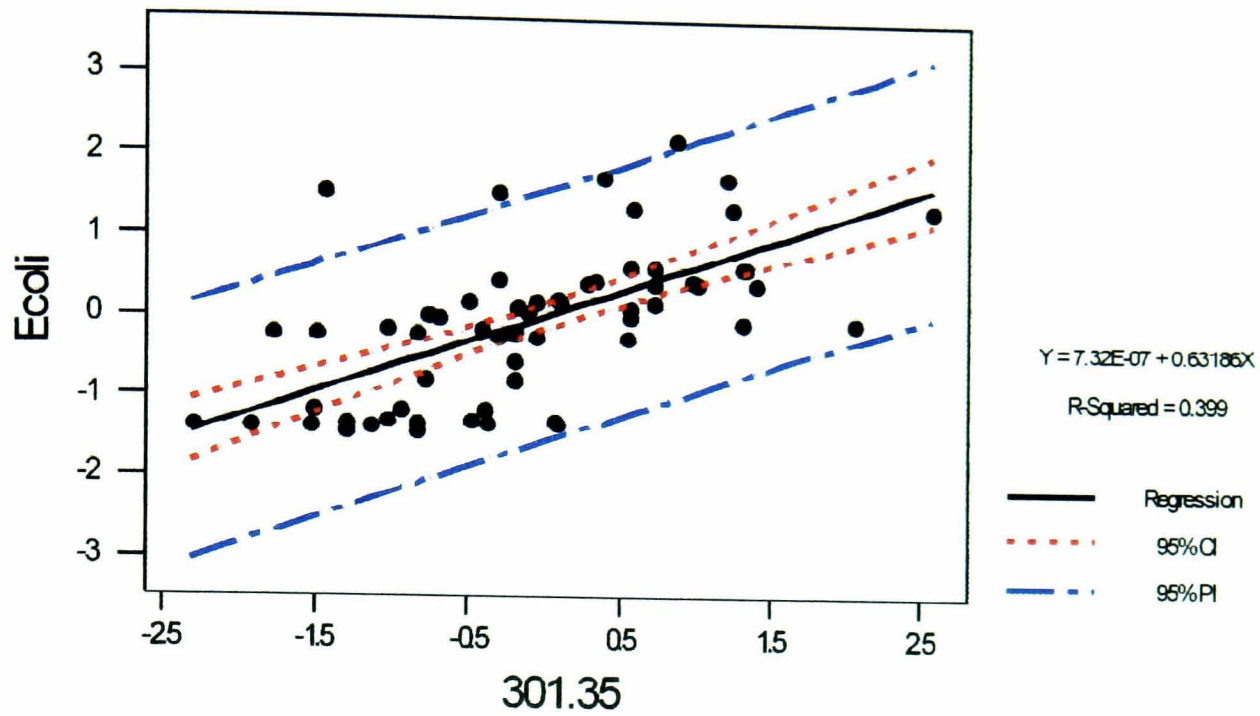
Table 8. 11 Regression analysis using the standardised subset data for E.coli

The regression equation is

Ecoli = 0.0000 + 0.632 301.35

Predictor	Coef	StDev	T	P
Constant	0.00000	0.07830	0.00	1.000
301.35	0.63186	0.07870	8.03	0.000

S = 0.7791   R-Sq = 39.9%   R-Sq(adj) = 39.3%

Although there was a positive relationship (Figure 8.24 and Table 8.12), the results of the regression did not offer strong support for the relationship. An investigation of the outliers did highlight several samples that were significantly different from those collected in the same data collection period, but these did not have any clearly identifiable characteristic (such as low water, or weather conditions) that had suddenly changed. They may have been the result of a temporary variation in water content, cloud cover or any of a wide range of physical changes that can affect recorded

reflectance (Milton *et al.*, 1995). The removal of the outliers cannot be given any great value as they were not removed by a set rule or method other than a significant change from their surrounding samples. The result of the regression analysis using this edited data set was dramatically improved as illustrated below.

The samples removed were 2a1-3, 2c1, 2d4, 2h3-5, 2h10, 3d1, 3h3, all of which were from days 2 and 3 of the data collection period. They were removed as obvious anomalies (i.e. distinctly changed from neighbouring reflectance data values) and the resulting improved regression is illustrated in Figure 8.25 and Table 8.13.

Figure 8.25 Regression of E.coli and 301.35nm with outlier samples 2a1-3, 2c1, 2d4, 2h3-5, 2h10, 3d1, 3h3 removed
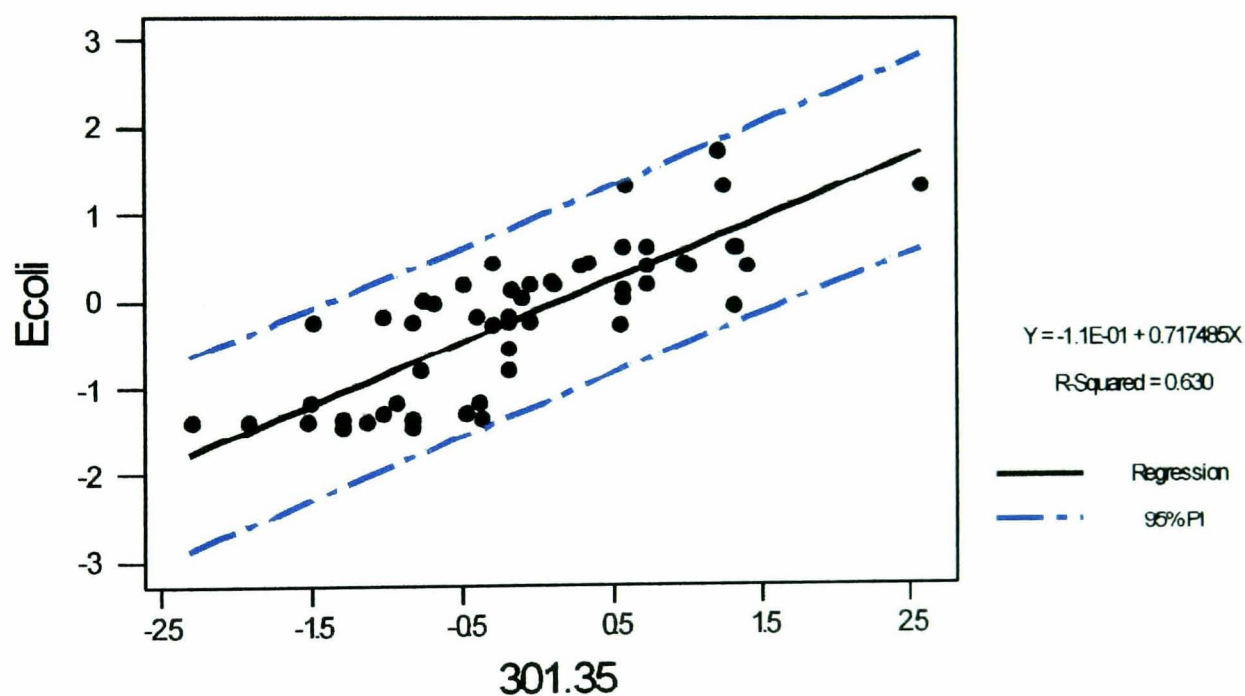
Table 8. 12 Regression analysis using the standardised subset data for E.coli

Regression Analysis

The regression equation is

Ecoli = - 0.113 + 0.717 301.35

Predictor	Coef	Stdev	t-ratio	p
Constant	-0.11304	0.05792	-1.95	0.054
301.35	0.71749	0.05929	12.10	0.000

s = 0.5434   R-sq = 63.0%   R-sq(adj) = 62.6%

Regression analysis was performed on the full data set producing a much weaker but still positive relationship and the result is shown in Figure 8.26 and Table 8.13. The weaker relationship can in part be explained by the fact that some of the best sampling conditions were not days when the micro-bacterial samples were collected, therefore the influence of cloud conditions was greater than for parameters such as dissolved oxygen that were collected on every day.

Figure 8.26 Regression of E.coli and 301.35nm using the full data set

Regression Plot

$Y = -40.3103 + 14.8452X$
$R\text{-}Sq = 0.295$
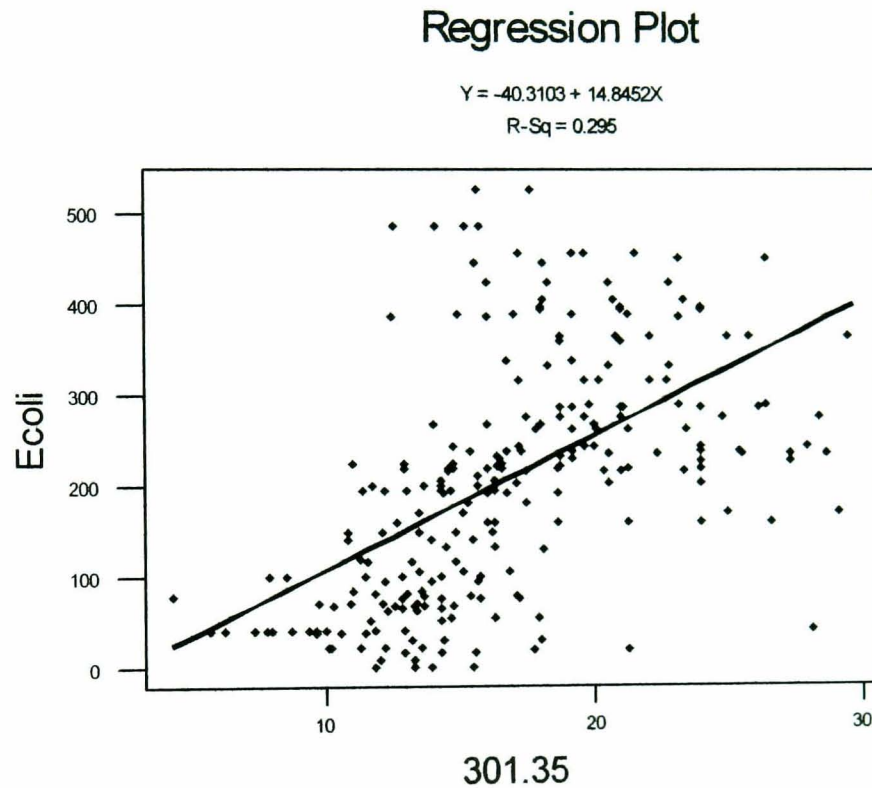
Table 8. 13 Regression analysis using the full dataset for E.coli

Regression				
The regression equation is				
$y = -40.3 + 14.8\ x$				
495 cases used 298 cases contain missing values				
Predictor	Coef	StDev	T	P
Constant	-40.31	18.51	-2.18	0.030
x	14.845	1.023	14.51	0.000
S = 109.3	R-Sq = 29.9%	R-Sq(adj) = 29.8%		

The visual analysis and statistical analysis consistently showed 301.35nm to be a potential optimum wavelength to identify E.coli. The level identified by the COM860(2000)Final (21.12.2000) policy statement proposed for the new EU Bathing Water Directives is 100counts per 100ml selected as guide and 200counts per 100ml selected as essential. These EU directive levels of E.coli were scaled to match the reflectance data (by subtracting the mean and dividing by the standard deviation shown below and plotted alongside the scaled subset of spectral and E.coli count field data (Figure 8.27).

- (100-219.2)/108.1 for 100 counts per 100ml = -1.102

- (200-219.2)/108.1 for 200 counts per 100ml = -0.177)

Figure 8.27 Standardised data: Ecoli samples, reflectance at 301.35nm,EU guide level (100counts per 100ml) and fail level (200counts per 100ml) for E.coli (COM860(2000) final for freshwater
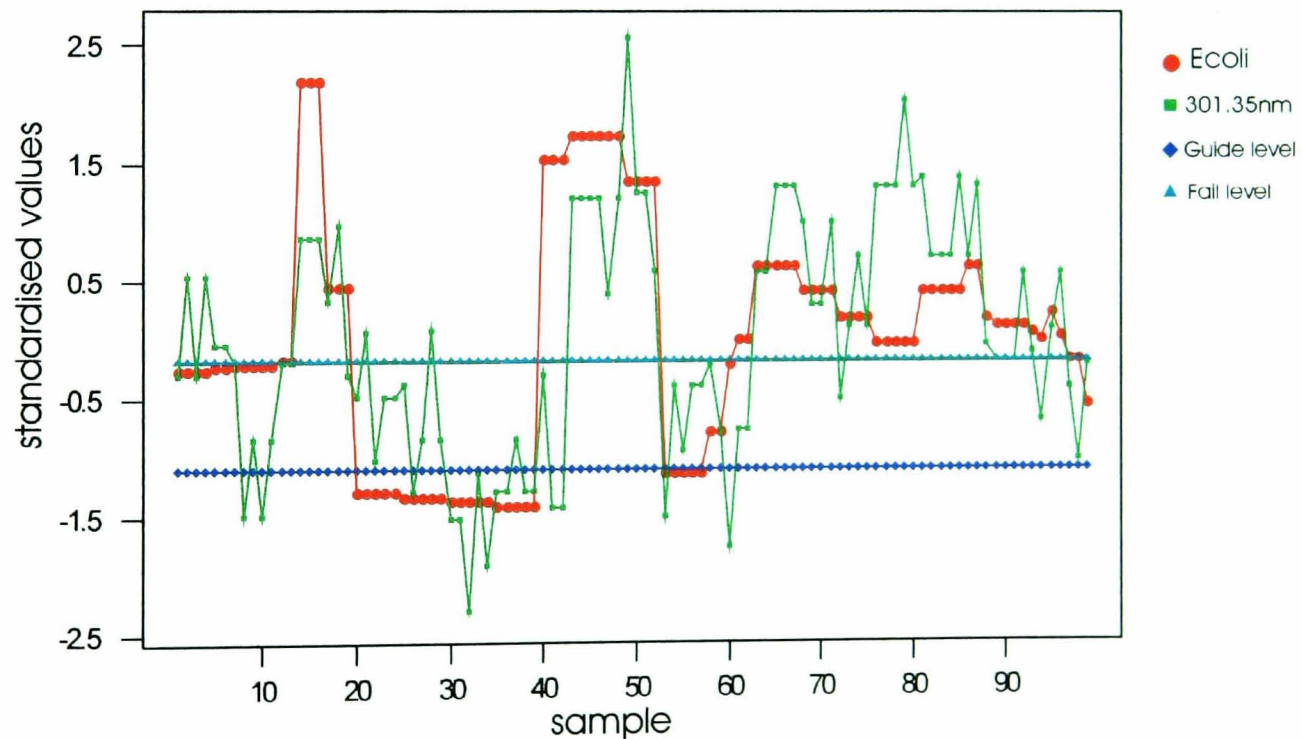
As Figure 8.27 illustrates the field data did exceed the proposed guide and fail levels of E.coli count during the field data collection period. In fact the majority of samples exceeded the guide level and so the fail level was selected to test the success of

reflectance at 301.35nm at predicting E.coli levels in excess of 200 counts per 100ml. As before the upper quartile of the reflectance data was used as the starting point in trial and error selection of the optimum level of reflectance to identify when E.coli fail level was exceeded. This process resulted in the selection of a reflectance threshold for the 200 E.coli count limit of 14.9537 as illustrated in Figure 8.28.

Figure 8.28 Standardised data: Ecoli samples, reflectance at 301.35nm,EU (COM860(2000) final for freshwater) guide level (100counts per 100ml) and fail level (200counts per 100ml) for E.coli and predictor reflectance level for 200count limit of 14.9537.
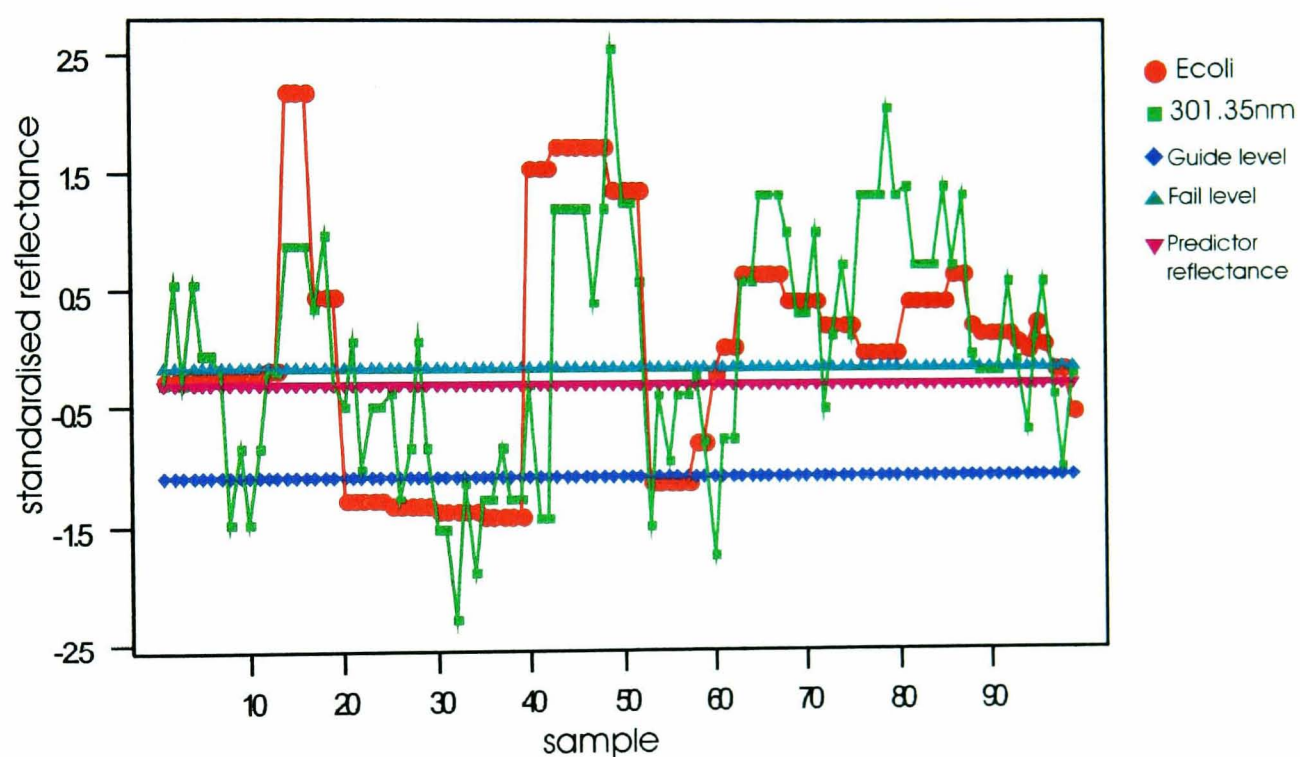
This reflectance threshold was applied to predict from the best data subset when E.coli exceeds the proposed EU fail standard (Figure 8.29). A high level of prediction of 81% was achieved when E.coli had exceeded the proposed EU standard as shown in Table 8.14.

Table 8. 14 Results of 301.35nm as a predictor for >200 counts of E.coli per 100ml

301.35nm CORRECT	%
82 correct	81
17 incorrect of which	17
4 underestimated	4
13 over-estimated	13

This threshold reflectance value (14.9537) was then applied as a predictor of E.coli counts in excess of 200/100ml against the full data set (494 samples). This still produced an exceptionally high prediction accuracy based on 494 samples as shown in Table 8.15.

Table 8. 15 Results of 301.35nm as a predictor for >200 counts of E.coli per 100ml

301.35nm CORRECT	%
389 correct	78.6
105 incorrect of which	21.4
28 underestimated	5.8
77 over-estimated	15. 6

Figure 8.29 Standardised data: Ecoli samples, reflectance at 301.35nm,EU (COM860(2000) final for freshwater) guide level (100counts per 100ml) and fail level (200counts per 100ml) for E.coli and predictor reflectance level for 200couint limit of 14.9537 shown as point graph.
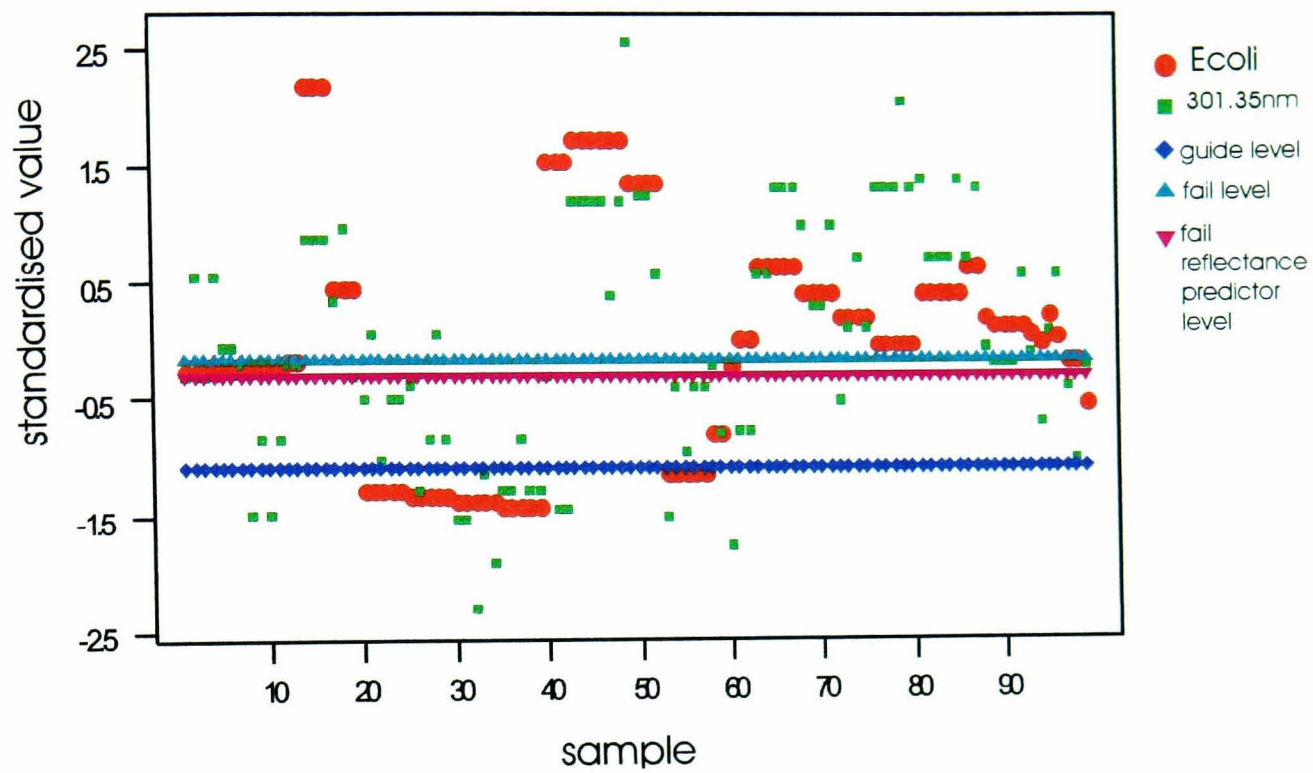
8.3 Non-Microbiological Water Quality Parameters

8.3.1 Nitrates

The results from the preliminary analysis showed no statistical relationship between nitrates and reflectance but the preliminary visual analysis using mean reflectance highlighted the ranges 450-580nm, 610-640nm and 730nm. Visual analysis (see appendix 4A5) of the standardised reflectance against the standardised nitrate levels showed no discernible relationship except at 911.88nm (Figure 8.30). While no relationship was evident when the full data set was used, a correlation analysis of just the scaled, best data subset showed a correlation coefficient of 0.448 and the regression analysis showed a weak positive relationship (Table 8.17).

Table 8. 16 Regression of nitrate and reflectance at 911.88nm using the scaled best data subset

The regression equation is
Nitrates = 0.0000 + 0.448 911.88

Predictor	Coef	StDev	T	P
Constant	0.00000	0.09034	0.00	1.000
911.88	0.44755	0.09080	4.93	0.000

S = 0.8989   R-Sq = 20.0%   R-Sq(adj) = 19.2%

Despite the lack of evident relationship between nitrates and reflectance using the full data set, 911.88nm was selected as the optimum wavelength as it had shown potential using the scaled data subset.

No guideline nitrate concentration value is provided by the EU Bathing Water directives. Nitrates are only measured if there is evidence that there has been a deterioration of the water quality. Then nitrate levels would be measured to check that they are normal for the local environment. During the field collection period there were no extreme values for nitrates and therefore none of the samples would have been sufficient to have flagged a need for more monitoring. Therefore the upper quartile was taken as the threshold for the evaluation of wavelengths i.e. if the upper quartile was exceeded then the nitrates level was designated as a failure requiring further monitoring.

The mean for nitrates from the field data set after all missing values had been removed was 2.151mgl-1 standard deviation 0.6932 and the upper and lower quartile values were 2.6 and 1.600mgl-1.

Figure 8.30 Nitrate level, reflectance at 911.88nm
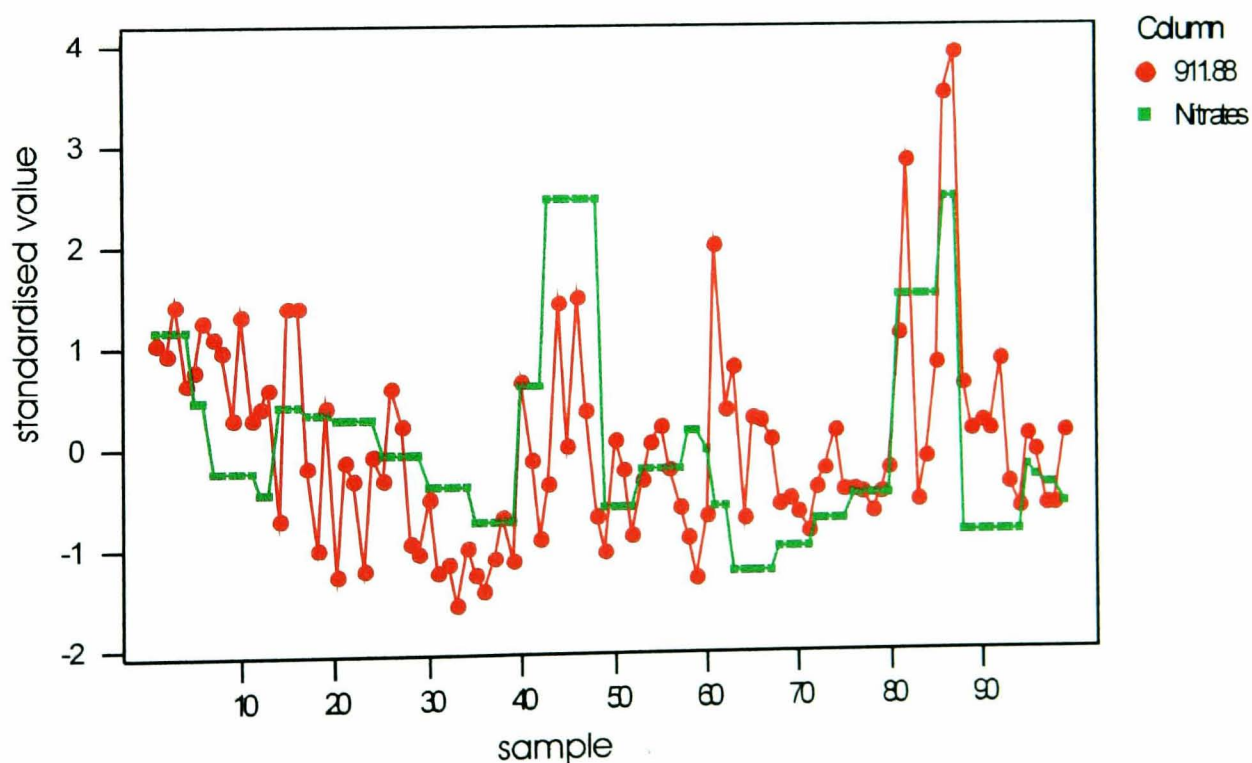
The threshold reflectance level of 911.88nm was established based on the upper quartile value of reflectance at 911.88nm to predict the samples taken that exceeded the upper quartile (2.6mg/l) of nitrate level. Table 8.18 shows the results of this prediction level using the best data sub set.

Table 8. 17 Results of 911.88nm as a predictor for >2.6mg/l-1 Nitrate

911.88nm CORRECT	%
186 correct	64.4
102 incorrect	35.3
of which	
14 underestimated	4.9
87 over-estimated	30.2

A 64.35% prediction rate using the best data set does show that there is a potential for monitoring a threshold level of nitrates but data not collected in optimum conditions shows no relationship with 911.88nm. However, the fact that of the 102 samples incorrectly identified 87 were overestimated was preferable for flagging if the water should be manually checked as only 4.9% of the samples were incorrectly underestimated which would mean only 4.9% would be considered to fail.

8.3.2 Phosphates

Visual analysis (see Appendix 4A8) of the standardised reflectance against the standardised phosphate levels (illustrated in Appendix 4A8) showed no discernible relationship within the range 300nm to 900nm between patterns of reflectance and

phosphate level. However, phosphates showed a similar pattern to nitrates in the range 890-920nm. Reflectance at 911.88nm was visually the best fit to levels of phosphates.

Figure 8.31 Standardised data: Reflectance against Phosphate at 891.45,895.84,900.22nm
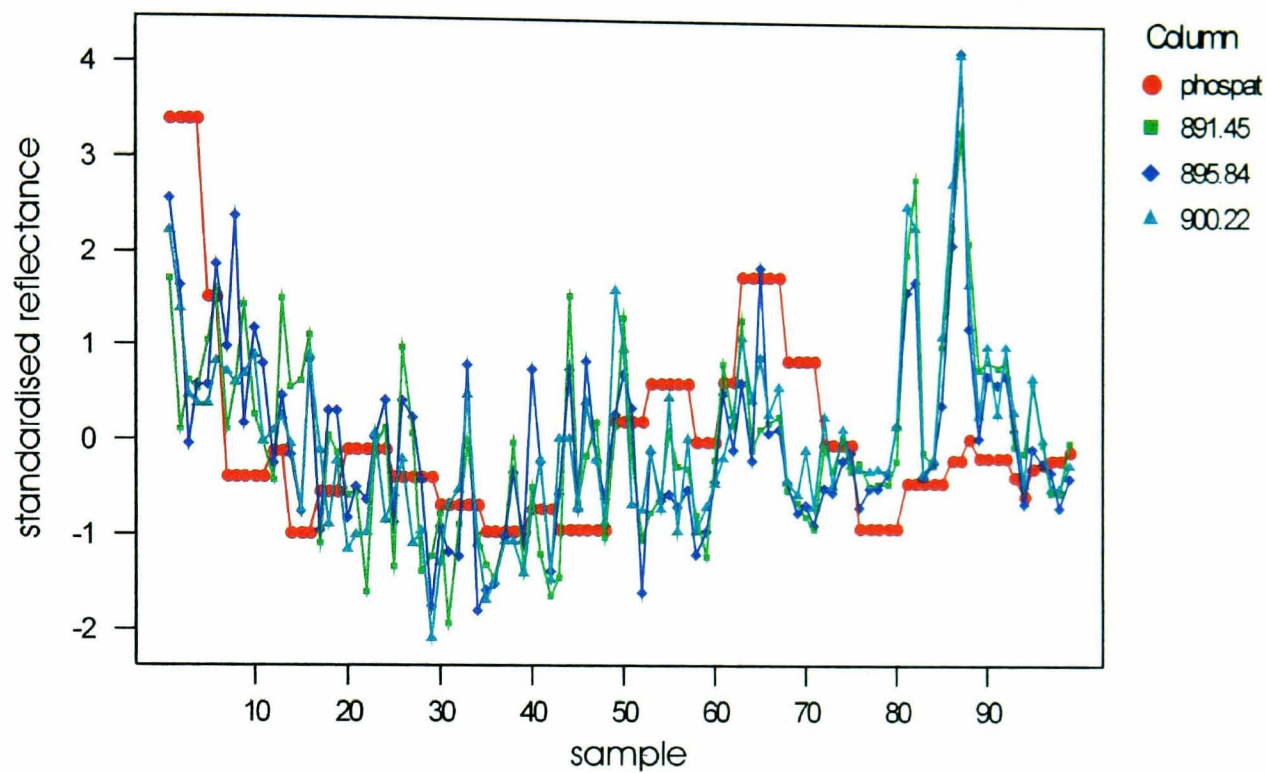
Figure 8.32 Standardised data: Reflectance against Phosphate at 904.59,911.88,916.24nm
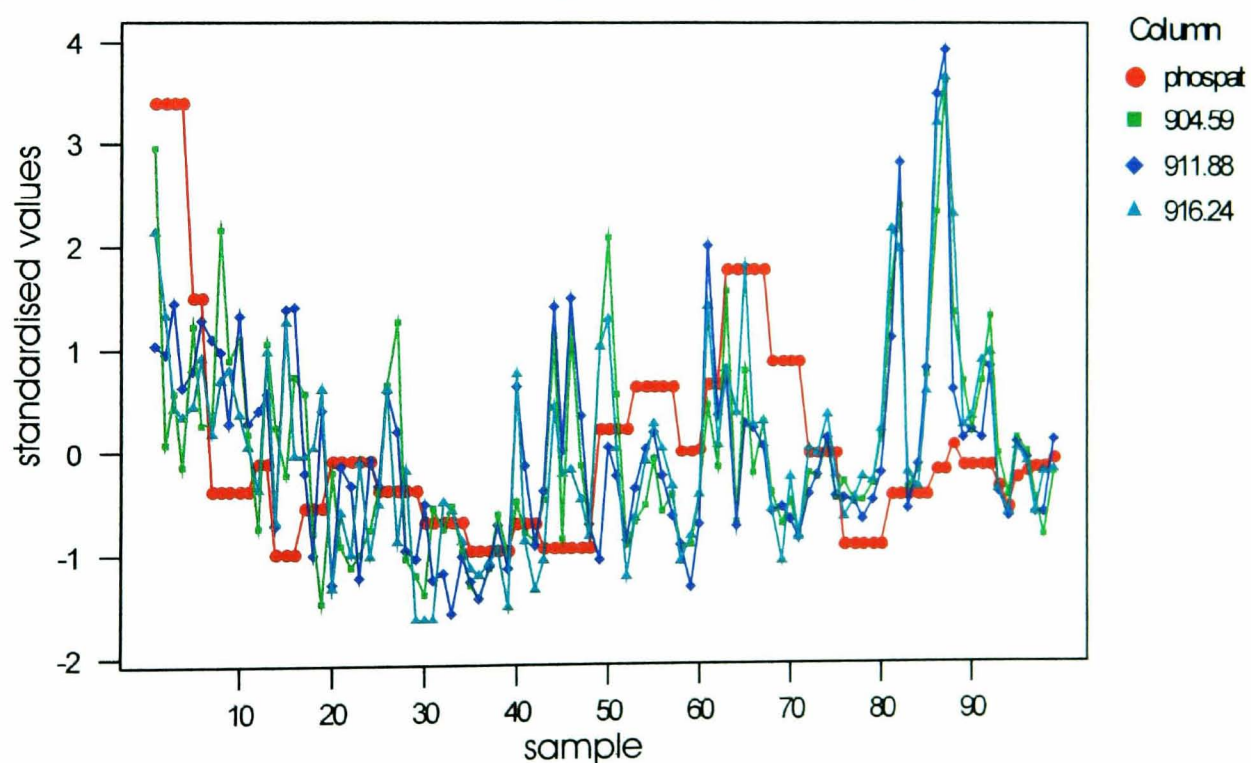
Preliminary correlation analysis showed no strong relationship from the data, especially at around 900nm where there was almost no correlation e.g. 911.88 had a correlation

value of only -0.012. However, through the range 625.51-633.05nm there was a noticeable increase in correlation with a low negative correlation, but still the relationship was only very slightly correlated with low correlation values of just -0.202 to -0.210. A very low negative correlation level of –0.2 was taken as a threshold for phosphates to identify potential predictor wavelengths and this gave the wavelengths shown in Table 8.19.

Table 8. 18 Correlation coefficient values for reflectance against phosphates

Wavelength (nm)	Correlation Coefficnient
625.51	-0.202
627.15	-0.205
628.78	-0.209
630.05	-0.21
632.05	-0.209
633.69	-0.204

This range of wavelengths were supported by the previous visual analysis using mean reflectance where the range 610nm-640nm was highlighted as showing a negative relationship to phosphates. The other ranges highlighted by the earlier visual analysis (450-580nm and 730nm) showed lower correlation values. Despite this, the visual analysis of standardised reflectance showed that 911.88nm (see Figures 8.33 and 8.34) had some similarities in pattern with phosphates when compared with the other wavelengths (albeit with several strong differences in some samples).

Figure 8.33 Standardised reflectance at 911.88nm against Phosphates
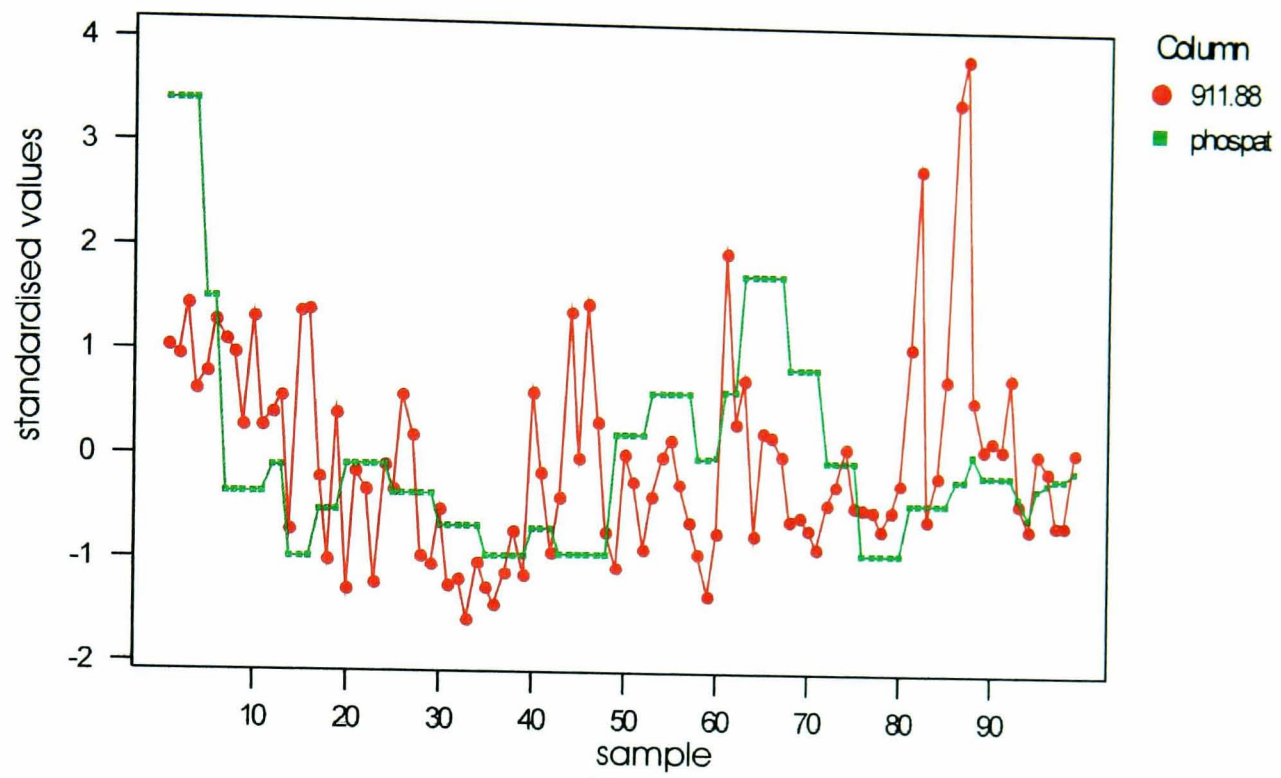
Figure 8.34 Standardised reflectance 625.51nm against Phosphates
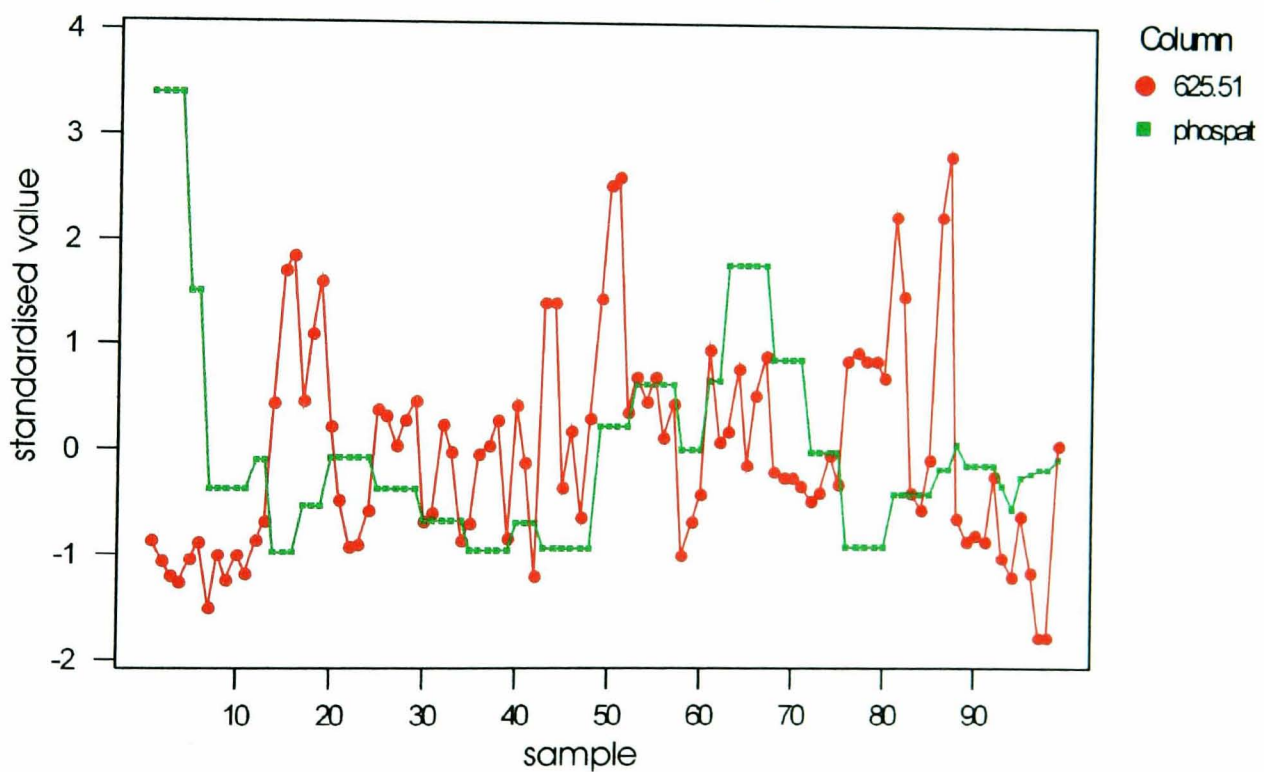
Unlike nitrates statistical support for phosphates was not strong for 911.88nm with no relationship evident when using the full data set. A correlation analysis of just the scaled, best data subset showed a correlation coefficient of 0.214 (which is only

significant to 0.05 and much weaker than nitrates). Regression analysis showed almost no relationship (Table 8.20).

Table 8. 19 Regression of phosphate and reflectance at 911.88nm using the scaled best data subset

The regression equation is
phosphates = 0.0000 + 0.214 911.88

Predictor	Coef	StDev	T	P
Constant	0.00000	0.09868	0.00	1.000
911.88	0.21395	0.09918	2.16	0.033
S = 0.9819	R-Sq = 4.6%	R-Sq(adj) = 3.6%		

Despite the lack of evident relationship between phosphates and reflectance using the full data set, 911.88nm was selected as the optimum wavelength as 911.88nm had shown some potential using the scaled subset of data from the visual analysis.

No guideline phosphate concentration value is provided by the EU Bathing Water directives. Phosphates are only measured if there is evidence that there has been a deterioration to the water quality, at which point phosphate levels would be measured to check that they are normal for the local environment. During the field collection period there were no extreme values for phosphates and therefore none of the samples would have been sufficient to have flagged a need for more monitoring. Therefore the upper quartile was taken as the threshold for the evaluation of wavelengths i.e. if the upper quartile was exceeded then the phosphates level was designated as a failure requiring further monitoring.

The threshold reflectance level of 911.88nm was established based upon the upper quartile value of reflectance at 911.88nm to predict the samples taken that exceeded the upper quartile (1.310mg/l) of phosphate level (Figure 8.35). Table 8.21 shows the results of this prediction level using the best data subset.

Table 8. 20 Results of 911.88nm as a predictor for >1.310mg/l-1 Phosphate

CORRECT	%
173 correct	60
115 incorrect	40
of which	
59	20.9
underestimated	
55	19.1
over-estimated	

A 60% prediction rate using the best data set does show that there is a potential for monitoring a threshold level of phosphates but data not collected in optimum conditions shows no relationship with 911.88nm. The fact that of the 115 samples incorrectly identified 59 were under-estimated means that for flagging of failing water quality, the water would not be manually checked for 20% of the samples that were failing.

Figure 8.35 Standardised data: reflectance at 911.88nm, phosphate level, upper quartile for phosphates, reflectance upper quartile
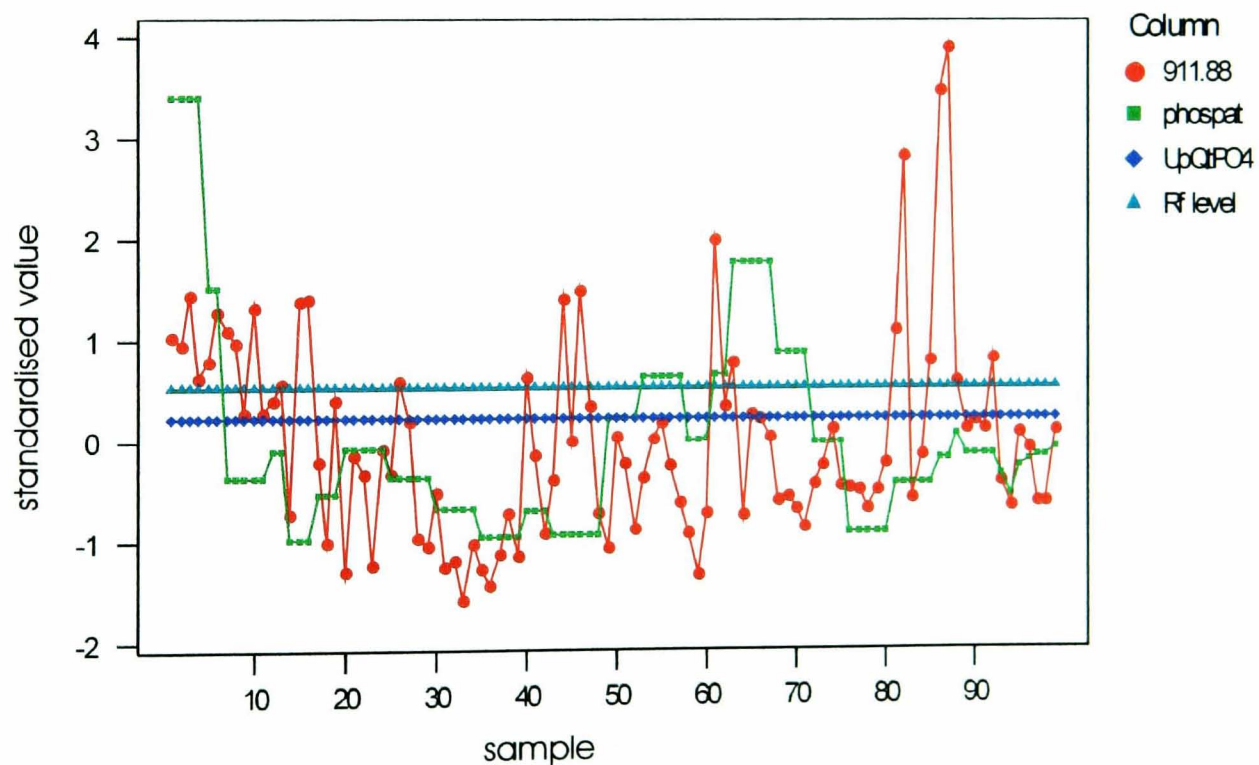
With a level of accuracy of only 59% and 20% underestimation, phosphates cannot be monitored by direct light reflectance in field conditions using the range 300-1100nm in the field. Phosphates, therefore, must be included amongst those parameters that

require the development of a spectral physical model and rely on its relationship to secondary water quality parameters with possible support from information gained at 911.88nm.

8.3.3 Chlorophyll and Suspended Sediment and Turbidity

Chlorophyll and suspended sediment were not treated in the same way as the other variables. Both these variables have been extensively investigated by other studies such as Matthews and Boxall, 1994; Groom,1991; Dekker, 1993) using both laboratory analysis, large scale field studies and 'real world' application of remote sensing to monitor these variables. Their inclusion in the data set was because of the widespread monitoring knowledge that has been acquired for these variables. The strength and depth of knowledge about their relationships to both reflectance and other water quality parameters meant they were perfect for inclusion as possible secondary relationships to designated EU bathing water quality parameters. Only suspended sediments are included in the EU directives. Therefore the main interest applied to these parameters was in regard to their relationship with the other water quality parameters and their possible inclusion in the spectral physical model.

Only limited data collection was undertaken for chlorophyll as this required access to the laboratory at the Enfield Campus and it was only possible to collect six days of data (see Chapter 4). This was not seen as a significant problem as the relationship between chlorophyll and water quality parameters such as phosphates, nitrates, bacterial counts should not be a contentious issue. Study of the chlorophyll data revealed that there were

only 25 samples taken on good spectral data collection days. Inevitably expected relationships from such small sample numbers were hard to derive. The expected relationships are as follows:

1. Gordon and Morel proposed an algorithm using a pigment algorithm in 1983 (van der Piepen *et al.*, 1991) using a "weighted ratio of the reflectance near the absorption maximum and absorption minimum of chlorophyll-a" (van der Piepen *et al.*,1991), typically in case I waters these would be 443nm and 550nm (van der Piepen *et al.*,1991).

2. The relationship between reflectance and chlorophyll-a can be summarised as:

- 430-450nm chlorophyll-a and hums absorption

- 500-510nm lower chlorophyll absorption

- 630nm cynobacteria absorption

- 680-710nm (peak depends on pigment development possibly related to life cycle stage)

(information sources: Dekker *et al.*, 1993; Boxall and Matthews, 1994)

3. Van der Piepen (1991) suggested that the additional salts and minerals in Case 2 waters makes the relationship more complex. "In Case 2 waters the green/blue ratio does not only depend on the chlorophyll concentration but also on the suspended matter and yellow substance contents"(van der Piepen *et al.*1991). The use of the wavelengths at around 685nm have proved successful from airborne measurements using the following algorithm (van der Piepen *et al.*1991):

$C=D*(R_{685}-E*R_x)$ (van der Piepen *et al.* 1991)

Where c= chlorophyll concentration

R_{685}=reflectance at 685nm

Rx= the average reflectance in neighbouring channels above and below 685nm

D & E are constants determined empirically by means of simulation models (van der Piepen *et al.* 1991)

The relationships suggested by previous research were tested with the data collected in 1995, and the Tables 8.22-8.27 contain the results.The following wavelengths were tested as a predictor to identify chlorophyll levels over the upper quartile (324 samples mean=11.22, median 11.02 upper quartile 16.53).

- 444.27nm in the range 430-450nm for chlorophyll-a and hums absorption

- 700.98nm in the 680-710nm chlorophyll-a absorption

- 759.8nm in the surface vegetation range 700-800nm. (Surface green weed is

  common in the estuary)

Only a low number of samples (three days only per week) for chlorophyll were collected when spectral data conditions were good, giving at total sample of 105 in ideal conditions. Therefore data collected in non perfect conditions had to be included to increase the sample number. Therefore weather conditions were not considered for chlorophyll and the upper quartile values were taken for both reflectance level and chlorophyll levels.

- The upper quartile for 444.27nm was 10.02

- The upper quartile for 700.98nm was 8.831

- The upper quartile for 759.98nm was 9.339

- The upper quartile for chlorophyll was 16.53

Table 8. 21 444.27nm as a predictor

CORRECT	%
182 correct	56.2
141 incorrect	43.5
of which	
70 underestimated	21.6
71 over-estimated	21.9

Table 8. 22 Using the relationship between 444.27nm and 550nm (upper quartile -1.626)

CORRECT	%
196 correct	60.5
127 incorrect	39.2
of which	
63 underestimated	19.4
64 over-estimated	19.8

Table 8. 23 Using 700.98nm

CORRECT	%
166 correct	51.2
157 incorrect	48.8
Of which	
79 underestimated	24.4
79 over-estimated	24.4
158	

Table 8. 24 Using the relationship between 700.98nm and 550nm (upper quartile -3.061)

CORRECT	%
190 correct	58.6
133 incorrect	41.0
of which	
67 underestimated	20.7
67 overestimated	20.7

Table 8. 25 Using 759.98nm as predictor

CORRECT	%
187 correct	57.9
135 incorrect	41.8
of which	
68 underestimated	21.1
67 over-estimated	20.7

Table 8. 26 Using the relationship between 759.98nm and 550nm (upper quartile -1.389)

CORRECT	%
208 correct	64.2
115 incorrect	35.5
of which	
58 underestimated	17.9
58 over-estimated	17.9

Suspended sediments were collected for every sample but as expected in the highly turbid Thames Estuary, the turbidity and suspended sediment levels were consistently high with turbidity only ranging 1m-1.5m in all but one sample throughout data collection periods (and in all NRA data for the previous decade). The suspended sediments had a similarly limited variation with the upper quartile at 55mgs/l and the lower quartile at 42.35mgs/l (see Figure 8.36).

Figure 8.36 Histogram of Suspended Sediment Samples

Variable	Count	Minimum	Low Quart	Median	Up Quart	Maximum
s.s. mgs	780	25.00	42.35	49.00	55.00	77.00

Histogram
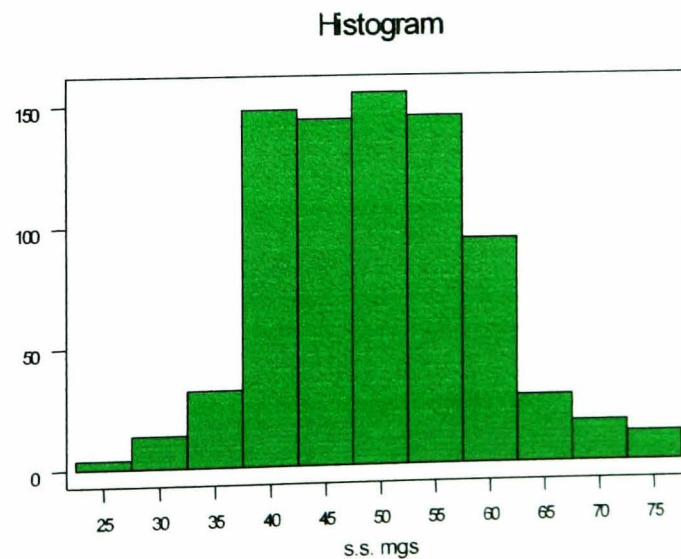
Inevitably the lack of any variation in the turbidity level or in the level of suspended sediment means that there are no excessive levels to predict using reflectance information. This is further complicated by the relationship between salinity and suspended sediments which would indicate a relationship to the tidal flow. In a similar way to chlorophyll, there is an abundance of laboratory and field based research into monitoring suspended sediments. Research using Landsat TM and MSS data by Forster (1994), Dekker (1993) and the LOIS (NERC, 1994) project have shown that there is a strong relationship between suspended sediment concentrations and MSS Band 5 TM band 3, the range 600-800nm (Xia, 1993). Research involving airborne spectroradiometers has shown relationships between the peak in reflectance at 575nm (Forster *et al.*, 1994) with varying levels of sediment level.

Whilst disappointing, the lack of support from the data collected in 1995 does not exclude the use of suspended sediments from the construction of a spectral physical model. The 575nm wavelength was used as a predictor but, with almost no correlation between any wavelength suspended sediments almost certainly due to the lack of variation in suspended sediments, and with no correlation values exceeding 0.2, there was a very poor prediction level. The results of predicting the higher levels of sediment were amongst the poorest of all the parameters predicting 35% correctly using 575nm.

8.3.4 Ammonia

Visual analysis of normalised reflectance against the ammonia/nitrogen levels showed no discernible relationship (Appendix 4A10). This finding was supported through correlation analysis which showed no appreciable relationship. In fact for most of the range 300-980nm correlation analysis showed that there were no relationships at all e.g correlation analysis of 303.35nm and ammonia produced a correlation coefficient of just 0.008 and values rarely exceed 0.1. The ranges from 981nm to1034.44nm and 1079.92nm to 1099.63nm were found to have very low correlation values, peaking in the range 1027.27nm-1034.44nm, with a very low mean correlation value of just 0.195.

To ensure that all possibilities were investigated the standardised reflectance at 1030.14nm (the wavelength with highest correlation value between reflectance and ammonia level) was plotted against standardised ammonia levels. The initial visual analysis of mean reflectance with high and low levels of ammonia highlighted 800-880nm and 900-915nm as related wavelengths. However, correlation and subsequent visual analysis of standardised data clearly showed there to be no true relationship. Closer inspection of reflectance at 1030.14nm through visual and regression analysis (Figure 8.36 and Figure 8.37) also demonstrated a lack of any relationship.

Figure 8.36 Standardised reflectance at 1030.14nm and Ammonia level
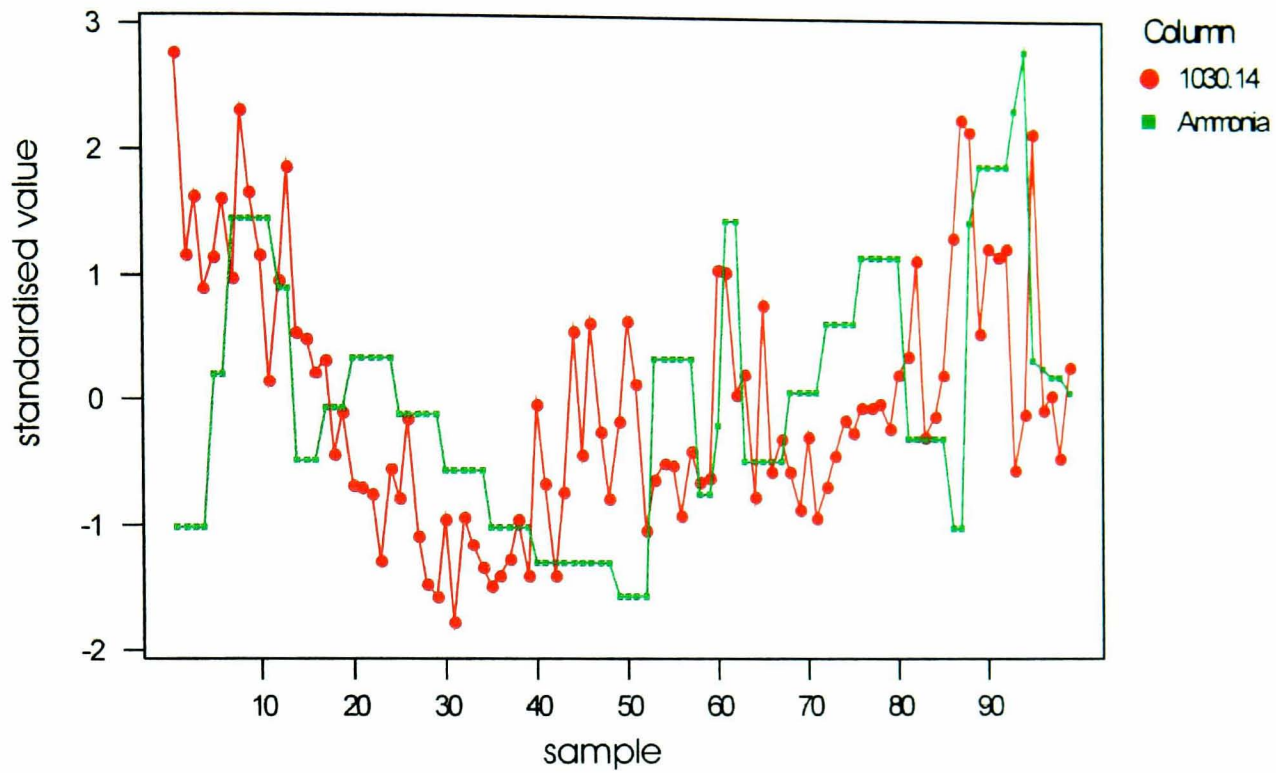
Figure 8.37 Regression of ammonia and reflectance at 1030.14nm

$Y = 1.20239 + 1.06\text{E-}02X$

$R\text{-Squared} = 0.032$
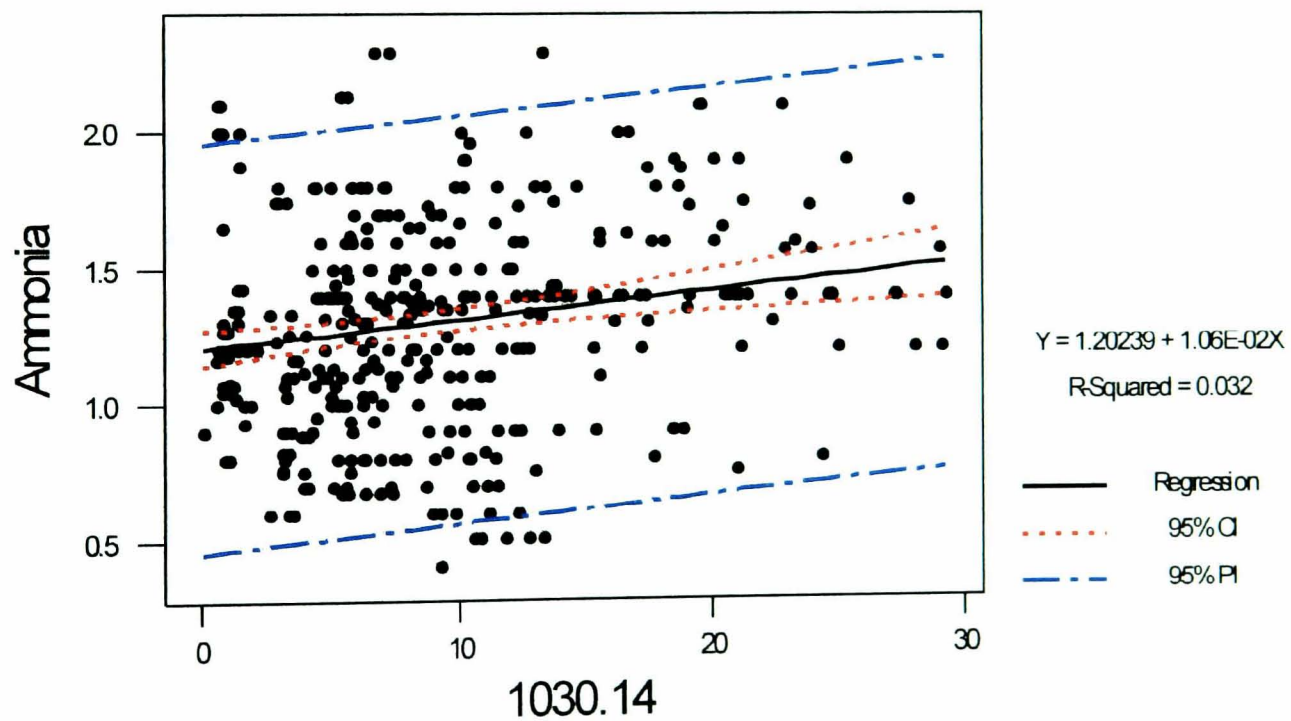
The second stage analysis clearly showed that Ammonia/nitrogen could not be measured directly by reflectance using the range 300-2500nm in the field. Therefore

Ammonia would have to estimated through the application of a water quality model using related water quality parameters i.e. secondary water quality parameters suggested through the water quality model in Chapter 7.

8.3.5 Biological Oxygen Demand (BOD)

The preliminary visual analysis of mean reflectance had highlighted possible relationships in the range 450-650nm and 1100-1300nm. Wavelengths above 1100nm had been excluded because of the low level of reflected light at these longer wavelengths and the corresponding poor quality of data obtained above 1100nm. Furthermore, the range 450-650nm showed no statistical relationship of any significant level and was therefore also discounted. The correlation analysis produced no high, or even modest correlation coefficients (Table 8.28) (see Appendix 3A1 for full details) and thus a threshold of 0.2 was selected which according to Bryman and Cramer (1996) could be described as a low, rather than a very low, value. This selected 313.26nm, 317.21nm and 352.34nm wavelengths.

Table 8. 27 Summary of correlation of BOD against Reflectance

nm	301.35	303.35	305.33	307.32	309.29	311.28	**313.26**	315.24
Correlation coefficient	0.161	0.168	0.159	0.172	0.192	0.18	**0.202**	0.158
nm	**317.21**	319.19	321.16	323.12	325.09	327.04	329.01	330.97
Correlation coefficient	**0.247**	0.197	0.182	0.185	0.18	0.186	0.173	0.184
nm	348.48	350.41	**352.34**	354.27	356.2	358.12	360.05	361.97
Correlation coefficient	0.19	0.191	**0.209**	0.191	0.178	0.185	0.18	0.18

The visual analysis of standardised data showed no clear relationship between BOD and reflectance (see Appendix 4A11) and was supported by the lack of any correlation values of any significance (Table 8.28). The three wavelengths 313.26nm, 317.21nm, 352.34nm with the highest correlation values were investigated through regression analysis. However, as the low correlation values and standardised data visual analysis suggested, regression analysis (Figures 8.38, Table 8.29), proved that there were no remotely detectable relationships between reflectance and the BOD and that the only way of monitoring BOD would be through monitoring other related parameters and modelling BOD.

Figure 8.38 Regression of BOD and reflectance at 313.26nm
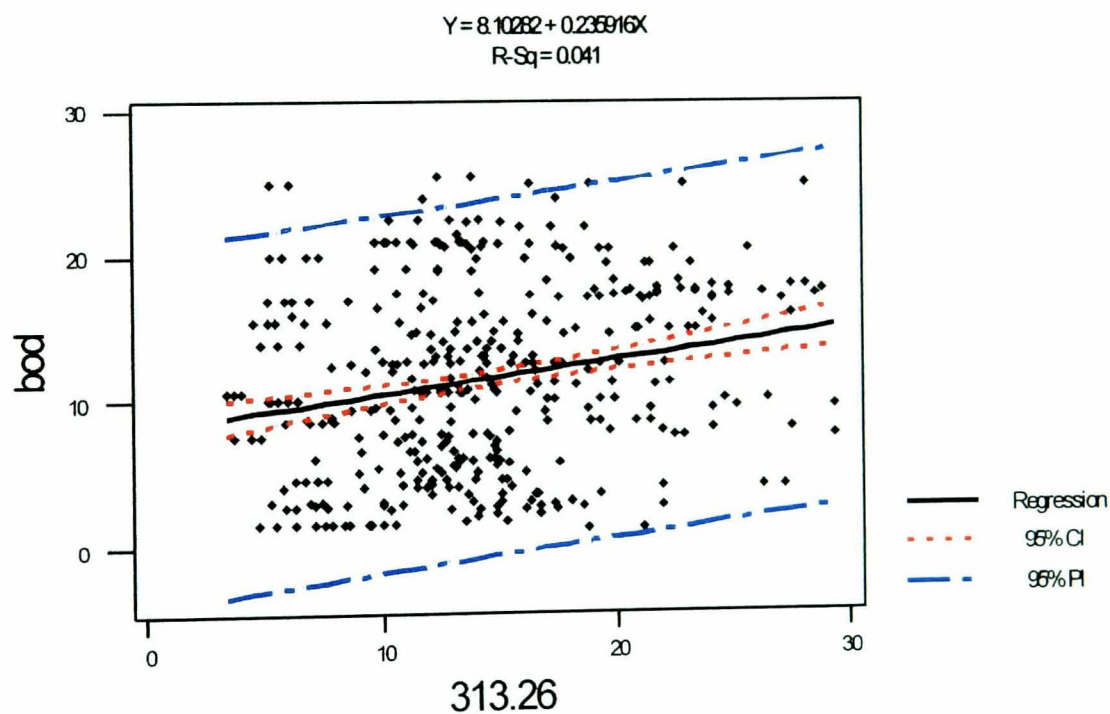
Table 8. 28 Regression of BOD and reflectance at 313.26nm using the scaled best data subset

The regression equation is

y = 8.10 + 0.236 x

647 cases used 146 cases contain missing values

Predictor	Coef	StDev	T	P
Constant	8.1028	0.7103	11.41	0.000
x	0.23592	0.04493	5.25	0.000

S = 6.246   R-Sq = 4.1%   R-Sq(adj) = 4.0%

Figure 8.39 Regression of BOD and reflectance at 317.21nm

Y = 8.15808 + 0.230688X
R-Sq = 0.048
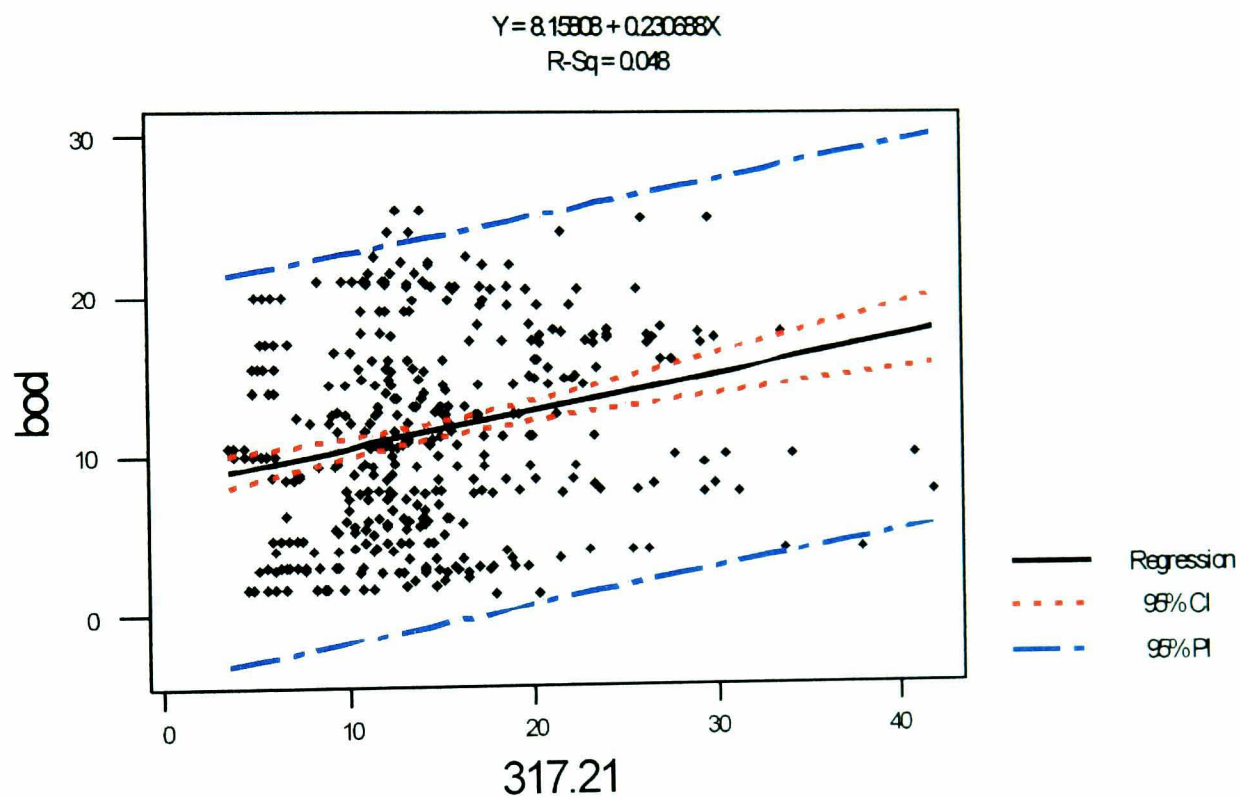
Table 8. 29 Regression of BOD and reflectance at 352.34nm using the scaled best data subset

The regression equation is

y = 8.16 + 0.231 x

647 cases used 146 cases contain missing values

Predictor	Coef	StDev	T	P
Constant	8.1581	0.6504	12.54	0.000
x	0.23069	0.04036	5.72	0.000

S = 6.223   R-Sq = 4.8%   R-Sq(adj) = 4.7%

Figure 8.40 Regression of BOD and reflectance at 352.34nm
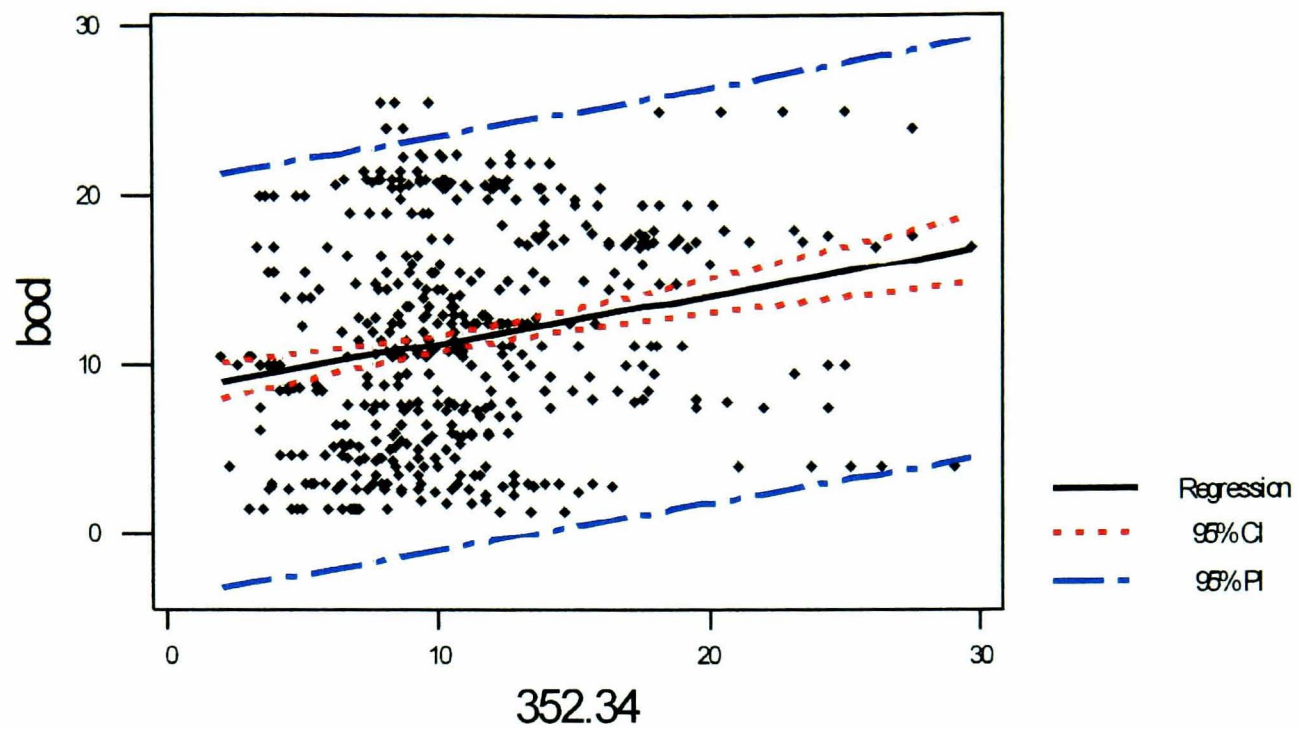
Table 8. 30 Regression of BOD and reflectance at 352.34nm using the scaled best data subset

The regression equation is				
y = 8.45 + 0.281 x				
647 cases used 146 cases contain missing values				
Predictor	Coef	StDev	T	P
Constant	8.4468	0.6313	13.38	0.000
x	0.28138	0.05187	5.42	0.000
S = 6.238	R-Sq = 4.4%	R-Sq(adj) = 4.2%		

8.3.6 Dissolved oxygen

The preliminary visual analysis of mean reflectance had highlighted the range 940nm, 440-575nm and 300-320nm as potential ranges of interest. 440nm was supported through the results of the correlation analysis which showed a slight rise in correlation at 440nm but only with a low coefficient of 0.228. 940nm showed no correlation (0.064) and was therefore not taken any further as a possible wavelength. A low correlation level threshold of +ve or −ve 0.3 was used for dissolved oxygen to select the most highly correlated wavelengths (Table 8.32).

Table 8. 31 Selected examples of correlation of wavelength and Dissolved Oxygen

Wavelength(nm)	Correlation Coefficient from Preliminary Analysis
303.35	0.311
317.21	0.315
319.19	0.304
321.16	0.309
323.12	0.308
338.77	0.301

Visual analysis of the standardised data showed no evidence of any significant relationship from the field data (Appendix 4A11) and this was supported by the lack of any strong relationship from correlation analysis. Investigation of the wavelengths highlighted in the preliminary analysis (Figures 8.41-8.46) through visual analysis of standardised reflectance against the dissolved oxygen levels showed no discernible relationship to any wavelength.

Figure 8.41 Standardised DO levels with reflectance at 301.35nm
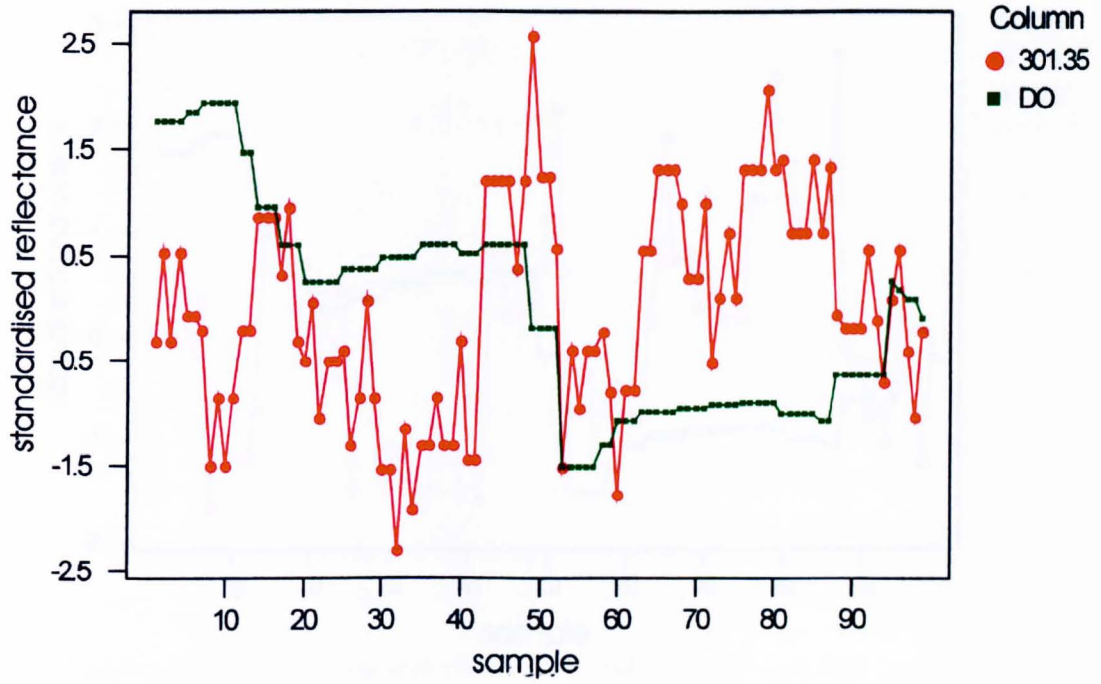
Figure 8.42 Standardised DO levels with reflectance at 317.21nm
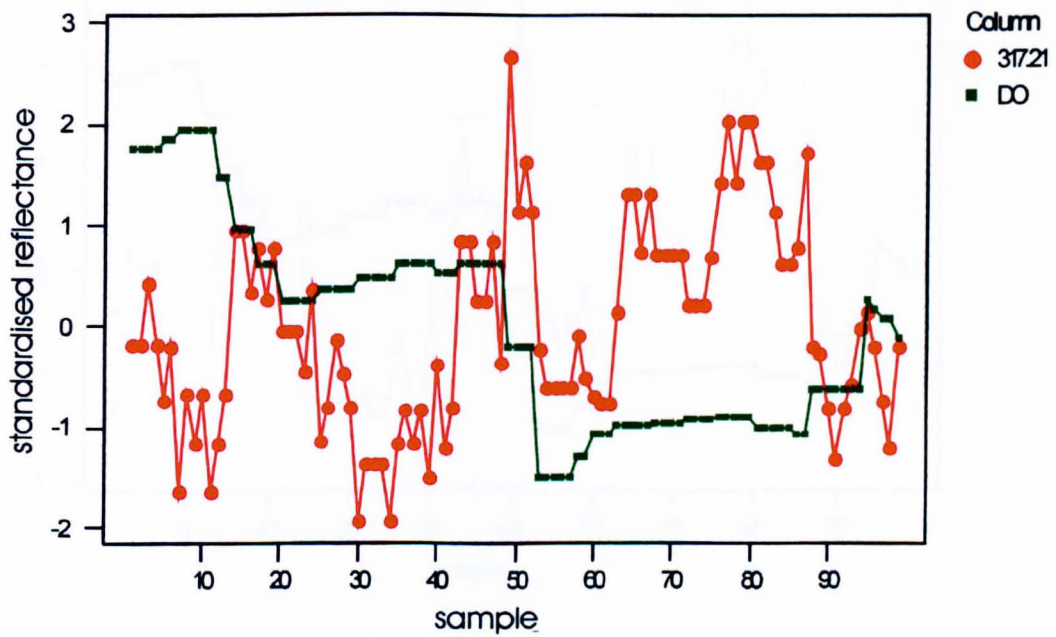
Figure 8.43 Standardised DO levels with reflectance at 319.19nm
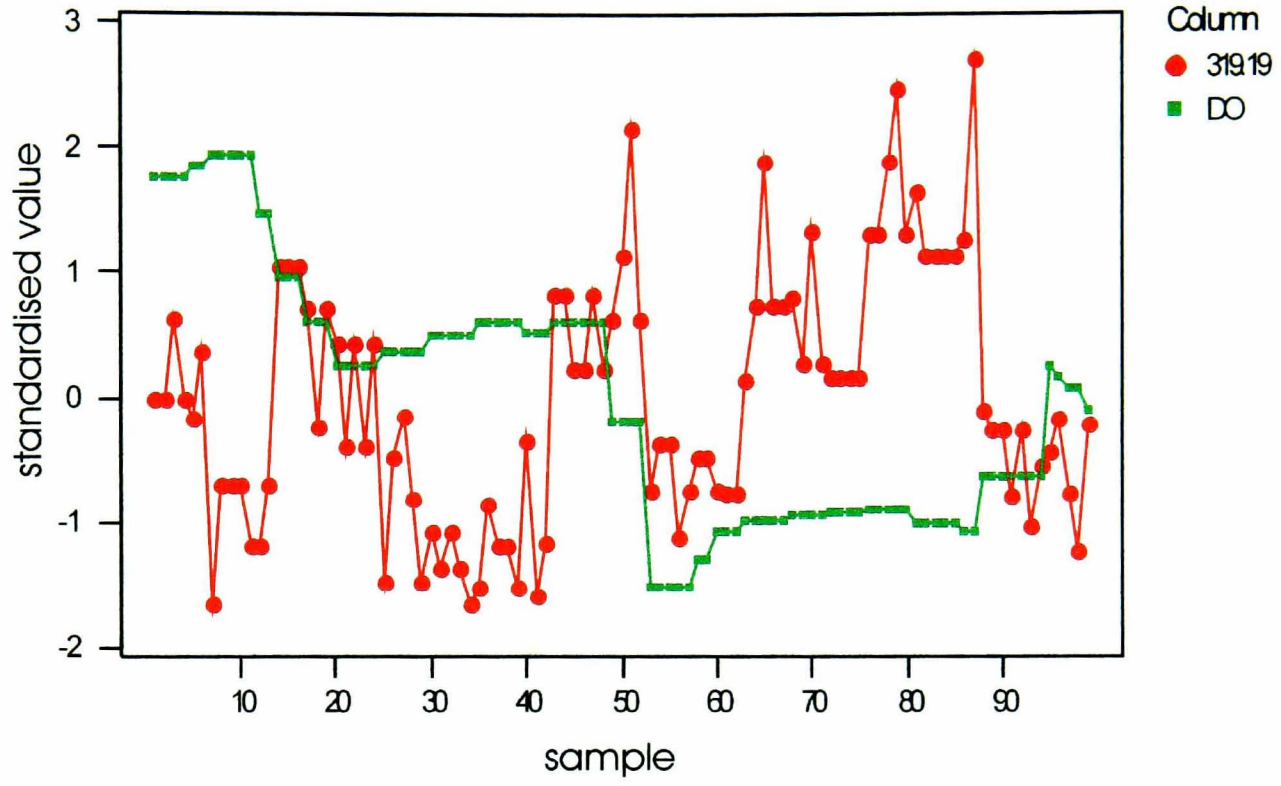
Figure 8.44 Standardised DO levels with reflectance at 321.15nm
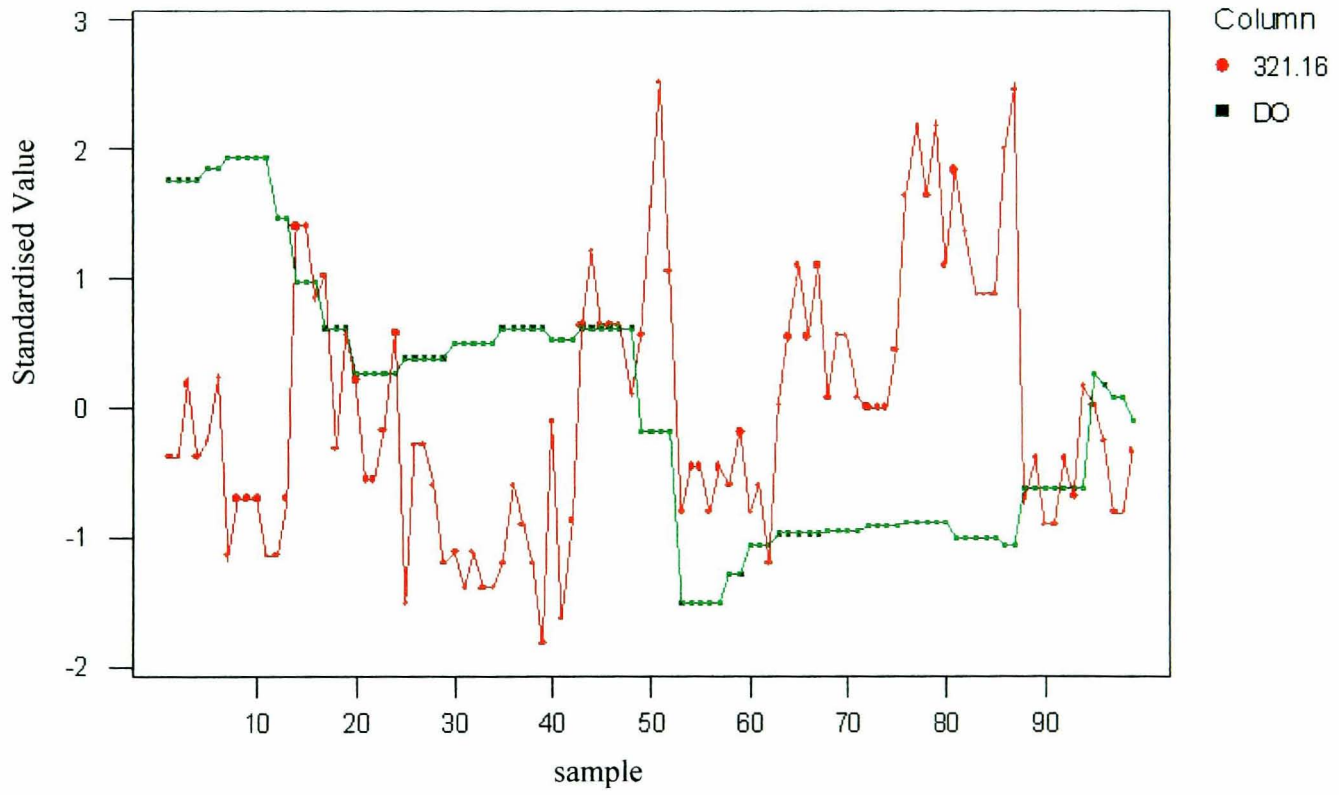
Figure 8.45 Standardised DO levels with reflectance at 323.12nm
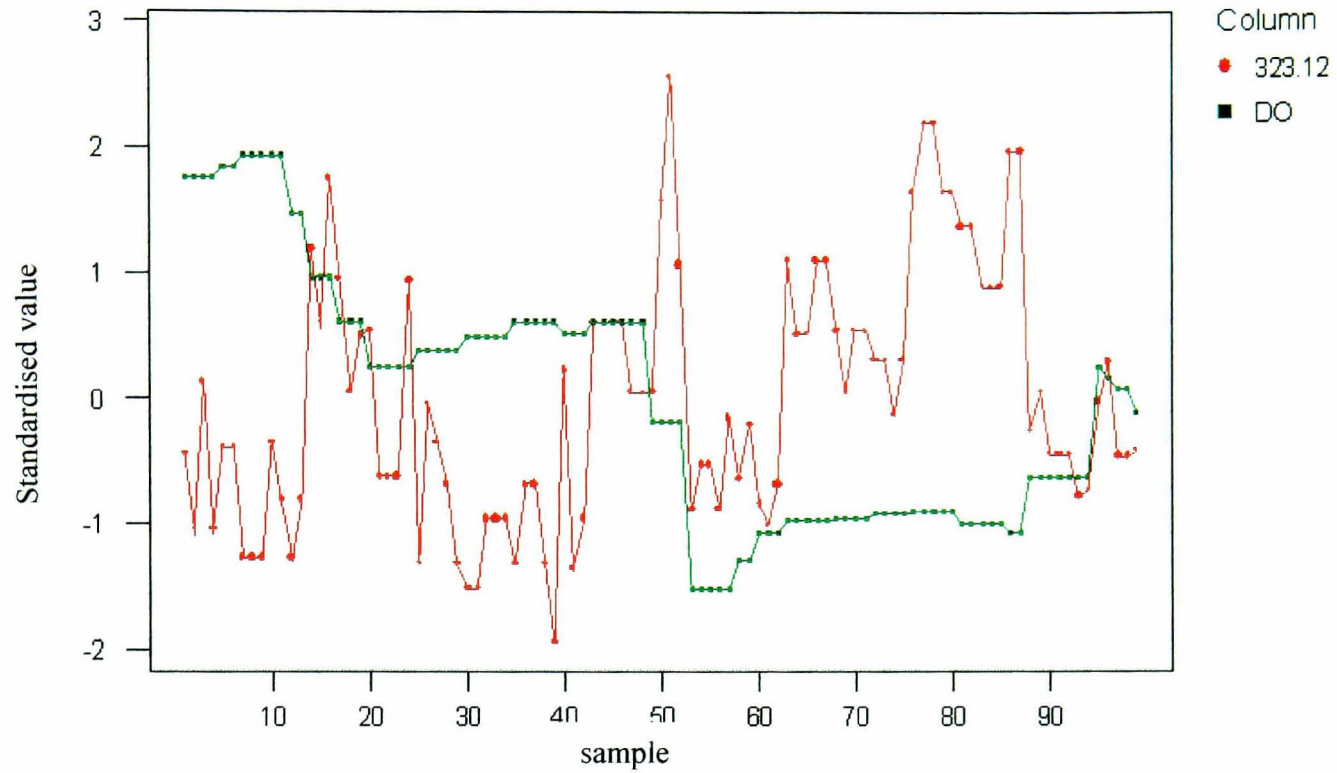
Figure 8.46 Standardised DO levels with reflectance at 338.77nm
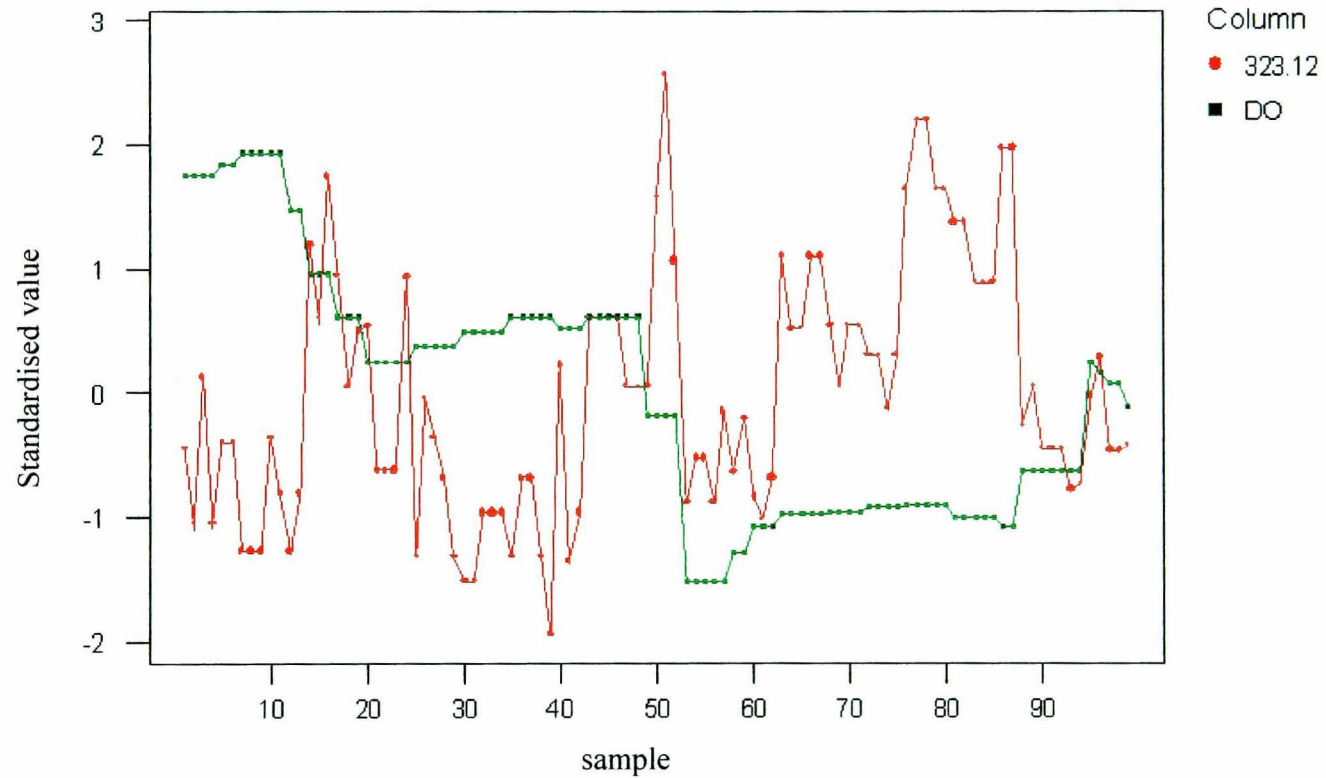
Regression analysis was carried out on each of the wavelengths identified using the best data subset and this again showed no evidence for any relationship between dissolved oxygen and reflectance (Appendix 4A13).

The data showed that the only possible way of monitoring dissolved oxygen would be through indirect relationships with secondary (related water quality parameters) and that

there was no direct relationship with reflectance in the field in the range 300-2500nm. Therefore this parameter must be estimated through a water quality model based on other parameters that can be directly recorded, such as chlorophyll, sediment load and bacterial counts.

8.3.7 pH

Visual analysis of standardised reflectance against pH showed no clearly discernible relationship (see Appendix 4A14). This was supported by the lack of any statistical evidence of a correlation between reflectance and pH (correlation values only exceed 0.150 in the range 305.33nm-315.24nm but never exceed 0.190). The initial visual analysis comparing mean reflectance at high and low pH levels indicated that when pH levels were highly alkali (within the range collected) reflectance between 400nm-700nm could be related. This indication was shown to be false by the subsequent correlation and standardised visual evidence and was therefore excluded from further consideration. There was such a small change in pH during the entire data collection periods (and the previous and subsequent Environment Agency data from 1993-2001) that it was highly improbable that any relationship between pH and reflectance or with any other water quality parameter could be determined.

8.4 General Chapter Summary

The best data set was standardised and a detailed visual analysis (described in Section 8.1.1) of the standardised visual and water quality data was undertaken which identified the wavelengths that showed a similar pattern in distribution to the water quality

parameter concentrations. The analysis was carried out at intervals of 10nm and at specific wavelengths that were identified in the results from the visual analysis and statistical analysis in Chapter 6. If more than one wavelength was found to show a strong similarity in pattern to the water quality parameter concentration then these were then compared through regression analysis. The strongest (and most significant for remote sensing) of the identified wavelengths were then tested to try to predict (against the best data set and then the full data set) when the water quality parameters exceeded either the upper quartile of the data collected or above an identified threshold. The result produced an optimum wavelength for each water quality parameter and an accurate evaluation of the predictive accuracy of that wavelength. The results of each process are summarised in a table at the end of each sub section. The wavelengths that showed no relationship through this analysis were determined to require a secondary parameter to assist in the prediction of failing water quality and are derived in Chapter 9 using the results from Chapter 7.

Chapter 9

Analysis of Water Quality Parameters Requiring a Secondary Water Quality Parameter

9.1 Overview

The water quality parameters that showed no significant relationship to any wavelength through the final analysis in Chapter 8 were identified as requiring a secondary parameter(s) to assist in the remote sensed prediction of failing water quality. The parameters identified were salinity, total coliform, nitrogen/ammonia, pH, and phosphates. These water quality parameters and their secondary parameters (identified from the water quality model and results of Chapter 7) are analysed in Chapter 9.

9.2 Application and Testing

The second stage analysis showed that salinity, total coliform, nitrogen/ammonia, pH and phosphates could not be directly related to reflectance. Consequently, the water quality model for the Thames Estuary (Figure 7.16) was used to select the secondary parameters that could predict high levels of salinity, total coliform, nitrogen/ammonia, pH and phosphates. The secondary water quality parameters in the water quality model were tested to estimate the confidence that could be placed on each of them using the same approach used for testing the relationship between reflectance and each water quality parameter in Chapter 8. Each parameter was tested to see the number of correct and incorrect predictions when the target water quality parameter was in it's upper

quartile. A second prediction test was then run to estimate the percentage of incorrect and correct predictions when the secondary predictor water quality parameter predicted a target water quality parameter level in excess of its upper quartile. i.e. If the model was to be used as a flagging system to request a manual sample to be taken, this second test would estimate the percentage of those flagged occasions that in reality would not need a manual survey.

9.2.1 Phosphates

Phosphates show no significant relationship with any of the other water quality parameters. The only way of predicting excessive levels of phosphates would therefore be by the use of 911.88nm as suggested through the secondary analysis. However, this analysis produced only a 60% success rate at predicting instances of high phosphate levels (based on upper quartile of field data) using the best quality data subset. It was therefore not considered suitable for prediction.

9.2.2 pH

The water quality model showed that pH has relationships with three other water quality parameters: E.coli, temperature and ammonia and these are shown in Figure 9.1.

Figure 9.1 Relationship between pH, E.coli, Ammonia/Nitrogen and Temperature (all standardised by subtracting the mean and dividing by the standard deviation).
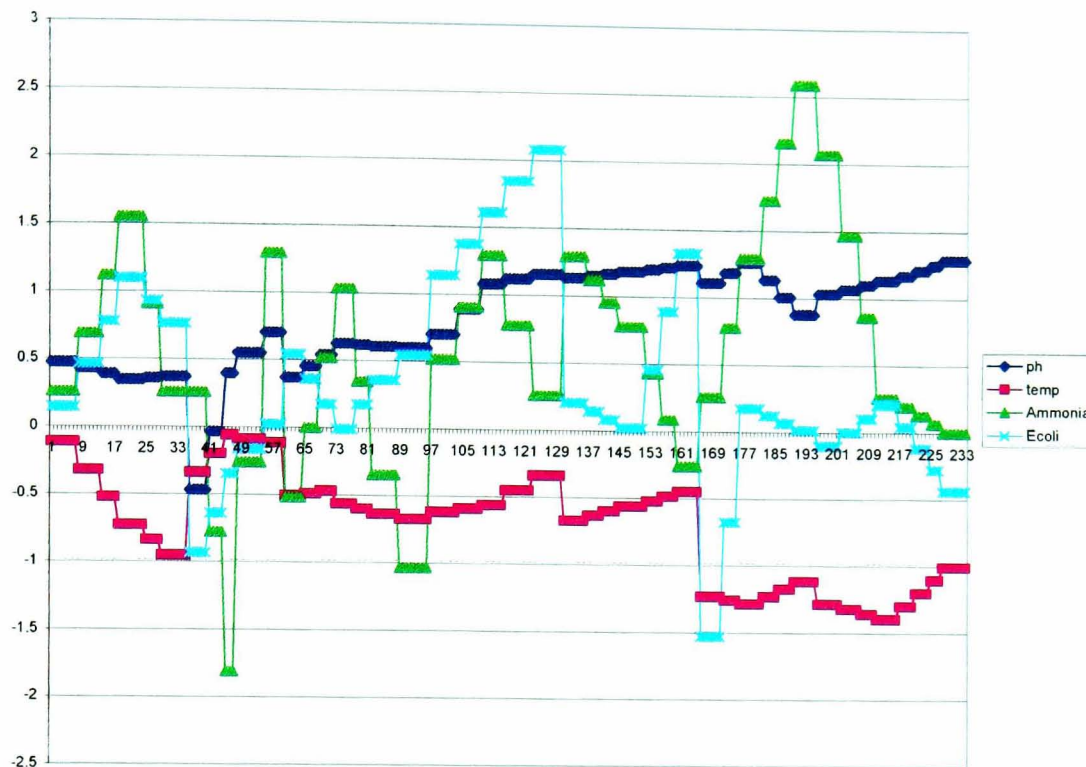
Temperature is naturally related to Thermal Infra-Red but Thermal Infra-Red was not within the range of any of the instruments used in the field. This means that confidence in temperature prediction cannot be tested using data collected for this investigation. However, numerous other research studies (Baban, 1993a-b; Parada *et al.*, 1998) can be relied upon to show that the level of accuracy of temperature measurement is widely accepted as being very good. The only accuracy consideration should be that the temperature measurements are only of the water surface, not of the water body because of the lack of penetration of light at these long wavelengths but studies such as that by Baban (1993a) show that surface measurements is reasonably accurate. Surface measurement was a consideration in data collection but with all water quality parameters samples being taken from within the upper 1m of the Thames estuary, this is similar to current sampling methods adopted by EU legislative authorities.

pH needs to be identified if it reaches either extreme alkali or acidic levels. Therefore, each of the related water quality parameters were tested as a predictor against the full data set to see if they could be used as an indicator of high and low pH. As described in section 9.2, the tests were repeated for the predictor water quality variables for a subset of data when the predictor variable was in its upper or **lower quartile (**dependent on whether low or high pH is trying to be predicted). The repeat of the test shows the accuracy of the predictor when pH has been indicated as extreme. The results of this test process are contained in Tables 9.1 and 9.2.

Table 9. 1 Prediction of high pH using secondary water quality parameters

High pH i.e. over upper quartile of 8.087						
Predictor Parameter	Using only samples with upper quartile value of predictor variable or full data set	Using only samples with upper quartile value of predictor variable or full data set	Number of correct predictions	% Correct	Number of incorrect predictions	% Incorrect
Ammonia	FULL SET	FULL SET	556	70.2	236	29.8
	YES		91	46	106	53.54
Temp-erature (inverse relationship)	FULL SET	FULL SET	615	77.6	177	23.3
		YES	102	51.3	97	48.7
E.coli	FULL SET	FULL SET	337	65.6	177	34.4
	YES>200Count/100ml		155	53.3	136	46.7

Table 9. 2 Prediction of low pH using secondary water quality parameters

Low pH i.e. below lower quartile of 7.58					
Predictor Parameter	Using only samples with upper quartile value of predictor variable or full data set	Number of correct predictions	% Correct	Number of incorrect predictions	% Incorrect
Ammonia	FULL SET	436	55.1	356	44.9
Temperature (inverse relationship)	FULL SET	653	82.4	139	17.6
	YES	129	65.2	69	34.8
E.coli	FULL SET	406	79	108	21
	YES	56	41.5	78	57.8

The results of these tests show that all three predictor water quality variables are reasonably good indicators of levels of pH when pH is alkali, with a 65-77% accuracy. Of the samples predicted as having potentially extreme pH, around 50% were actually extreme values. Temperature and E.coli were shown to be acceptable predictors for acid pH values, with an accuracy of 82% and 79% respectively. The reliability of extreme prediction was lower for E.coli, with only 41% of predicted high pH values actually being high. Temperature was a better predictor variable, with 65% of predicted high values actually being correctly identified as high.

9.2.3 Ammonia

The water quality model (Figure 7.16) showed that Ammonia has a positive relationship with pH and an inverse relationship with temperature (Figure 9.2). Again the predictor variables were tested against the data to test the accuracy of the predictions using the upper quartile of the predictor data to see if this predicted values in the upper quartile of the ammonia samples.

Figure 9.2 Relationship between Ammonia/Nitrogen and Temperature and pH (all standardised by subtracting the mean and dividing by the standard deviation).
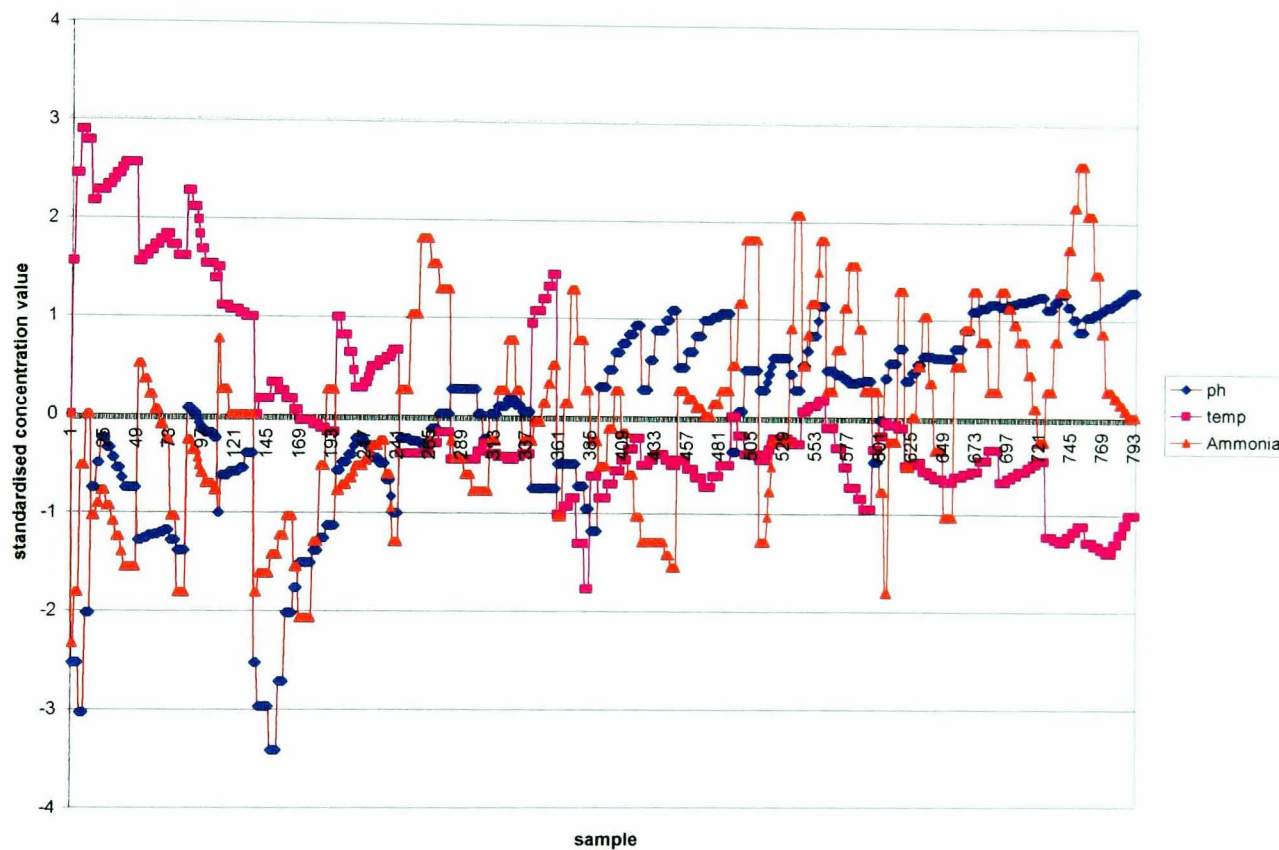
Using a threshold value based on the upper quartile of each predictor variable, the accuracy of the predictor variable was tested for both predictions below and above the threshold value. This was then repeated for just the data in the upper quartile to give the accuracy of high level predictions (see section 9.1). The results of this analysis are shown in the Table 9.3.

Table 9. 3 Prediction of high Ammonia concentration using secondary water quality parameters

High Ammonia/Nitrates i.e. over upper quartile of 1.567					
Predictor Parameter	Using only samples with upper quartile value of predictor variable or full data set	Number of correct predictions	% Correct	Number of incorrect predictions	% Incorrect
Temperature	FULL SET	556	70.2	236	29.8
(inverse relationship)	YES		45.4	119	54.6
pH	FULL SET	556	70.2	236	29.8
	YES	21	10	180	89

Although both predictor variables (temperature and pH) do enable a 70% correct prediction, pH has only a 10% accuracy of prediction in the upper quartile which is the range of interest to EU legislation. Therefore, only temperature could be viewed as potentially useful as a predictor variable with:

- a low but possibly useful 45% accuracy of high predictions using only samples within the upper quartile of the predictor data (55% would be over estimates)

- a 70% prediction accuracy using all data

.

9.2.4 Salinity

The water quality model (Figure 7.16) showed that salinity has a relationship with chlorophyll and suspended solids (Figure 9.3). Again, the upper quartile of the predictor variables were tested against the data to test the accuracy of the predictions to see if the predicted values were in the upper quartile of the salinity samples.

Figure 9.3 Relationship between Salinity and chlorophyll, and Suspended sediment (all standardised)
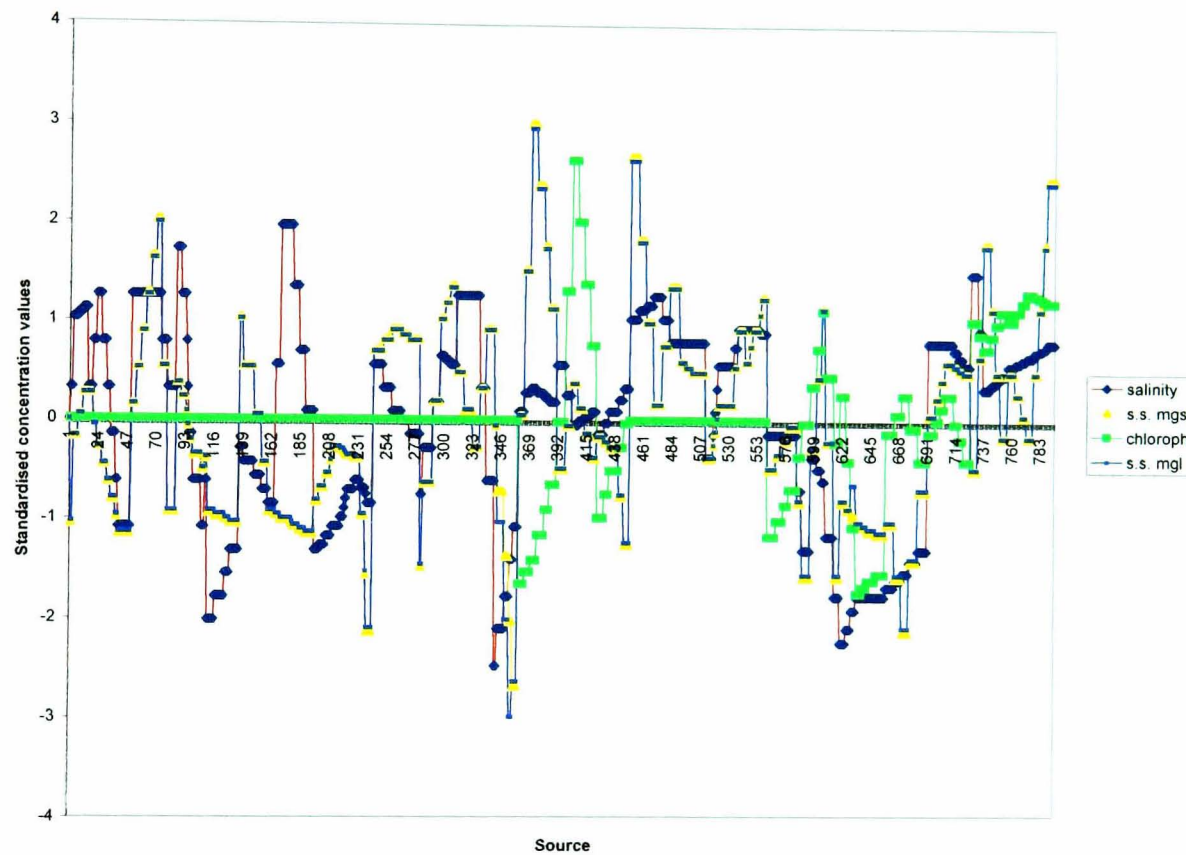
Using a threshold value based on the upper quartile of each predictor variable, the accuracy of the predictor variable was tested for both predictions below and above the threshold value. This was then repeated for just the data in the upper quartile to estimate the accuracy of high level predictions (see section 9.1). The results of this analysis are shown in Table 9.4. Both chlorophyll and suspended sediments enabled reasonably high numbers of correct predictions using the full data set. However, when

only samples in excess of the threshold upper quartile value (55mgs for suspended sediments and 16.53 for chlorophyll) were used, only suspended sediments produced a reasonable result of 47% correct with 52.5% being classified as false warnings.

Table 9. 4 Prediction of high Salinity concentration using secondary water quality parameters

High Salinity i.e. over upper quartile of 1.023					
Predictor Parameter	Using only samples with upper quartile value of predictor variable or full data set	Number of correct predictions	% Correct	Number of incorrect predictions	% Incorrect
Chlorophyll	FULL SET	234	72.4	89	27.6
	YES	13	16.9	64	83.1
Suspended sediment (mgs)	FULL SET	564	71.2	228	28.8
	YES	96	47.5	106	52.5

9.2.5 Total Coliform

The water quality model (Figure 7.16) showed that Total Coliform has an inverse relationship with both chlorophyll and faecal coliform (Figure 9.4). Again, the predictor variables were tested against the data to test the accuracy of the predictions using the lower (for chlorophyll) and upper (for faecal coliform) quartile of the predictor data to see if this predicted values in the upper quartile of the total coliform samples.

Figure 9.4 Relationship between Total Coliform and chlorophyll, and Faecal coliform (all standardised).
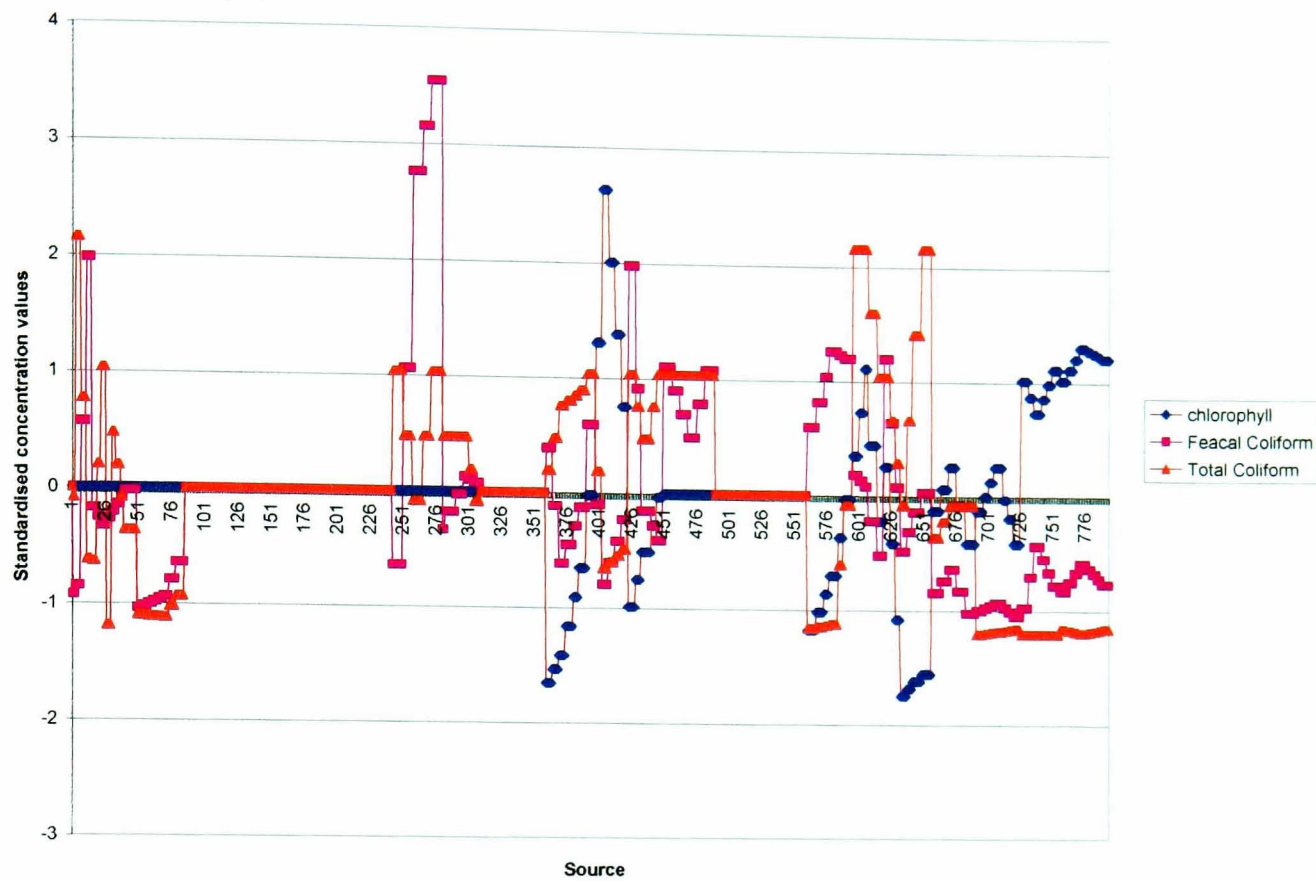
Using a threshold value based on the relevant quartile value of each predictor variable, the accuracy of the predictor variable was tested for both predictions below and above the threshold value. This was then repeated for just the data in the upper quartile to give the accuracy of high level predictions. The results of this analysis are shown in Table 9.5. Both chlorophyll and faecal coliform showed reasonably high numbers of correct predictions using the full data set. However when only samples in excess of the threshold quartile value (55mgs for suspended sediments and 16.53 for chlorophyll) were used, only faecal coliform with a 72% correct prediction using the full data set, produced a reasonable result of 45.5% correct i.e. 54.5% would be false warnings.

Table 9. 5 Prediction of high Total Coliform count using secondary water quality parameters

High Total Coliform i.e. over upper quartile of 457count /100ml					
Predictor Parameter	Using only samples with upper quartile value of predictor variable or full data set	Number of correct predictions	% Correct	Number of incorrect predictions	% Incorrect
Chlorophyll	FULL SET	218	67.5	105	35.5
	YES	21	26.6	58	73.4
Faecal coliform	FULL SET	370	72	144	28.02
	YES	60	45.5	72	54.5

9.2 Chapter Summary

Secondary water quality parameters were used to identify the remaining water quality parameters (pH, ammonia, total coliform, and salinity) whose above threshold levels could not be identified directly. The secondary water quality parameters had been identified in Chapter 7 through the production of the water quality model (Figure 7.16). Each secondary parameter was tested against the data to identify the percentage of correct prediction of high (above upper quartile) primary (pH, ammonia, total coliform, and salinity) water quality parameters. The results were summarised for each parameter in terms of percentage correct and percentage incorrectly identified and under estimated and are shown in the five Tables 9.1-9.5.

It was found that the following secondary parameters were the most successful at flagging high levels of each parameter :

❖ For pH the secondary parameters were temperature, and E.coli both of which have been shown to be reliable primary parameters

❖ For total coliform the most supportive secondary parameter was faecal coliform

❖ For ammonia the secondary parameter was identified as temperature

Chapter 10

Summary and Evaluation of Results, Conclusions and Recommendations

10.1 Overview of results

A water quality model (reproduced here as Figure 10.1 from Figure 7.16) was constructed through the water quality analysis of this investigation's data (Chapter 7) and application of existing water quality research. The second stage analysis (Chapter 8) identified the water quality parameters that can be monitored directly from remotely sensed data and estimated the level of accuracy that could be achieved in predicting high water quality parameter concentrations. The results of this analysis are summarised in Table 9.6 and shows seven parameters that have the potential to be monitored by remote sensing (Chapter 8) and a further four parameters that showed potential (Chapter 9) for prediction through the use of secondary water quality parameters (identified in Chapter 7).

All the results from Chapters 8 and 9 are summarised in Table 10.1 and form the basis of the spectral physical model (Figure 10.1). Table 10.2 summarises the wavelengths that have been identified as showing potential for use in a remotely sensed flagging system and, where necessary, which secondary parameter(s) can be used to estimate when that parameter concentrations are excessive. Where prediction through reflectance data is possible, no secondary parameter is required in order to make a eventual operational system as efficient as possible.

Figure 10.1 Water quality model for Thames Estuary
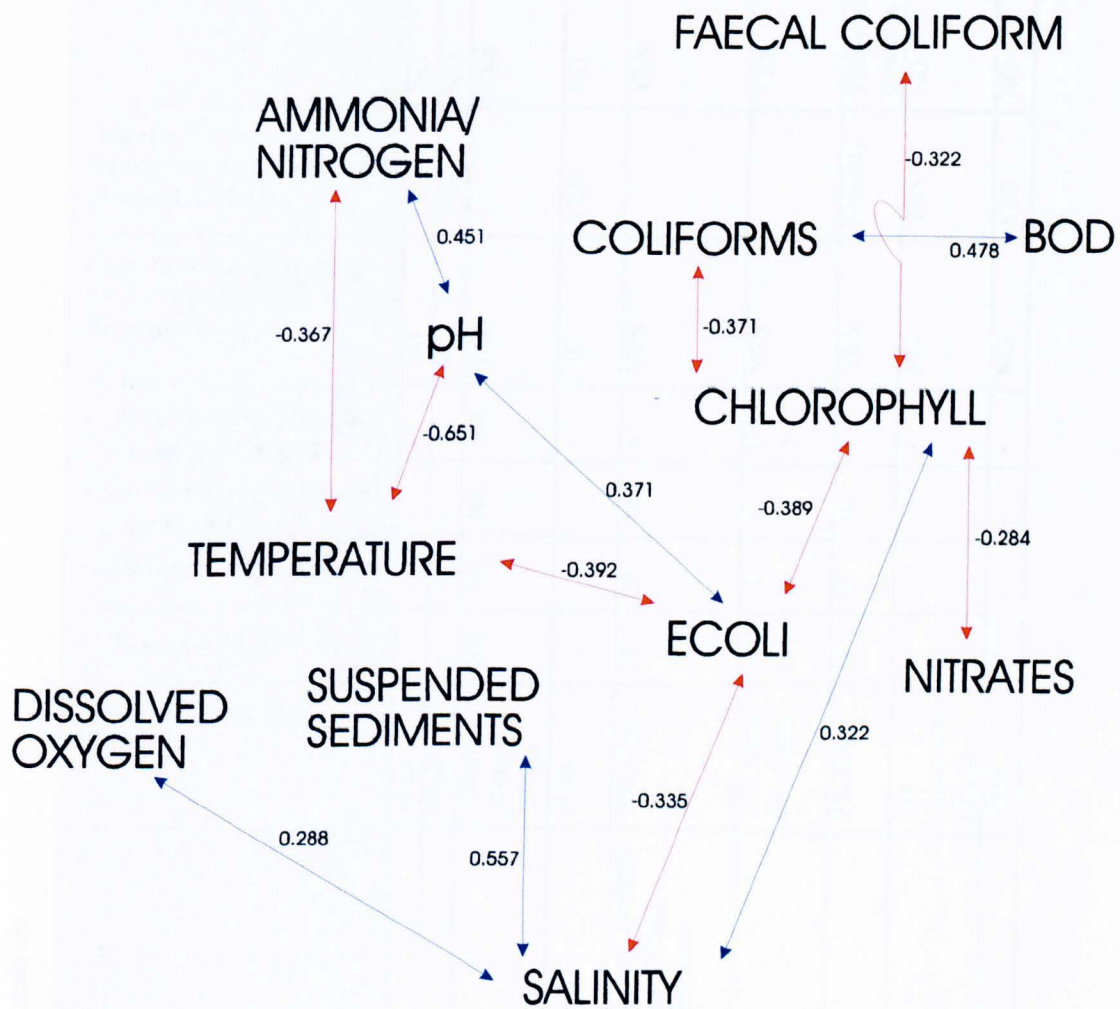
Table 10.1 **Summary of Second Stage Analysis**

Parameter	EU Directive level (1976)	EU COM(2000) 860 Final 21.12.2000	Potential Monitoring Wavelength	% correctly identified	% incorrectly identified	% incorrectly identified (over-estimated)	% incorrectly identified (under-estimated)	Remote sensing can be used to identify high threshold load	Require Secondary Parameter within spectral physical model		Can operate as a secondary parameter
Ammonia	Yes (3)	Yes(3)	None	-	-	-	-	NO	YES		NO
BOD	No	Yes(4)	None	-	-	-	-	NO	YES		NO
Chlorophyll	No	Yes(4)	444nm 700nm 759nm	NA	NA	NA	NA	YES	-		YES
DO	Yes 80-120% saturation	Yes	None	-	-	-	-	NO	YES		NO
E. Coli	No	Yes freshwater possibly 400 counts per 100ml Coastal enterococci 50/100ml	301.35nm	79	22	16	6	YES	-		YES
Faecal Coliforms	Guide 100count Fail 2000 counts per 100ml	Yes	338.77nm 633.69nm	69 64	30 36	22 31	8 5	YES	-		YES
Nitrates	No	Yes (4)	911.88nm	64	35	30	5	YES	Possibly		YES with collaborating evidence
Nitrogen	Yes (3)	Yes	See Ammonia results	-		-	-	NO	YES		NO
pH	Yes 6-9	Yes (2)	None	-	-	-	-	NO	YES		NO

Parameter	EU Directive level (1976)	EU COM(2000) 860 Final 21.12.2000	Potential Monitoring Wavelength	% correctly identified	% incorrectly identified	% incorrectly identified (over-estimated)	% incorrectly identified (under-estimated)	Remote sensing can be used to identify high threshold load	Require Secondary Parameter within spectral physical model	Can operate as a secondary parameter
Phosphates	No	Yes (4)	911.88nm	60	40	20	20	Possibly	Possibly	NO -although could be used to collaborate with other parameters
Salinity	No	Yes (2)	None	-		-	-	NO	YES	NO
Suspended Sediment	No	Yes (2)	575nm	NA	NA	NA	NA	YES	-	YES
Temp	Yes	Yes (2)	Thermal IR	NA	NA	NA	NA	YES (Surface only)	-	YES
Total Coliform	Yes 500counts per 100ml guide, 10000 counts per 100ml Fail	Yes	649.93nm	56	44	4	40	Possible with corresponding data	Possibly	NO
Turbidity	Yes Guide 2m Fail 1m with local exceptions allowed	Yes (4)	None	NA	NA	NA	NA	Possibly	YES	Possibly

2 Concentration to be checked when area shows the quality of water has deteriorated

3= When there is a eutrophication tendency

4 "Divergence from the normal....a change..from normal conditions for the bathing area in question would, in any case, indicate that there is/has been an influx of 'strange' water - for example rainwater or wastewater - worth investigating" (COM(2000)860 Final 21.12.2000)

Figure 10.2 The suggested spectral physical model

Spectral Physical Model
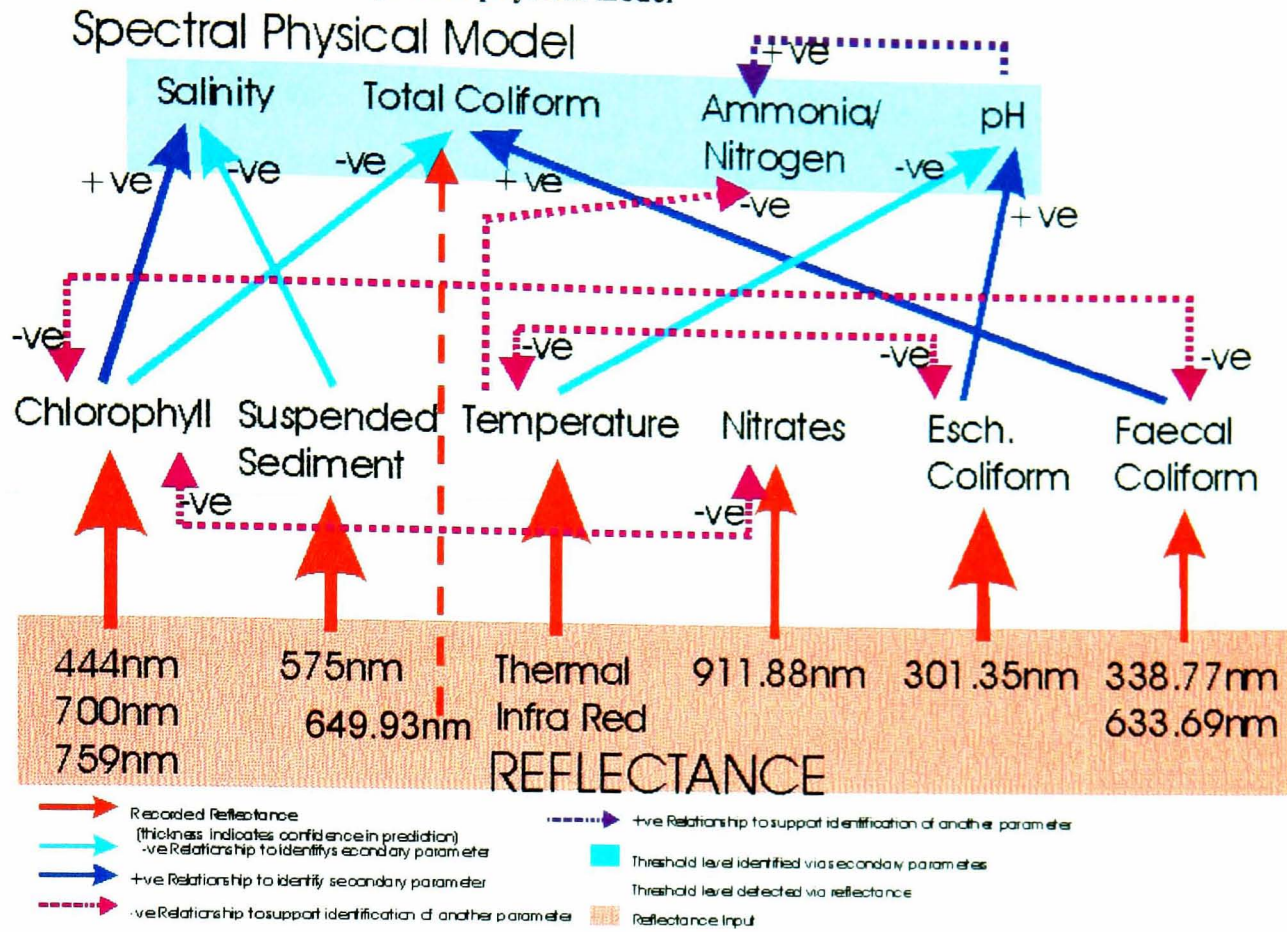
Table 10.2 Summary of predictors for each water quality parameter selected for remote monitoring of EU Bathing water (chlorophyll, salinity and BOD were selected from the outset as secondary parameters)

Water Quality Parameter	Predictor Wavelength	Predictor Secondary Water Quality Parameter
Dissolved Oxygen	None	None
pH	None	Temperature E.coli
Nitrogen /Ammonia	None	Temperature
Temperature	Thermal IR	Not required
Suspended Solids	575nm	Not required
Nitrates	911.88nm	Not required
Phosphates	None (911.88nm)	None
Total Coliform	649.93nm	Faecal Coliform
Faecal Coliform	338.77nm 633.69nm	Not required
E.coli	301.35nm	Not required
Turbidity	(see Suspended sediment)	Not required

10.2 Brief Supporting Evidence/Explanation for Predictors

Where available a hypothesis was found to support each predictor for the water quality parameters identified in Table 10.2. This was to support the findings and therefore methodology of this study and to provide further supporting evidence to encourage future research.

10.2.1 pH, Ammonia/Nitrogen, and Nitrates

E.coli and temperature were identified as the secondary water quality predictors for pH (Table 10.3). This is explained because E.coli is widely accepted as an indicator of recent human effluent (Kay *et al.*, 1999). In the study area the most likely source of human effluent are the sewer outfall. As discussed in Chapter 4, pH will be increased by domestic waste within the sewer discharge which will contain increased concentrations of ammonia amongst other substances (EU, 2000). Temperature is the secondary water quality predictor for ammonia. These parameters are plausibly related due to the effect on water body temperature from the sewer outfall plumes itself. There is no supporting evidence for the identification of 911.88nm as a potential predictor for nitrates. This could potentially be produced through a detailed laboratory investigation into the spectral signature of nitrates in a similar way to that undertaken by Matthews *et al.* (1994) with chlorophyll-a.

10.2.2 E.coli, Faecal Coliform and Total Coliform

Faecal coliform has been identified as the secondary water quality predictor for total coliform. Total coliform is by its nature inclusive of faecal coliform and therefore related to faecal coliform. Total coliform is included in the EU Bathing Water Directive as an indicator of sewage pollution, though its accuracy as an indicator has been debated

(Fleischer, 1992) as it occurs naturally. This in part may also explain the imperfect relationship between faecal coliform and total coliform.

E.coli, faecal coliform and total coliform are accepted as indicators of sewage effluent (Fleischer, 1992). This investigation has identified reflectance at 301.35nm to be related to E.coli; 338.77nm and 633.69nm to be related to faecal coliform; and possibly 649.93nm related to total coliform (using faecal coliform as a secondary parameter).

Pinnick et al. (2002) undertook an investigation of airborne particles and found a peak in reflectance at 310nm and 340nm for the amino acids found in bacterial particles and further smaller peaks at 635nm and 670nm. Pinnick's study used dried E.coli and found that one of the amino acids, trytoplan, had a fluorescence peak around 350nm. In a biophysics study of molecular structure using E.coli, Vickery et al. (1997) found fluorescence peaks for two E.coli proteins at around 300nm (specifically 303nm) and 340nm (specifically 337nm) which are all highly supportive of the results of this study. While the concentrations of any one bacterium will be low, these studies suggest similar relationships are found in other coliform and possibly other biological matter (Pinnick et al., 2002). These will be present in high concentration because E.coli is a highly specific indicator of recent human effluent. Therefore if E.coli levels are high, it is likely that a sewage plume is being sampled and therefore very high microbiological levels will be present. Petrenko et al. (1997) in a study of sewage plumes in Mamala Bay, Hawaii and laboratory study of sewage samples observed maximum fluorescence between 280-340nm with 340nm found to be a good identifier of older plumes where faecal coliform is likely to be a better indicator of sewage pollution. The similarity in reflectance peaks in Petrenko et al.'s (1997) study of Mamala Bay to those observed by

this investigation are also supportive of the data collection and methodology applied in this investigation. Furthermore, E.coli does not have a long life-span in the open environment and therefore faecal coliform is likely to be a better indicator of older plumes which again supports the results reported in the current study.

10.2.3 Suspended Sediments, Turbidity and Chlorophyll

Suspended sediments and turbidity are inevitably closely related but the very limited variation in turbidity in the Thames Estuary (particularly in view of the level of accuracy of the traditional method of measurement (Sechi disk)) has disguised this relationship. However, in some Case 2 bathing waters variation in turbidity may be greater and a relationship evident between suspended sediment and turbidity may allow the use of remotely sensed monitoring.

Other research involving airborne spectroradiometers has shown relationships between the peak in reflectance at 575nm with varying levels of sediment level (Forster *et al.*, 1994) and a strong relationship between suspended sediment concentrations and reflectance in the 600-800nm range (Xia, 1993).

Van der Piepen *et al.*, (1991) used a "weighted ratio of the reflectance near the absorption maximum and absorption minimum of chlorophyll-a" based on the Gordon and Morel pigment algorithm from 1983. Typically in Case 1 waters these would be 443nm and 550nm but, van der Piepen (1991) suggested that the additional salts and minerals in Case 2 waters made the relationship between reflectance and chlorophyll-a more complex and the use of the wavelengths at around 685nm proved more successful from airborne measurements using the algorithm in Equation 2.

Equation 2 Remote Sensing of Chlorophyll (van der Piepen *et al.*, 1991)

$$C=D*(R_{685}-E*R_x)$$

Where c= chlorophyll concentration

R_{685}=reflectance at 685nm

Rx= the average reflectance in neighbouring channels above and below 685nm

D & E are constants determined empirically by means of simulation models

10.2 Evaluation of Results

This research has identified the need for a remotely sensed flagging system for EU designated bathing water quality and shown wavelengths and parameters that can be used to successfully identify failing water quality. In order for a remote sensing flagging system, designed to highlight when a water quality parameter is in excess of directive limits, to be successful the percentage of correct predictions is obviously important (Table 10.1). However, if the intention for such a system is to indicate potential failure and prompt manual sampling, the percentage of incorrectly underestimated samples is equally significant. Therefore the performance of a predictor should be viewed in the light of both the percentage of correct predictions and the percentage of incorrect underestimates. In order to interpret the results of the current study, a rating was assigned to each predictor variable for each water quality parameter. This predictor rating was calculated by the formula shown in the following equation:

Equation 3 Predictor Rating

Predictor Rating = % correctly identified / % incorrectly underestimated

A high predictor rating therefore indicates a high correct prediction with a low number of underestimates. Table 10.3 summarises the resulting predictor ratings.

Table 10. 3 Bathing Water Quality Predictor Ratings

Parameter	EU Directive level (1976)	EU COM (2000) 860 Final 21.12.2000	Potential Monitoring Wavelength or Parameter	• % correctly identified	• % incorrectly identified	• % incorrectly identified (over-estimated)	• % incorrectly identified (under-estimated)	Relationship rating (%correctly identified/ % incorrectly underestimated)
Ammonia	Yes (3)	Yes(3)	Temperature	70	30	15	15	4.6
BOD	No	Yes(4)	None	-	-	-	-	0
Chlorophyll	No	Yes(4)	444nm 490nm 665nm 681.25nm 759nm	NA	NA	NA	NA	NA
DO	Yes 80-120% saturation	Yes	None 753.75nm/ 760nm (MERIS)	-	-	-	-	0
E.coli	No	Yes freshwater possibly 400 counts/ 100ml	301.35nm	79	22	16	6	13.2
Faecal Coliforms	Guide 100 count/ 100ml. Fail 2000 counts/ 100ml	Yes	338.77nm 633.69nm	69 64	30 36	22 31	8 5	8.6 12.8
Nitrates	No	Yes (4)	911.88nm	64	35	30	5	12.8
Nitrogen	Yes (3)	Yes	Temperature (See Ammonia results)	70	30	15	15	4.6
High pH	Yes 6-9	Yes (2)	E.coli Ammonia Temperature	66 70 78	34 29 22	11 2 12	23 27 10	6 2.6 7.8
Low pH	Yes 6-9	Yes (2)	Temperature Ecoli	82 79	17 21	9 15	8 5	10.25 15.8
Phosphates	No	Yes (4)	911.88nm	60	40	20	20	3
Salinity	No	Yes (2)	Chlorophyll Suspended sediment mgl	72 71	28 29	8 14	15 15	4.8 4.7
Suspended Sediment	No	Yes (2)	575nm	NA	NA	NA	NA	NA
Temperature	Yes	Yes (2)	Thermal IR	NA	NA	NA	NA	NA
Total Coliform	Yes 500counts per 100ml guide, 10000 counts per 100ml Fail	Yes	649.93nm Faecal Coliform	56 72	44 28	4 14	40 14	1.4 5.14
Turbidity	Yes Guide 2m Fail 1m (local exceptions)	Yes (4)	None	NA	NA	NA	NA	NA

Key :2= Concentration to be checked when area shows the quality of water has deteriorated

3=When there is a eutrophication tendency

4= "Divergence from the normal....a change from normal conditions for the bathing area in question would. in any case, indicate that there is/has been an influx of 'strange' water - for example rainwater or wastewater - worth investigating" (COM(2000)860 Final 21.12.2000)

The predictor ratings were used along with the suggested spectral physical model (Figure 10.1) to produce a final threshold model for identifying high levels of EU bathing water quality parameters (Figure 10.3). The final threshold model shows that through the measurement of reflectance at ten wavelengths (or similar corresponding narrow wavebands) an estimation of bathing water quality could potentially be established that would incorporate a number of water quality parameters. The thickness of arrow indicates the confidence level in the threshold exceedance prediction that was possible using the field data.

The accuracy of prediction is inevitably going to be higher for the primary parameters E.coli, suspended sediments, faecal coliform, nitrates, chlorophyll an temperature. These primary water quality parameters would be highly indicative of water quality and would in most instances be adequate to produce an operational bathing water quality flagging system with an acceptable degree of reliability. The levels set for the threshold level of each parameter would need to decided by the monitoring authority involved. A threshold level set below the legal requirement would ensure a safer system but would also incur more false alarms and therefore cost of manual survey. It would seem likely that a monitoring authority might set critical parameters such as E.coli, and faecal coliform with lower thresholds so that most instances of failure would be detected but parameters such as nitrates could be set to a higher threshold level that is close to the legal guide level.

Figure 10.3 The Final Spectral Physical Model for EU bathing Water Quality

301.35nm

Thermal IR

575nm

444nm 700nm 759nm

338.77nm 633.69nm

649.93

911.88nm

E.Coli

Suspended Sediment
High confidence in accuracy using reflectance info from other research

Faecal Coliform

Nitrates

High pH

Low pH

Chlorophyll
High confidence in accuracy using reflectance Info from other research

Total Coliform

Phosphates

No relationship
BOD
DO
Turbidity

Temperature
High confidence in accuracy using reflectance info from other research

Arrow thickness based on the relationship rating (%correctly identifed/%incorrectly underestimated). Red arrows and parameters are based on other existing research.

Ammonia

Salinity

Spectral Physical Model of Thames Estuary Bathing Water

10.3 Conclusions and Recommendations

Remote sensing of water and, in particular coastal waters. is in its infancy and has been generally limited to quantifying a handful of water quality parameters. namely chlorophyll (and gelbstoff) (Matthews et al., 1994), suspended sediments (LOIS 1993) and temperature (Uncles, 2001). Work towards the 2002 launch of the instrument MERIS by Doerffer et al. (1997) started the move towards the development of operational remote sensing of coastal areas. Nevertheless, the only significant investigation into the use of remote sensing of the coastal environment by the EU was with the recently published European Environment Agency (EEA, 2002) report on the monitoring of algal blooms. Moreover. previous studies have concentrated on precisely identifying all levels of a water quality parameter and this research has shown that this is beyond the accuracy needed for operational purposes. The proposal that remote sensing be used as a flagging system to trigger manual sampling in certain areas is a cost effective, efficient and, more importantly, an achievable objective that can lead to an operational system with current levels of expertise. A remote sensed flagging system would require a new approach by the EU in future directives concerning bathing water quality monitoring. But. it could potentially lead to the ability to react to pollution events in near real time (an issue raised in EU COM2000) and to the improvement in safety standards of the coastal environment whilst reducing overall monitoring costs, especially in those countries with good water quality (itself an incentive for improving coastal water quality). Taking Italy as an example. if a flagging system had been running in 2001, only 213 of its approx.4500 beaches should have been flagged for manual monitoring (EU bathing water reports 2001). The number of beaches in each country will inevitably increase in the future and therefore there will be an increased potential to save costs.

This research has shown (Figure 10.3) the potential for the development of a remotely sensed flagging system for bathing water quality monitoring and has identified temperature, suspended solids, low pH, nitrates, chlorophyll, faecal coliform, and E.coli as the most likely water quality parameters that could be included in an operational system. Arguably the most important parameters for bathing water (particularly for public interest/health and therefore economic and political reasons) are the bacterial parameters. Of these E.coli and faecal coliform are potentially the most useful as they are accepted as good indicators of effluent pollution, which is the main problem in most bathing waters. For example, the Southend-on-Sea bathing samples have only ever failed on bacterial counts over the last eight years. Indeed, the new EU directive which will come into operation in 2004 only includes two microbiological parameters (E.coli and faecal streptococci). The results from this research have shown an exceptionally good predictive result with E.coli over a 200 count/ml level (78% correct) and a good result with faecal coliform proving the potential for an operational system.

10.3.1 The need and policy context of a remotely sensed flagging system

The increasing economic importance of bathing water quality and near coastal waters has led to recent revision in EU policy with the EU openly soliciting advice in the development of this policy to "streamline the European environmental water legislation....that will ensure the same environment ... but at the same time will take into account new approaches and new science and technologies" (EU COM(2000)860 p4) in order to accommodate the increasing numbers of coastal areas that need to be monitored. Indeed the EU 2000 policy document COM(2000) 860 Final specifically refers to an idealistic but realistically unobtainable objective that all EU coastal waters should be monitored. However, remote sensing has the potential to make this an obtainable objective. The

development of a remotely sensed system that produces a solution to a real world problem would also command developmental interest in the remote sensing community. For this to be accepted, the EU bathing water directives would need to accommodate a new approach. and include the secondary parameters, but the EU has already acknowledged that its policy will need to take account of new approaches and technologies in the COM(2000) 860 policy document. As stated in the introduction of this study. environmental remote sensing's ultimate goal must be to produce reliable, routine information that assists and improves the management of the environment. This objective was supported in EU policy concerning the funding and development of EU space policy through the 1992 EU communication document COM(92) 360 Final which placed strategic emphasis on the "operational uses of earth observation data that assist in the development of policies and procedures for the effective deployment and use of resources in the environment" (Sloggett, 1994, p26). The development of a remotely sensed flagging system would be a significant step toward this objective.

10.3.2 Contribution toward an operational system

The results of this research show that remote sensing could potentially be used to predict exceedance of threshold values for the main EU directive water quality parameters (with the exception of phosphates) in the Thames Estuary. This is especially true for the microbiological parameters (E.Coli has a 78% correct prediction at 200 counts /100ml in this study). and these are the parameters that the new 2002 directive (introduced in 2004) has decided are of paramount importance. indeed E.Coli and faecal streptococci are the only parameters that need regular testing in most coastal areas from 2004 onwards. If the results from this research were used to develop a remotely sensed "warning system" that triggers laboratory testing of an area when failure was predicted.

then the percentage of inaccurate predictions would be critical to the costs and accuracy of that system and this research's predictor ratings, summarised in Table 10.3, indicate how these could be evaluated for inclusion into an operational system. A remotely sensed flagging system would achieve a wide geographical coverage that would be both financially prohibitive and practically impossible to achieve through traditional manual spot sampling. Therefore a remotely sensed flagging system is likely to reduce costs if coverage is broadened as suggested by the EU in EU COM1994 and COM2000.

A wide coverage would allow both early identification of problems and identify sources and distribution of pollution and addresses the need for greater understanding of bathing water area quality for long term management. The implementation of a remote sensing warning system would allow comprehensive testing of problem areas by reducing the need for, and therefore costs of, manual surveys of all bathing water areas. This would allow spot sampling resources to be directed to any areas highlighted as being of questionable water quality. False alarms would obviously entail a financial cost (Table 10.3 gives an indication of the likely number) but if overall laboratory testing was reduced due to the warning system being employed in place of regular spot sampling, it could present an economy as well as an improvement to the service.

The supporting evidence of Petrenko *et al.* (1997), and Pinnicks *et al.* (2002), and the good predictive results of the microbiological parameters (E.coli and faecal coliform) suggest at the very least that an effluent flagging system could be achieved. The similarity of the current findings to those reported by Petrenko *et al.* (1997) is also highly supportive of the research methodology applied in this study.

This research has produced four sets of results which are a step toward the development of a fully operational monitoring system. This thesis has:

1. Identified which bathing water quality parameters could potentially be monitored through remote sensing in relation to the EU Bathing Water Directive

2. Identified optimum wavelengths for monitoring bathing water quality to meet EU directive guidelines and estimated the reliability of each wavelength by testing the reflectance data as a predictor for each water quality parameter

3. Identified secondary parameters for monitoring bathing water quality to meet EU directive guidelines and estimated the reliability of each by testing the reflectance data as a predictor for each water quality parameter

4. Developed a proposed spectral physical model (Figure 10.3) consisting of three separate components which can be used to develop accurate remote sensing water quality monitoring (flagging) models.

This thesis has applied a significantly different approach to remote sensing of water quality in a multi-parameter study (which is itself a significant departure from the vast majority of remote sensing studies). It has also proposed an original, practical approach to water quality monitoring and demonstrated the potential of remote sensing as a tool for a practical real world problem.

10.3.3 Limitations and further research

The research reported here has identified an approach to the application of remote sensing to a real world problem where present methods are both inadequate and

expensive, and where there is an increasing demand for the service from the EU and the public. While the results of this study show that remote sensing could be used as a warning or flagging system, they also indicate that it is highly unlikely that precise concentrations of the various EU water quality parameters could be measured. However, where the correct prediction percentages are very high, such as for E.coli, it is not inconceivable that with further advances in research, methods of measuring concentrations could be developed in the same way that suspended sediment, temperature and chlorophyll have been estimated in the past two decades. The reliability and efficiency of a threshold monitoring system or warning system would be dependent on improvements to the accuracy of the spectral physical model.

This research forms only the first part of a sequence of research that would be required before an operational system could be put in place. In the immediate future, a priority would be for similar research to be repeated for other Case 2 bathing water areas, to see if these research findings are applicable to other bathing water areas, or whether they are specific to the Southend-on-Sea study area. It is likely that different categories of coastal area would need a modified model to enable accurate prediction. Likely categories would be Case 2 estuary dominated (e.g. Southend-on-Sea, Clacton, Tynemouth, Grimsby); Case 2 coastal (e.g. Brighton, Frinton, Scarborough); Mediterranean; Atlantic coast; and Case 1 coastal waters. If this proved to be the case, different models might be needed for different bathing water zones. This would not prohibit the development of a remotely sensed flagging system for bathing water quality, as modern computing systems could process the data based on location given by a global positioning satellite system. Perhaps more significantly, the development of beach categories would answer the EU COM(2000) 860 Final communication document

call for the development of a beach profile, quantifying and identifying any local sources of pollution or contamination, and there by creating localised models for water quality management.

The significant implications of weather, environmental and atmospheric conditions discussed in Chapter 5 also need to be resolved for data to be collected by airborne or satellite sensor. However, it should be noted that researchers using CASI, SeaWiFS and MERIS data have forced progress on this issue over the last few years. Other potential approaches to data collection include the use of low-cost in-situ measuring devices recording selected wavelengths, which could prove ideal for areas like the UK where cloud cover is a problem. Spectral data collection could use existing buoys or platforms in bathing water areas, with the data sent periodically to a central computer in a similar way to the Bermuda Testbed Mooring Program (Ocean Physics Laboratory, 2002). For in-situ measurement, an artificial light source could be employed to eradicate the affects of both weather and atmospheric change. In-situ measurement would, however, return the sampling policy to point sampling removing the potentially increased accuracy in overall monitoring of an area that zone sampling using air based recordings could achieve (see Milton et al. (1995) for further discussion). The use of air-based recording also removes the need for duplication of equipment with one set of equipment potentially covering many bathing water zones.

Once the reliability and applicability of remote sensing of bathing water quality parameters has been proven, the integration of a predictive water quality model would allow the prediction of secondary parameters to be improved and also aid the

development of beach profiles (suggested by the EU in COM2000) for their management.

In summary, this research has proposed and successfully investigated a new approach to bathing water quality monitoring. The successful results should promote further research in this field and are a significant first step toward the development of an operational system.

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Abbreviations

CZCS	Coastal Zone Colour Scanner
CASI	Canadian Airborne Spectrographic Instrument
DEFRA	Dept. of Environment, Food and Rural Affairs Surveys
EA	Environment Agency
EC	European Commission
EOS	Earth Observation System
ESA	European Space Agency
EU	European Union
IR	Infra-Red
MERIS	Medium Resolution Imaging Spectrometer (normally referred to as MERIS)
NIR	Near Infra-Red
NERC	Natural Environment Research Council
NRA	National Rivers Authority

Satellite programmes/sensors referred to in the text:

CZCS
ENVISAT
ERS
Landsat
MERIS
MOS
Nimbus-7
SeaWiFS
SPOT

APPENDIX 1A Specifications

APPENDIX 1A1 EU Bathing Water Quality Directive

EU directives and some implications for remote sensing

The EU directives concerning the coastal zone and estuaries are broken down into several areas of concern. The first of these, dated the 7th of February 1975, included the quality of bathing water. This directive concerns all water where bathing is either practised by large numbers or is explicitly authorised and was intended to improve health problems, aesthetic attractiveness, amenity and quality of the environment. It was adopted in December 1975. The second set of environmental directives that concern the estuarine and coastal environments are for areas of shellfish waters. These were set out in a directive in November 1979 (following a meeting on October the 30th). These areas will generally tend to be more localised and therefore manual survey methods at the specific locations would be lower cost and more accurate. Some vary with the regularity required for the monitoring, because all parameters are surveyed irrespective of pollutant changes.

The EU directives also set out two extensive lists of 129 toxic metals, (lists I and II) which must not exceed very low levels (literally measured in parts per million). In most circumstances these are closely monitored at source. They are not tested for by the Environment Agency on a regular basis at bathing waters unless there are exceptional circumstances. Indeed, these substances only need sampling when "the quality of the water has deteriorated" (EU Directives). These substances have to be monitored using particular laboratory analysis methods. It would be futile to try to simulate such monitoring using remote sensing as it would never offer a real alternative. However, remote sensing can assist when these levels are higher through suspended solid levels/turbidity around outfall areas of these substances. This could be used in conjunction with laboratory testing and action by the appropriate authorities.

Table 1A1 is a detailed list of the parameters and when and how often they should be monitored (all information taken from the EU directives).

Table 1A.1 EU water quality directives in bathing and shellfish waters
The table sets out the frequency of testing and the method of analysis used in monitoring each parameter.

Key to frequency.

1=When a sample is taken in previous years produced results which were appreciably better than the set limits, and when no new factors are likely to lower the water quality, sampling may be carried out half as frequently (once a month in most cases).

2=Concentration to be checked when an inspection shows that the substance may be present or if the water quality appears to have deteriorated.

3= Only to be checked when there is a tendency toward eutrophication

PARAMETER	Frequency Bathing (Shellfish Directive only)	Current method of monitoring
MICRO BIOLOGICAL		
Total coliform	1	lab analysis
Faecal coliform	1	""
Faecal Streptococci	2	""
Salmonella	2	""
Entero Viruses	2	""
PHYSICAL CHEMICAL		
PH	2	Electronic
Colour	1 then 2	Visual
Mineral oils	1	Visual
Surface active substances reacting with methylene blue	1 then 2	no lasting foam -visual
Phenols	1 then 2	odour or spectrometry
Transparency	1	Sechi's disc
Dissolved oxygen	2	Winklers method
Tarry residues and floating debris	1	visual
Ammonia mg/l NH₄	3	only eutrophic waters
Nitrogen mg/litre N	3	only eutrophic waters
Heavy metals e.g.arsenic, cadmium, mercury,lead	2	Extraction
Nitrates and Phosphates	2	Laboratory
Pesticides mg/litre	2	Laboratory
Cyanides	2	Laboratory
Temperature	(Shellfish)	
Suspended sediments	(Shellfish)	

APPENDIX 1A2 GER SIRIS Specification

Geophysical Environment Research INC. Single FOV IRIS (SIRIS) is a high performance field spectroradiometer comprising two units: an optical head and portable computer.

- Extended wavelength operation: from 300nm-3000nm
- High spectral resolution: 2nm over 300-1000nm, 4nm over 1000-1800nm and 5nm over 1800-3000nm

Instrument samples an area of 34cm x 13cm from a height of 1.5m; angular field of view of 13 x 5 degrees. A boresight allows the SIRIS to be positioned over target. Single field of view means target and reference measurement are measured sequentially. Typical delay is one minute. Operation of the optical head is via software on the microcomputer which performs essential signal processing and hardware control to ensure good spectra under a wide range of illumination conditions. Pre-processing normalises spectra for variations in gain. The large field of view of the SIRIS means the instrument is better suited to field measurements than many other instruments.

Scan duration: typically 1 minute

Power source: 12v 5.7Ah battery and 6v 95Ah battery

Weight: optical head 6kg, case and ancillary equipment 17kg. Complete case designed to fit beneath aircraft seat.

Environmental limits: 0 to 50 degrees C. Housed in two metal cases. Weatherproofed and sealed against dust.

APPENDIX 2A Data Collection

APPENDIX 2A1 Sample Dates and Times

Three samples were taken each day.

Date	1st sample time	High/low(L) tide times.	Final sample time	Burnham Micro-biology Laboratory arrival	Enfield laboratory arrival	Chlorophyll BOD
21	S'PTON	NERC	EPFS			
August 95						
22	8.41	10.41	12.41	14.00	-	BOD Frozen
23	9.38	11.38	13.38	15.00	-	BOD Frozen
24	10.00	12.24	14.00	15.00	-	BOD Frozen
25	11.02	13.02	15.02	-	-	BOD Frozen
26S	11.38	13.38	15.38	-	-	BOD Frozen
27S	12.12	14.12	16.12	-	-	BOD Frozen
28	12.47	14.47	16.47	-	-	BOD Frozen
29	13.22	15.22	17.22	-	-	BOD Frozen
30	13.30	15.59	17.30	-	-	BOD Frozen
31L	8.30	10.30L	12.30	14.00	-	BOD Frozen
Sept 1995						
1L	9.00	11.05L	13.00	14.30	-	BOD Frozen
2LS	9.40	11.40L	13.40	-	-	BOD Frozen
3LS	11.00	13.00	15.00	-	-	BOD Frozen
4L	12.00	14.00	16.00	-	-	BOD Frozen
5*	8.25	9.25	12.25	13.30	15.00	BOD+chlorophyll
6	8.44	10.44	12.44	14.00	15.00	BOD+chlorophyll
7	9.49	11.49	13.49	15.00	16.00	BOD+chlorophyll
8	10.00	12.42	14.00	15.00	-	
9S	11.27	13.27	15.27	-	-	
10S	12.08	14.08	16.08	-	-	
11	12.42	14.47	16.47	-	-	
12	13.25	15.25	17.25	-	-	
13L	8.15	10.00	12.15	13.30	15.00	BOD+chlorophyll
14L	8.30	10.30	12.30	13.45	15.00	BOD+chlorophyll
15L	8.40	11.40	12.40	14.00	15.30	BOD+chlorophyll
16LS	9.00	11.40	13.00	-	-	
17LS	10.14	12.14	14.14	-	-	
18*	8.15	7.11	12.15	13.15*	14.00	BOD+chlorophyll
19*	8.00	8.29	12.00	13.15	14.30	BOD+chlorophyll
20	8.15	9.53	12.13	13.15	15.00	BOD+chlorophyll
21	8.59	10.59	12.59	14.30	16.00	BOD+chlorophyll
22	9.49	11.49	13.49	-	-	

L = Low tide day
S = Saturday or Sunday

* means times have been adjusted to conform with laboratory times.

APPENDIX 2A2 WATER ANALYSIS METHODS

Turbidity was measured using Sechi Disk with a rope with 0.25m delimination marked to a depth of 3metres.

Biological samples (E.coli, Faecal Coliforms, Total Coliforms) were analysed by the Microbiology Laboratory, Burnham on Crouch, Essex using the membrane filtration methods. Results are simple counts per 100ml. 400ml samples were used in the laboratory work, and samples were analysed within 3hrs of collection. samples were stored prior to this in a closed cool bag to maintain temperature as far as possible and to prevent UV light from entering.

All other analysis was carried out using the following methods at Middlesex University.

DETERMINATION OF TOTAL PHOSPHORUS IN WATER USING THE HACH DR2000 SPECTROPHOTOMETER (Acid persulfate digestion Method)

INTRODUCTION:
Samples were frozen on day of extraction and analysis carried out in September/October 1995. Phosphorus occurs in natural water and wastewater mainly as phosphate. Phosphates may enter water from agricultural run-off and biological and industrial wastes. A certain amount of phosphate is essential for most plants and animals, but too much phosphate in water can contribute to eutrophication, especially when large amounts of nitrogen are also present.

EQUIPMENT:
HACH DR2000 Spectrophotometer, hot plate and water bath, 25ml graduated measuring cylinder, 50ml conical flask, 1ml calibrated dropper, 2 x 25ml. sample cells and clippers.

MATERIALS:
Potassium persulfate powder pillow (SSDS No. P19) Sulphuric acid standard sol. 5.25 N (SSDS No. S27), Sodium hydroxide sol. 5.0 N (SSDS No. S26)

Warning: These chemicals may be hazardous to the health of the user and others if inappropriately handled. Sulphuric acid 5.25 N must only be used within a fume cupboard. Read relevant substance safety data sheets (SSDS) before use.

PRECAUTIONS:
Use in a working fume cupboard. Wear disposable gloves and safety goggles. Do not breathe chemicals.

METHOD:

Follow method 8190 on page 441 of the DR2000 Spectrophotometer Manual, followed by either method 8048 on page 433 (att.40(l)) or method 8178 on page 419 (att.40(h)) depending on the expected total phosphorus concentration range.

After the completion of testing discard contents of 25ml. sample cells into waste drain and wash with distilled water. Remove disposable gloves and wash hands thoroughly when testing activity is completed.

DETERMINATION OF NITRATES (range 0 - 4.5mg/l) IN WATER USING THE HACH DR2000 SPECTROPHOTOMETER

INTRODUCTION:
Samples were frozen on day of extraction and analysis carried out in September/October 1995. Nitrates in water are commonly derived from soils (in association with the use of nitrogenous fertilisers or the application of sewage sludge to the land), from vegetation and due to discharge of sewage effluent. In addition, nitrates can be atmospherically derived.

EQUIPMENT:

HACH DR2000 Spectrophotometer and 2 x 25ml. sample cells with stoppers.

MATERIALS:
NitraVer R 5 powder pillows (SSDS No. N2)

Warning: This chemical may be hazardous to the health of the user and others if inappropriately handled. Read relevant substance safety data sheets (SSDS) before use.

PRECAUTIONS:
Use in a well ventilated area or in a fume cupboard if available. Wear disposable gloves and safety goggles. Do not breathe chemicals.

METHOD:

As the samples were taken from sea water, the DR2000 instrument was manually calibrated to standards (with salinity to comparable levels to those of samples by raising chloride levels) at concentrations of :

standard	concentration of standard	absorbance set to
0	0	0.000
1	0.9	0.250
2	3.0	0.750
3	4.8	1.125

Follow method 8171 on page 313 of the DR2000 Spectrophotometer Manual.

After the completion of testing immediately discard contents of 25ml. sample cells into waste drain and wash thoroughly with distilled water. Remove disposable gloves and wash hands thoroughly when testing activity is completed.

SUSPENDED SEDIMENT CONCENTRATIONS

INTRODUCTION:

There are two stages in the determination of suspended sediment concentrations in streams. The calculation of a filter correction factor is necessary because filter papers themselves actually lose weight on wetting and drying. This weight loss must therefore be quantified for each filter paper before completing the filtration.

EQUIPMENT:

Drying oven or Microwave oven, Analytical balance, Buchner filter funnel and flask assembly connected by rubber hose to water jet pump, Whatman filter papers, 500ml. graduated measuring cylinder, forceps, glass petri dishes and an indelible pen.

METHOD:

Filter Correction Factor (FCF)

1. Accurately weigh a labelled Whatman filter paper to at least 3 decimal places on the analytical balance.

2. Place the filter paper into the Buchner filter assembly and dampen with distilled water.

3. Measure 400mls. of distilled water in the graduated measuring cylinder and pass through the filter assembly. This is done by pouring the distilled water into filter assembly and then turning on the water jet pump which will draw the distilled water through the filter.

4. Once all the distilled water has passed through the filter, using the forceps carefully remove the filter from the funnel and place on a glass petri dish. Then place in either a drying oven at 90°C for two hours to dry, or place in microwave oven on high power for approximately three minutes or until dry.

5. Remove from oven and re-weigh.

$$FCF = \frac{\text{Weight of filter paper after filtration}}{\text{Weight of filter paper before filtration}}$$

Suspended Sediment Concentration

1. Replace filter paper into filter assembly.

2. Dampen with distilled water.

3. Accurately measure 400mls. of vigorously shaken river water sample.

4. Pass river water sample through the filter paper in the filter assembly. Always pour slowly into the centre of the filter paper. Keep swirling and shaking the sample as you pour to ensure that no sediment is left on the sides of the measuring cylinder. If necessary use a small amount of distilled water to flush out the measuring cylinder.

5. Once all the water has passed through the filter remove the filter paper and dry in either the drying oven or the microwave oven and finally re-weigh the dry filter paper to three decimal points.

SS (gms.) = (wght of filter paper + sediment) - (FCF x wght of filter paper at beginning of filtration)

$$SS \text{ (mgs.)} = \frac{SS \text{ (gms.) x 1000}}{\text{volume of sample}}$$

SS (mgl-1) = mg x 1000

MEASURING BIOCHEMICAL OXYGEN DEMAND (BOD) OF RIVER WATER

INTRODUCTION:
BOD is a measure of the oxygen removed by organisms using the dissolved or even particulate organic matter in river water, and gives an approximate index of organic pollution. BOD is commonly carried out by measuring the dissolved oxygen concentration in river water samples before and after incubation in darkness at 20C. for 5 days. Preliminary dilution and aeration of the sample may be necessary to ensure that not all the O2 is used during incubation. Excess dissolved Oxygen must be present during the whole incubation period, and samples absorbing more than 6mgl-1 of O2 should therefore be diluted.

EQUIPMENT:
Checkmate system meter with Dissolved Oxygen probe. Incubation bottles of known capacity and an incubator thermostatically controlled at 20°C. + 1°C., from which all light is excluded. An automatic shaker, fridge, a large capacity plastic container, 4 X 1ml. pipettes, 1 litre measuring cylinder and various pipettes for dilution of sample.

MATERIALS:
Dissolved oxygen electrolyte (SSDS No. D5)
Zero oxygen solution (SSDS No. O2)
Phosphate buffer solution (SSDS No. P18)
Magnesium sulphate solution (SSDS No. M13a)
Calcium chloride solution (SSDS No. C11a)
Ferric chloride solution (SSDS No. F6a)

Warning: These chemicals may be hazardous to the health of the user and others if inappropriately handled. Read relevant substance safety data sheets(SSDS) before use.

PRECAUTIONS:
Use in a well ventilated area. Wear disposable gloves and safety goggles.

METHOD:
1. Measure 1 litre of distilled water(using the measuring cylinder) and pour into a large plastic container. Ensure that the distilled water has been thoroughly aerated, as near to saturation level as possible. This is done by shaking container of distilled water on an automatic shaker, keeping it as cool as possible. If necessary place occasionally in fridge. Be sure to avoid supersaturation, by checking the DO value of the distilled water by using the Checkmate system DO probe.

2. Prepare dilution water by adding 1ml.(using the 1ml. pipettes) of each of the nutrients in the following order; ferric chloride sol., calcium chloride sol. magnesium sulphate sol. and phosphate buffer sol., into the plastic container holding the aerated distilled water. Screw on lid and mix thoroughly.

3. The sample should be diluted according to the expected BOD range, following the guidelines below. It will be seen that most samples will require dilution in order to obtain accurate results.

Typical sample	BOD range (mgl-1) (parts)	Vol sample (parts)	Vol dilutent (parts)
Clean river	0 - 6	1	Nil
River	6 - 20	1	2
Sewage Effluent 10 - 30		1	4
Poor Effluent	20 - 60	1	9
Bad Effluent	40 - 120	1	19
Raw Sewage	100 - 300	1	49

4. Carry out dilution by pipetting 1 part undiluted sample and placing into an incubation bottle, and making up the volume with dilution water.

5. Measure the initial dissolved oxygen content (mgl-1) of the diluted sample, by lowering the checkmate DO probe into the sample and taking a direct reading.

6. Ensure that the incubation bottle is completely filled by topping up with dilution water. Insert the stopper making sure that no air is trapped in the bottle.

7. Place bottle containing diluted sample water into the incubator which must be set at 20oC. Leave bottles in incubator for a period of exactly 5 days(120 hours).

8. At the end of the incubation period, again measure the amount of dissolved oxygen content (mgl-1). by lowering the Checkmate DO probe into the sample and taking a direct reading.

9. Calculation   BOD mgl-1 = D0 - D1

Where   DO = Initial Dissolved Oxygen concentration (mgl-1).
D1 = Dissolved Oxygen level after 5 days incubation(mgl-1)
F = Dilution factor (e.g. if 5 times dilution, then F = 1/5).

10. After the completion of the test discard samples into waste drain with plenty of running water. Remove disposable gloves and wash hands thoroughly when testing activity is completed.

Measuring pH, Conductivity/TDS and Dissolved Oxygen using the Checkmate System

INTRODUCTION:
The Checkmate system allows the analysis of pH, Conductivity/TDS. and Dissolved Oxygen of water samples to be determined quickly and efficiently in either the lab or the field.

EQUIPMENT:
Checkmate meter M90 with three interchangeable electronic probes to measure pH, Conductivity/TDS and, Dissolved Oxygen. Small beakers(for calibration).

MATERIALS:
pH electrode filling solution (SSDS No. P2)
pH 4 Buffer solution (SSDS No. B6)
pH 7 Buffer solution   (SSDS No. B7)
Conductivity Standard solution 12.88ms. (SSDS No. C6)
Conductivity Standard solution 1413us. (SSDS No. C7)
Dissolved Oxygen Electrolyte (SSDS No. D5)
Zero Oxygen solution (SSDS No. O2)

Warning: These chemicals may be hazardous to the health of the user and others if inappropriately handled. Read relevant substance safety data sheets(SSDS) before use.

PRECAUTIONS:
Use in a well ventilated area. Disposable gloves and safety goggles are available for use in the lab or field.

METHOD:
Measurement of pH:
1. Attach the pH probe to the meter via a series of pins and push firmly together.

2. Remove wetting cap from the tip of the probe, and slide down the vent sleeve to reveal the fill hole. Ensure that the probe is filled to a level no lower than 1cm. below the fill hole with pH electrode filling solution, and tap gently to remove any air bubbles which may be present.

3. Press MODE once to switch the probe onto pH mode.

4. To calibrate pH probe: Lower probe into a small beaker containing pH 7 Buffer solution and press CAL once. An 'A' symbol will be displayed, and will stop flashing when 7 is displayed. Remove probe from solution, and rinse thoroughly with distilled water, and gently dab dry with tissue. Press CAL again and lower probe into a beaker containing pH 4 Buffer solution. The 'A' symbol will appear again and will stop flashing when 4 is displayed. The probe is now calibrated, and will require rinsing with distilled water before testing samples. If any difficulty arises with calibration ask a member of staff for assistance.

5. To read a sample, lower probe into water to be tested. Press READ and the pH of the sample will be shown. Ensure that probe is thoroughlyrinsed with distilled water between each sample tested.

6. When analysis is complete press MODE twice to turn the probe off. Replace wetting cap containing fresh pH 7 Buffer solution back onto the probe's tip, and reposition vent sleeve to cover over the fill hole.

Measurement of Conductivity/TDS:
1. Attach the Conductivity/TDS probe to the meter via a series of pins and push firmly together.

2. Ensure that the probe's outer sheath is in place when measuring.

3. Press MODE once to switch the probe onto Conductivity mode. or press MODE twice for Total Dissolved Solids mode.

4. To calibrate Cond/TDS probe: Press CAL once and wave probe gently in free dry air. an 'A' symbol will be displayed, and will stop flashing when 0 is displayed. Press CAL again and lower probe into a beaker containing either of the standard solutions(12.88ms. or 1413us.), ensuring solution is above cell chamber rings and below vent hole. The 'A' symbol will appear again and will stop flashing when 12.88ms/1413us is displayed whilst in the Conductivity mode, or 6.44gl-1 /706mgl-1 whilst in the TDS mode. Remove probe from calibration solution, and rinse thoroughly with distilled water. If any difficulty arises with calibration ask a member of staff for assistance.

5. To read a sample, lower probe into water to be tested. Press READ and the Conductivity or the TDS concentration for the sample will be given. Ensure that probe is thoroughly rinsed with distilled water between each sample tested.

6. When analysis is complete press MODE twice if in conductivity mode or once if in TDS mode. to turn the probe off. Rinse probe and outer sheath thoroughly with distilled water,and disconnect probe from meter and return both back to carrying case.

Measurement of Dissolved Oxygen:
1. Attach the Dissolved Oxygen probe to the meter via a series of pins and push firmly together.

2. Remove wetting cap from the tip of the probe. Ensure that the probe's anode tip is clean and that the membrane is filled with Dissolved Oxygen electrolyte. Gently tap the probe to remove any air bubbles which may be present within the membrane.

3. Press MODE once to switch the probe onto DO % saturation mode, or press MODE twice for DO mgl-1mode.

4. To calibrate DO probe: Press MODE once to obtain DO % saturation mode. Lower probe into a small beaker containing Zero Oxygen solution(ensure that the probe is submerged to just above the small hole), and press CAL once. An 'A' symbol will be displayed, and will stop flashing when 0%o is displayed. Remove probe from solution and, rinse thoroughly with distilled water. Press CAL again and gently wave probe about in free air. The 'A' symbol will appear again and will stop flashing when 100% is displayed If any difficulty arises with calibration ask a member of staff for assistance.

5. To read sample, lower probe into water to be tested. Press READ and the concentration for the sample will be given in either % saturation or mgl-1. Ensure that probe is thoroughly rinsed with distilled water between each sample tested.

6. When analysis is complete press MODE twice if in % saturation mode or once if in mgl-1 mode, to turn the probe off. Rinse probe thoroughly with distilled water, and replace wetting cap containing fresh distilled water back onto the probe's tip.

7. Always ensure that the checkmate is returned back to it's case with the DO probe attached in order to retain polarization of the DO probe.

8. Wash hands thoroughly once all testing activity is completed.

DETERMINATION OF CHLOROPHYLL-a IN WATER

INTRODUCTION:
An estimate of the green plant matter in a water body can be obtained by measuring the chlorophyll-a content of the water body. The chlorophyll-a content is determined by extraction of the pigment into acetone followed by the measurement of its visible absorbance.

EQUIPMENT:
Jenway 6105 uv/vis spectrophotometer, Buchner filter funnel and flask assembly connected by rubber hose to water jet pump. Ultrasonic water bath, centrifuge, 15ml centrifuge tubes. tube rack. 500ml

measuring cylinder. GF/C 5.5cm glass fibre filters, forceps, 10ml pipette, pipette filler, pasteur pipette, glass cuvettes, glass dropper and an indelible pen.

MATERIALS:
Acetone (SSDS No. A3)
2M Hydrochloric acid (SSDS No. H3)

Warning: These chemicals may be hazardous to the health of the user if inappropriately handled. Read all relevant substance safety data sheets(SSDS) before proceeding. Acetone is highly flammable therefore keep away from sources of ignition.

PRECAUTIONS:
Use in a well ventilated area. You must wear a lab coat, disposable gloves and goggles.

METHOD:
Note: Before commencing with the extraction, turn the Spectrophotometer on as it takes up to 30 minutes to warm up.

1. Using the measuring cylinder, measure out between 100 - 500mls of water sample.

2. Place a GF/C 5.5cm glass fibre filter paper into a Buchner filter assembly and carefully pour your measured water sample through the filter. Record the volume of water sample filtered.

3. Using forceps carefully remove the filter paper from the Buchner filter. Roll the filter into a cigarette shape and place it carefully into a clean and labelled 15ml centrifuge tube.

4. Using the 10ml pipette add enough acetone to cover the filter paper. Record the exact amount of acetone used.

5. Place the centrifuge tube in the tube rack and place into the ultrasonic water bath for 15 minutes.

6. Remove the 15ml centrifuge tube from the ultrasonic water bath and place it into the centrifuge and spin for 3 minutes at 3000rpm.

7. Calibrate the spectrophotometer in the absorbance mode to zero with distilled water. When recording results the sample area lid must be closed to ensure accurate results are obtained.

8. Using a pasteur pipette transfer some of the extract from the centrifuge tube to a 1cm glass cuvette. Place the cuvette into the spectrophotometer and record the absorbance at 665 and 750nm. Subtract the 750nm value from the 665nm value. The 750nm value serves to correct for any turbidity.

9. Using a glass dropper, add one drop of 2M Hydrochloric acid (made by adding 10mls HCL to 40mls distilled water) to the cuvette. Mix by inverting the cuvette and stand for one minute.

10. Place the cuvette back into the spectrophotometer and record the absorbance values again at 665 and 750nm. Again subtract the 750nm value from the 665nm value. The remaining figure is taken as the absorbance value due to pigments other than chlorophyll-a.

11. Calculate the chlorophyll-a concentration using the following formula:

$$\text{CHL-a (ug/l)} \quad = \quad \frac{29(A - Aa \times \text{vol. extract})(\text{ml})}{\text{vol. sample (L)}}$$

Where	A	=	corrected absorbance value at 665nm before acidification
	Aa	=	corrected absorbance value at 665nm after acidification.
	Vol. extract	=	is the amount of acetone in mls.
	Vol. sample	=	is measured in Litres.

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DETERMINATION OF AMMONIA NITROGEN IN WATER
(Using the HACH Ammonia Nitrogen test kit model No. NI-8)

INTRODUCTION:
Ammonia(NH_4) is the most common end point of the nitrogen cycle in soils. In waterlogged or arid environments it is readily leached from soils as it is highly soluble. In addition, it constitutes a major source of pollution from fertilizer application, slurry, sewage effluent and silage.

EQUIPMENT:
HACH Ammonia nitrogen test kit model No. NI-8 containing: colour comparator with Ammonia nitrogen colour disc 0-3 ppm, 2 x colour viewing tubes with stoppers, and a dropper.

MATERIALS:
Nesslers reagent (SSDS No. N1)

Warning; the chemical used in this activity is both toxic and corrosive, and therefore hazardous to the health of the user and others if inappropriately handled. Read the relevant substance safety data sheet (SSDS) before performing test.

PRECAUTIONS:
Use in a well ventilated area(i.e. in the field): use a fume cupboard when working in the lab. Disposable gloves and safety goggles must be worn. Do not breathe chemicals.

METHOD:
Note: A sample temperature of 20°c provides the best results. Warmer samples will give high results, cooler samples will give low results.

1. Fill the two sample tubes to the 5ml. mark with the water to be tested. Add 3 drops of Nesslers reagent to one of these tubes and swirl to mix.

2. Allow at least 10, but not more than 25 minutes for colour developement. If Ammonia nitrogen is present a yellow colour will develop.

3. Insert the tube of treated sample into the right hand opening of the colour comparator and the tube of untreated sample into the left hand opening.

4. Hold the comparator upto a light source and view through the two openings in the front. Rotate the colour disc to obtain a colour match and read the mgl-1 Ammonia nitrogen(N) through the scale window.

5. To express results as mgl-1 Ammonia(NH_3) multiply the mgl-1 Ammonia nitrogen by 1.2. To express result as mgl-1 Ammonium ion(NH_4) multiply the mgl-1 Ammonium nitrogen by 1.3. Note: 1ppm. = 1mgl-1

6. After the completion of the test discard sample onto the soil on the bank of the river tested(field).*

7. Remove disposable gloves and wash hands with tap water when available once testing is completed.

Although the chemical in this kit is labeled toxic and corrosive the small quantity used is likely to have a negligible effect on the water quality of the river. However if you are concerned discard sample into an appropriately labelled sample bottle.

DETERMINATION OF NITRATE IN WATER (0-50mgl-1)
(Using the HACH Nitrate test kit model No. N1-11)

INTRODUCTION:
Nitrates in river water are commonly derived from soils(in association with the use of nitrogenous fertilizers or the application of sewage sludge to the land); from vegetation; and due to discharge of sewage effluent. In addition, nitrates can be atmospherically derived.

EQUIPMENT:
HACH Nitrate test kit model No. N1-11, containing colour comparator with Nitrate colour disc. 2 x colour viewing tubes with stoppers.

MATERIALS:
NitraVerR5 powder pillow (SSDS No. N2)

Warning: This chemical may be hazardous to the health of the user and others if inappropriately handled. Read relevent substance safety data sheets (SSDS) before performing test.

PRECAUTIONS: Use in a well ventilated area. Wear disposable gloves and safety goggles. Do not breathe in chemicals.

METHOD:
1. Rinse the 2 colour viewing tubes several times with the water to be tested, then fill to the 5ml. mark.

2. Open one NitraVerR5 powder pillow and pour contents into one of the tubes containing the water to be tested. Stopper and shake vigorously for one minute. If Nitrate is present an amber colour will develope.

3. Allow to stand for one minute, and then place the tube into the right hand opening of the comparator. Place the other tube containing the untreated water sample into the left hand opening of the comparator.

4. Hold comparator upto a light source and view through the openings in the front. Rotate the disc until a colour match is obtained, then read the mgl-1 Nitrate Nitrogen(N) through the scale window.

5. Test results can be converted from mgl-1 Nitrate Nitrogen(N) to mgl-1 Nitrate(NO$_3$) by multiplying the scale reading by 4.4

6. After the completion of the test, discard sample on to the soil on the bank of the river tested (field).*

7. Remove disposable gloves and wash hands with tap water when available once testing activity is completed.

The quantity and nature of the chemical in this test will have a negligible effect on the water quality of the river. However if you are concerned, discard sample into an appropriately labelled sample bottle.

DETERMINATION OF PHOSPHATE IN WATER (0-50mgl-1)
(Using the HACH Phosphate test kit model No. PO-19)

INTRODUCTION:
Phospates in river water are commonly derived from the application of NPK fertilizer, detergents and sewage.

EQUIPMENT:
HACH Phosphate test kit model No. PO-19 containing; colour comparator with PhosVer R3 colour disc. 2 x colour viewing tubes with stoppers and dropper with 0.5 ml and 1ml marks.

MATERIALS:
PhosVer 3 Phosphate reagent powder pillows   (SSDS No. P4)

Warning: This chemical is classed as an irritant and therefore may be hazardous to the health of the user and others if inappropriately handled. Read relevant substance safety data sheet(SSDS). before performing test.

PRECAUTIONS:
Use in a well ventilated area. Wear disposable gloves and safety goggles. Do not breath in chemical powder.

METHOD:

Low range test : 0-5mgl-1
1.   Rinse the two colour viewing tubes several times with the water to be tested, then fill both tubes to the 5ml. mark.

2.   Open one PhosVerR3 powder pillow and pour contents into one of the tubes. Swirl to mix and allow at least one minute, but not more than five minutes for colour developement. If Phosphate is present a blue-violet colour will develop.

3.   Place the treated tube into the right opening of the comparator and the other tube containing original water sample into the left opening.

4.   Hold comparator up to a light source and view through the openings in the front. Rotate disc until a colour match is obtained, then read the mgl-1 in the scale window and divide by 10 to obtain the mgl-1 Phosphate (PO$_4$). To obtain the value as mgl-1 Phosphorous (P). divide the phosphate (PO$_4$) value by 3.

High range test : 0-50mgl-1
This method is similar to that for the low range test, but only 0.5ml. of water sample is used.

1. Fill the dropper to the 0.5ml. mark with the water to be tested. Discharge 0.5ml. of water into each of the two colour viewing tubes, and then top up to the 5ml. mark with distilled water.

2.   Follow instructions 2 to 4 as for the low range test. Read directly the mgl-1 Phosphate through the scale window. To obtain the value as mgl-1Phosphorous(P), divide the Phosphate(PO$_4$) value by 3.

3. After the completion of the test, discard sample on to the soil on the bank of the river tested.*

4.   Remove disposable gloves and wash hands with tap water when available once testing activity is completed.

* The quantity and nature of the chemical in this test has a negligible effect river water quality.

APPENDIX 3A Analysis

All the tables containing the correlation data are held on the attached CD entitled "CD1. Alex Moon. PhD Remote Sensing of Bathing Water Quality Appendix 3A1, 3A2, 3A3, 4A1- 4A13 . CD1"

- ❖ *APPENDIX 3A1 Correlation Analysis Summary Data*

- ❖ *APPENDIX 3A2 Water Quality Quartile Data for Each Parameter*

- ❖ *APPENDIX 3A3 Water quality data distribution*

Each Appendix is in a separate PDF file.

APPENDIX 4 Second Stage Analysis Additional Information

All the supporting figures of analysis at 50nm intervals and regression analysis figures are held on the attached CD1 entitled "CD1. Alex Moon. PhD Remote Sensing of Bathing Water Quality. Appendices 3A1, 3A2, 3A3, 4A1- 4A13. CD1"

All Appendices 4A1-4A13 are contained within one PDF file.

❖ *APPENDIX 4A1 Faecal Coliform p.1*

❖ *APPENDIX 4A2 Faecal Coliform Regression p.11*

❖ *APPENDIX 4A3 Total Coliform p.23*

❖ *APPENDIX 4A4 Total Coliform Regression p.33*

❖ *APPENDIX 4A5 Nitrates p.47*

❖ *APPENDIX 4A6 Nitrates Regression p.62*

❖ *APPENDIX 4A7 Phosphates p.65*

❖ *APPENDIX 4A8 Phosphates Regression p.74*

❖ *APPENDIX 4A9 Ammonia p.80*

❖ *APPENDIX 4A10 BOD p.89*

❖ *APPENDIX 4A11 Dissolved Oxygen p.98*

❖ *APPENDIX 4A12 Dissolved Oxygen Regression p.108*

❖ *APPENDIX 4A13 pH p.113*