An Investigation into changes in the phytoplankton community in Loch Creran, a Scottish sea loch

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0.2 Authorship

Part of this work (chapter 11) was carried out in collaboration with members of the SPICOSA project and I am grateful for all the help I received from them. The model used to determine phytoplankton growth in Loch Creran (chapter 10) was developed by the Comprehensive Studies Task Team (CSTT) with additional work by Celine Laurent (Laurent 2006). The author was responsible for reprogramming this model into EXTENDSIM7 and further enhancing it to include an anti-fouling compartment, a silicon compartment, and an integrated economic model. I am grateful for the MATLAB scripts used to calculate the Phytoplankton Community Index (chapter 3) which, were kindly provided by Paul Tett.

0.3 Abstract

Short term and irregular sampling in Loch Creran over recent decades suggested that changes may be occurring in the phytoplankton community in the loch. This study sought to confirm this suggestion. After instigating a regular sampling regime during 2008 and 2009 it became clear that significant changes had occurred, relative to information from the 1970s, in both the numbers of phytoplankton in the loch and in their biomass, particularly during the time of the spring bloom. Utilising a tool to assess change in the phytoplankton community, it also became clear that significant changes had occurred in the composition of the phytoplankton in Loch Creran. Work was undertaken to explore possible explanations behind these changes.

The effect that toxic, anti-fouling compounds, arising from an increase in leisure boating in Loch Creran, were having on the productivity of phytoplankton in the loch was considered by adapting an existing assimilative capacity model for phytoplankton growth. It was found, that at present levels of boating activity, the concentration of anti-fouling products present in the loch, would not be great enough to significantly impact on phytoplankton growth.

Nutrient samples collected during 2009 showed no significant changes in the concentration of silicate or nitrate in the loch, but phosphate levels were found to be significantly lower. A review of the effects of grazing on phytoplankton by farmed mussels in Loch Creran indicated that, at current levels, this would not account for the decrease in phytoplankton numbers observed in the loch.

Significant changes were observed in the water temperature in the loch and in the intensity and pattern of local rainfall. Increased levels of rainfall in the first three months of the year were found to be high enough to influence the rate of flush-

ing and the rate of phytoplankton washout from the loch. A correlation was found between the availability of light in the surface layers of the loch and the concentration of phytoplankton present in these layers. This correlation was found to exist, throughout the year and not only, as previously thought, during the winter months.

In conclusion, the observed decline in phytoplankton numbers in Loch Creran, was attributed to changes in local weather patterns, that had an impact on the physical structure of the water column, washout rates, the pattern and intensity of heterotrophic grazing and the availability of light.

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Chapter 1

Introduction

1.1 The Studentship

This studentship was funded by SPICOSA part of the European Unions Sixth Framework Programme. SPICOSA, an acronym for Science and Policy Integration for Coastal Systems Assessment that began in February 2007. The project involved 54 partners in 22 different countries collaborating to develop and test a framework that could be used to assess the different policy options available to coastal managers and policy makers. The aim was to apply a systems approach to the often socially complex issues involved in coastal zone management and to this end scientists from fields as varied as ecology, economics, social geography, mathematical modelling and sociology were brought together in an attempt to create an integrated approach to coastal zone science and attempt to enhance the link between science and policy.

Methods and tools developed during the project were tested at 18 study sites distributed across the member countries, each with its own unique ”issue”. The site chosen in the United Kingdom was the Clyde Sea on the West coast of Scotland. The study site was managed by Dr Tavis Potts a lecturer in marine policy at the Scottish Association for Marine Science and focussed on an issue raised by the Scottish Government in which, they called for an increase of between 50% and 100% in leisure boating and step ashore sites in the Firth of Clyde. This was to be accompanied by a similar increase in aquaculture. This issue resonated with local stakeholders who expressed concern that higher numbers of leisure boats and their crews could lead to an increase in pollution levels in the loch with detrimental effects on the local aquaculture.

While the site initially chosen was the Clyde Sea in reality this area proved too large for an effective study and so it was decided to focus on Loch Fyne in the upper reaches of the Clyde estuary. Given the limited time and resources allocated to this project it was also deemed necessary to refine the issue further. At the time there was a suspicion that changes were occurring in the phytoplankton community in Loch Creran a small sea loch approximately 50 miles to the North of Loch Fyne and that these changes were associated with an increase in anti-fouling compounds from the hulls of yachts and from the containment nets used on a local salmon farm. The issue of anti-fouling compounds and their effects in the local marine environment proved to be an acceptable focus for the SPICOSA study but unfortunately there was a lack of necessary data, particularly historic information on the ecological status of Loch Fyne. It proved advantageous therefore to move the initial parts of the study to Loch Creran where observations of the nutrient levels and phytoplankton community had been studied quite extensively during the 1970's, the mid 1980's and again in the early part of the 2000's.

An earlier study looking at the assimilative capacity of the loch (Laurent 2006) had found that nutrient levels in the loch had not significantly changed. However there were indications that some species of phytoplankton had decreased during certain times of the year. As part of the SPICOSA project it was hoped that each study site would develop an appropriately scaled integrated, ecological, economic and social model of the system they were studying. Given the difficulty in measuring concentrations of anti-fouling compounds *in situ* it seemed appropriate to concentrate one part of the ecological part of such a model on simulating the concentration of anti-fouling compounds in the loch when subjected to varying numbers of boats and to determine the effect that these loads would have on the growth of the phytoplankton community. The intention was that this model, concentrating on the growth of phytoplankton, would then be combined with an economic component and later integrated with a mussel growth model, programmed by a colleague. This integrated model will be discussed briefly in a later chapter.

As the model described in this thesis focusses on simulating the growth of phytoplankton in a sea loch it would seem appropriate to quickly summarise some of the key points regarding phytoplankton ecology as well as provide an introduction to the theories underlying the growth model and this can be found in the next section.

1.2 Phytoplankton

Plankton from the Greek adjective ($\pi\lambda\alpha\gamma\kappa\tau o\varsigma$) for ”errant” or ”wanderer” is, by convention, usually divided into three trophic levels or functional groups; plant (phytoplankton), animal (zooplankton) and bacteria (bacterioplankton). While some species are capable of swimming or altering their buoyancy (Villareal *et al* 1993) the speed and distances over which they can travel are generally overwhelmed by the natural horizontal and vertical turbulence found in the water column.

”*The sequence of populations* [of phytoplankton species] *is controlled by the physical environment, by advection and turbulence”* (Margalef 1978).

Marine phytoplankton comprising the photoautotrophic component of the plankton lives in the well lit surface waters of oceans, seas and estuaries, the photic zone (Simon *et al* 2009), where it obtains energy through photosynthesis. Most of the species, of marine phytoplankton of which there are estimated to be between 4000 and 5000 (Sournia *et al* 1991; Tett and Barton 1995) are single celled microscopic organisms (microphytoplankton) ranging between 20μm and 200μm and belong to the two domains: Bacteria and Eukarya (Simon *et al* 2009).

These organisms exhibit a wide variety of morphology, size and phylogenetic affinity and while there may be agreement on the classification of phytoplankton at the level of phyla, advances in the use of techniques such as gene sequencing, have led to a great deal of re-assessment when it comes to divisions within classes and even the legitimacy of what were believed to be well characterised species (Reynolds 2006).

In terms of their general morphologies the phytoplankton can be grouped into four broad categories; the diatoms with their ornamental frustules and spines, the dinoflagellates with transverse and longitudinal flagellum and a large nucleus, the coccolithophorids with cells covered in ornate calcite plates and the flagellates and monads comprised of naked or walled unicellular cells with one or more flagella.

Adl *et al* (2005) describes six eukaryote super groups four of which contain representatives from marine phytoplankton. These are further sub divided into eight divisions; Rhodophyta, Cryptophyta, Dinophyta (dinoflagellates), haptophyta, Heterokontophyta, Chlorophyta (green algae), Euglenophyta and zoomastigophora. Throndsen, *et al.* (2007). Of these, the haptophytes, the dinoflagellates (Dinophyta) and the diatoms (Heterokontophyta), dominate marine phytoplankton communities with the latter two comprising approximately 40% each of the species described in the literature. However while it is usual to make a functional distinction between phytoplankton and zooplankton this can, in some cases, be misleading particularly in the case of the dinoflagellates.

Approximately 50% of the species of recorded marine dinoflagellates contain chloroplasts nevertheless many of these also need organic substances such as vitamins, which they obtain from the surrounding environment and so should be characterised as auxotrophic while others will at times ingest organic particles including phytoplankton and should rightly be classed as mixotrophic. Indeed there are some species that utilise chloroplasts but first have to acquire them from ingested phytoplankters (Hoppenrath, Elbrachter and Drebes 2009). In general however any species that contains chloroplasts is considered to be phototrophic.

1.2.1 Phytoplankton and atmospheric composition

Based on isotopic fractionation of sulphur, oxygen began to accumulate in the atmosphere approximately 2.3 -2.4 billion years ago (Farquhar *et al* 2000). In evolutionary terms marine photoautotroph's appeared as early as 3.8Ga and biological biomarkers indicate that prokaryotic cyanobacteria and eukaryotic algae had evolved by 2700 Ma (Katz, Fennel and Falkowski 2007).

There is also a noticeable link between phytoplankton evolution and the carbon cycle. In today's oceans phytoplankton is a significant contributor to export production with larger eukaryotic phytoplankters accounting for a considerable part of the organic flux to the sea floor. Kooistra *et al* (2007), estimate that diatoms are responsible for approximately 60% of the sinking flux of particulate organic carbon in the oceans. Over hundreds of years this export of organic material from the ocean's surface to its depths helps to maintain a lower partial pressure of carbon dioxide in the atmosphere (Katz, Fennel and Falkowski 2007). On geological time scales however a part of this organic material will become incorporated into marine sediments, effectively removing it from the atmosphere. This can affect the redox potential of the oceans and can impact on the long term concentration of carbon dioxide in the atmosphere (Katz, Fennel and Falkowski 2007).

1.2.2 Primary production

While these primitive organisms have profoundly altered the biochemistry of the atmosphere and the oceans (Katz, Fennel and Falkowski 2007; Farquhar *et al* 2000) continual losses through grazing and sinking means that phytoplankton constitutes less than 1% of the planets photosynthetic biomass and yet it is responsible for approximately 46% of global net primary production (Reynolds 2006). Fenchel (1988) found that that in oligotrophic waters primary production tended to be governed by pico-plankton and nano-plankton and the microbial loop, whereby much of the energy flow and remineralisation is carried out by unicellular organisms and bacteria, formed the basis of the marine food web. Whereas in areas subject to inputs of nutrients, such as coastal areas, tidal fronts or seasonally affected temperate waters, larger phytoplankton has a tendency to dominate. These organisms are eaten by zooplankton or sink to the bottom sediments where they are broken down by benthic communities. In the latter case the food web generally has fewer trophic levels with more of the primary production being directed to larger organisms such as fish, (Fenchel 1988).

1.2.3 Seasonality

In temperate coastal waters, such as those found around the coasts of the British Isles, plankton exhibits an annual cycle (Tett 1987). During the winter months Lack of light leads to reduced growth. However, strong winds and turbulence mean nutrients and phytoplankton are well mixed throughout the water column. As light levels increase and mixing decreases during the spring a threshold is reached allowing phytoplankton to make use of the abundant supply of nutrients and for their numbers to increase rapidly. These high concentrations of phytoplankton quickly deplete the available nutrients and a combination of washout, where phytoplankton are removed from the loch by the outgoing surface flow of water, grazing and lack of nutrients causes their numbers to quickly decline. As the surface waters heat up during the summer, or as a result of freshwater inflow, the water column becomes increasingly stratified and the euphotic zone becomes depleted of nutrients, limiting phytoplankton growth. Towards the latter part of the year, as winds strengthen, increased turbulence in the water column may mix nutrients into the euphotic zone leading to a further smaller bloom during the autumn.

1.2.4 A theory to explain Phytoplankton growth

In 1844 Justus von Liebig, popularised a principle first developed by the German botanist Carl Sprengel, (Jungk 2009), stating:

"*When a given piece of land contains a certain amount of all the mineral constituents in equal quantity and in an available form, it becomes barren for any one kind of plant when, by a series of crops, one only of these constituents - as for example soluble silica - has been so far removed, that the remaining quantity is no longer sufficient for a crop,"* (Liebieg 1844).

This principle later became known as the law of the minimum. For phytoplankton to prosper they require a supply of nutrients, vitamins and light and the availability of these can affect the growth rate or determine the final biomass of a phytoplankton bloom. Droop (1974, 1975) applied the principle of the law of the minimum to chemostat studies when studying phytoplankton growth rates. He found that the growth of the haptophyte *Pavlova lutheri* was determined by the amounts of available vitamin B12 and phosphorous. Droop *et al.* (1982) later extended this principle of threshold limitation to include light.

Caperon (1968) and Droop (1968) also proposed that variations noted in the concentration of nutrients in phytoplankton cells could play a role in controlling their growth rate. Droop (1968) proposed a model where the cell quota (Q) is the ratio of nutrient (N) in a cell, which includes both free pool and structural nutrient components, to biomass (x). Each phytoplankton cell also has a minimum requirement for a given nutrient - the subsistence quota (kQ), below which growth will cease. Cell growth is determined by the nutrient which has the lowest ratio of Q:kQ.

"*The limiting nutrient is the one present in the cells in smallest amount relative to* *their need,"* (Droop 1975).

By separating nutrient uptake and growth, cell quota models allow the level of nutrients in a cell to vary between the subsistence quota and a maximum quota (Qm). This allows a cell, when a nutrient is plentiful, to take up more than necessary, (luxury uptake), particularly when another nutrient in short supply may be limiting growth. It should be noted that in cell quota models the uptake of a particular nutrient should be related to the algal biomass and not to the nutrient concentration in the algal cell, (Tett 1984).

1.2.5 Physical Processes

As mentioned above the movement of phytoplankton in the water column is largely the result of horizontal and vertical turbulence, and advection. Tett and Edwards (1984), Tett *et al* (1986) suggest that the distribution of phytoplankton is mainly due to vertical turbulence and argue that while horizontal mixing and advection may play a role it is a minor one. Non directional turbulence moves nutrients from deeper water, where they have undergone re-mineralisation, up into the photic zone where they can again be used by phytoplankton. The same process also acts in reverse moving phytoplankton cells out of the photic zone. The success of the phytoplankton largely rests with the degree of turbulence in the water column. Too severe and the rate of diffusion of phytoplankton out of the photic zone may be greater than its growth rate, too mild and nutrients will not diffuse into the photic zone quickly enough to support a large biomass, (Tett and Edwards 1984; Pingree *et al* 1976).

1.2.6 Algal Blooms

As already mentioned given ample light and sufficient nutrients, phytoplankters will have a tendency to grow, often exponentially, and this can sometimes cause a localised bloom with unfortunate consequences. Many human activities take place in and around estuaries, fjords, lagoons and embayment's, regions where the water is enclosed on three sides and exchange with the open sea is restricted. As human activities have increased the input of nutrients in the form of sewage or agricultural run-off has increased as has the tendency for eutrophic conditions to develop. At the same time these areas are increasingly being used for activities such as the culture of finfish and shellfish. In an attempt to ameliorate the effects of excessive algal growths the European commission introduced the Urban Waste Water Treatment Directive (CEC 1991). In 2003 the Commission for the Protection of the Marine Environment of the North East Atlantic, OSPAR also introduced its own strategy to combat eutrophication (OSPAR 2003).

While an algal bloom can be unsightly, appearing to stain the water for example, a deep red or brown, perhaps its biggest threat comes from the production of toxins. Certain species of phytoplankton, when gathered in sufficient numbers, release toxins into the water, known as harmful algal blooms (HABs), and these poisons can have detrimental impacts on other marine organisms and man. Shellfish filter organic particles including phytoplankters from the water column and will begin to accumulate any toxins present rendering a crop unsafe to eat and temporarily depriving a farmer of his livelihood. While many harmful algal species exist in relatively low concentrations, others can cause significant blooms. As these algae exhaust the supply of nutrients and begin to die, the decaying algal remains can quickly smother benthic organisms and lead through an increase in microbial activity to the development of hypoxic or anoxic conditions on the sea floor.

1.2.7 Eutrophication

Eutrophication, the process whereby water bodies are enriched, either through natural or artificial means, with nutrients, has long been regarded as a problem, and understanding the mechanisms linking it to the development of harmful algal blooms has been the topic of several research projects. The water Framework Directive (WFD 2000/60/EC) ratified in 2000 and transposed into UK law in 2003, lays down a framework to protect groundwater, inland surface waters and transitional and coastal waters. This directive has several objectives, amongst them the prevention of further deterioration of water resources, the sustainable use of these resources, an increase in protection and improvement of the aquatic environment, including a reduction in pollution, and efforts to reduce or at least mitigate flooding.

Paramount to these objectives is the aim to achieve good ecological quality status for all water bodies by 2015 (Borja *et al* 2005). Determining the status of a water body will be based on various factors including biological, hydromorphological and physico-chemical elements. Chief amongst these is the biological component which will include the status of the benthos, fish, macro algae and phytoplankton.

From the above it seems clear that phytoplankton plays an important role both in terms of global climate and, forming the basis of most marine food webs, in food supply. It is important therefore that an effort is made to understand the mechanisms and reasons underlying any observed changes in a phytoplankton community in an attempt to improve the understanding of the ecological functioning of these systems, particularly in instances where some unexplained change or ecological dysfunction has occurred.

Indeed this was the case in Loch Creran, a Scottish sea loch on the West coast of Scotland. Studies of the phytoplankton community in Loch Creran were started in the 1970's and continued until the early 1980's. There then followed a hiatus until 2003 when studies resumed. At this time it was noted that the concentration of chlorophyll, particularly during the spring bloom, appeared to have declined when compared with previous studies (Laurent 2006).

1.2.8 Aims

The aims of this study are twofold. First to compare the present physical and biological attributes of Loch Creran with historical data, to determine if there has been a significant change.

Second, if there has been a change in the community to attempt to understand the underlying causes that may have led to that change.

Due to their size and the environment they inhabit it can prove problematic to study phytoplankton in the field, often needing the use of expensive research vessels to allow samples to be taken. Additionally, it can prove difficult and costly to carry out experiments in the field to examine the effect of a change in one of the factors that may be controlling their growth. One possible approach, and the one chosen for this study, is to develop a mathematical model of the system. Through the use of such a model the different variables at play in the system can be easily manipulated and the outcomes predicted. This allows different scenarios to be simulated and can highlight those areas where further study may be profitably focussed. A description of this model can be found in chapter 10.

This thesis is therefore divided into several chapters which, are intended to stand alone and that in each case consider possible underlying causes for any observed change in the phytoplankton community. The testable hypotheses to be addressed are introduced at the beginning of each chapter.

Chapter 2

Evidence of Change

2.1 Introduction

A comparison of recent studies (Laurent *et al.*, 2006), with earlier ones (Tett and Wallis 1978; Tett, Heaney and Droop 1985), has suggested there may have been a change in the composition of the microplankton community, comprised of micro algae, protozoa and bacteria smaller than 200 micrometers (Tett *et al.* 1988), present in loch Creran, particularly in the abundance of the diatom *Skeletonema* spp. Major changes that have occurred in the loch include the introduction in 1983 of a fish farm and more recently an increase in mussel aquaculture and in the number of moorings available for leisure craft.

The growth of phytoplankton can be significantly affected by the concentration of available nutrients in a body of water. With the introduction of a fish farm in the 1980's it might be expected that the concentration of nutrients in the loch would increase. However, while nutrient inputs from fish farming have increased there has been no apparent increase in nutrient concentrations in the loch, (Laurent *et*

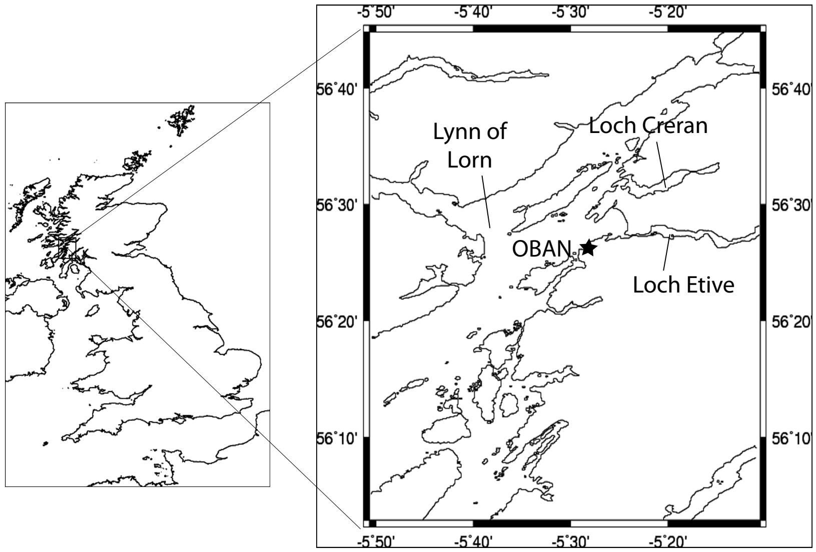


Figure 2.1: Location of Loch Creran, West coast of Scotland

al. 2006). This suggests that the reason for any observed decline in *Skeletonema* spp. may lie elsewhere. Changes in the level of precipitation, turbidity and flushing times and an increase in bivalve aquaculture are all possible causes while the introduction of a fish farm, combined with an increase in leisure boating and commercial boat traffic has led to speculation that an increase in the concentration of biocides, present in anti-fouling paints on boat hulls and aquaculture nets, may be contributing to a possible decline in diatoms (Gatidou and Thomaidis 2007; Evans *et al.* 2000; Brand *et al.* 1986; Morel *et al.*, 1978). The aim of this chapter is to compare the present physical attributes of the loch with historical data and attempt to determine if there has been any significant change in either the composition or the abundance of the phytoplankton community in the loch the null hypothesis being that there has been no such change.

2.2 The study site

Loch Creran is a small sea loch or fjord lying 16.5 km North of the town of Oban on the West coast of Scotland (Figure 2.1). This loch, approximately 13 km long and averaging 1.3 km wide, was extensively studied during the 1970's and 1980's and data were collected on its physical, chemical and biological characteristics.

Fjords in Scotland are generally formed where ancient river valleys have been scoured and deepened by glaciation (Bird 2008). As eustatic changes in sea level since the last ice age have occurred, these have then become inundated with sea water. They are distinctive in that they have relatively shallow sills, often the remains of morainic debris, and typically much shallower than the water in the loch, separating them from the open sea.

Loch Creran (see figure 2.2) has four sills, two with a mean water depth of 7.5 meters, at the entrance, a third at a depth of 15 meters dividing the main basin into two and a fourth, with a mean depth of 3.5 meters, separating the main basin from the upper basin. The average water depth in the loch is 13.5 meters, with a maximum depth of 49 meters in places and the tidal range is 3.3 meters (Edwards and Sharples 1986).

2.3 Water circulation in a typical Scottish sea loch

Fjords typically exhibit a two layer pattern of water movement; with an upper brackish layer, fed by inflowing rivers, moving outwards toward the open sea and deeper, higher salinity water flowing inwards, through tidal pumping (see figure 2.3). As this denser water moves up the loch it is gradually entrained into the upper brackish

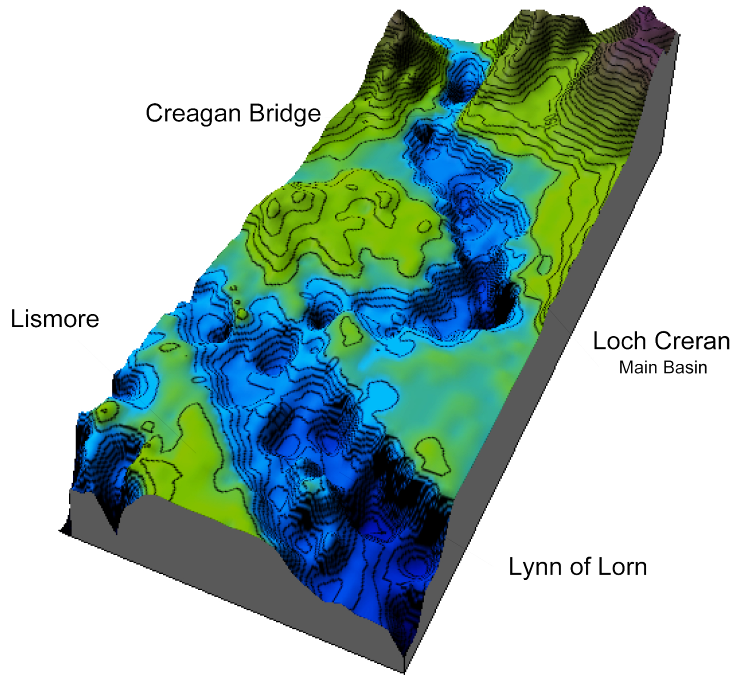


Figure 2.2: Contour plot of Loch Creran and part of the Lynn of Lorn illustrating the presence of shallow sills, those areas depicted in lighter blue shades, and deeper areas, those depicted in darker blue shades, within the loch. The plot is based on bathymetric data contained within admiralty chart 2378, *Loch Linnhe Southern part*. The vertical axis has been greatly exaggerated.

layers carrying its nutrient load with it. However the density of the water in the open sea at the level of the sill is not usually enough to displace water at the deepest levels of the loch and this dense bottom layer may persist for weeks or even months before it is replaced. As any detrital material in this deep layer is gradually broken down by microbial action, it is possible that the consumption of oxygen will cause this layer to stagnate, (Tyler, 1983).

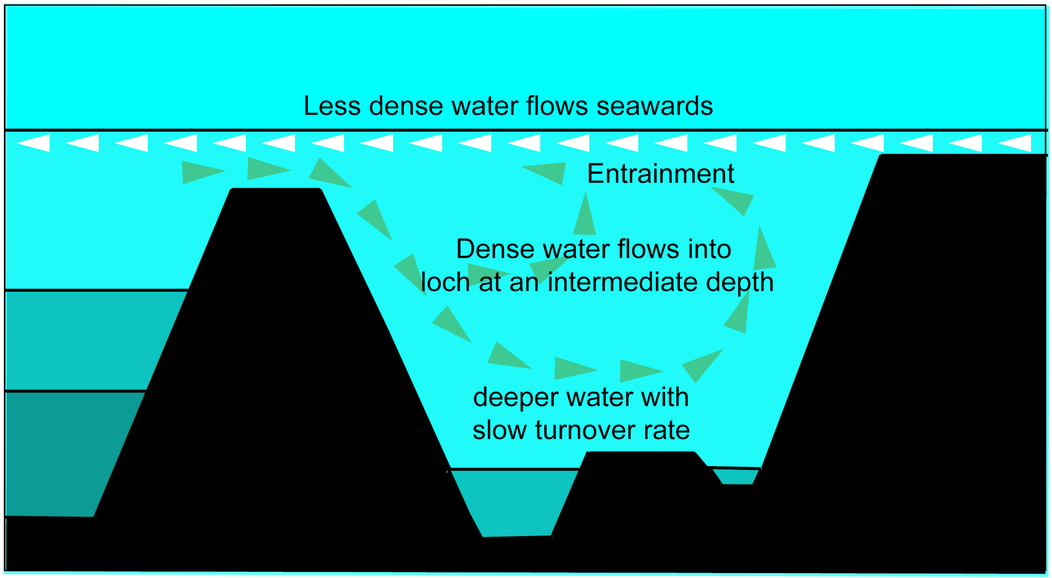


Figure 2.3: Cross section of a typical sea loch showing the shallow sill separating the loch from the open sea. Less dense, brackish water, from rivers or run-off, flows seawards as denser sea water flows into the loch and moves landwards at an intermediate depth. This denser water, carrying nutrients, is gradually entrained into the surface water.

2.4 Methods

2.4.1 Water Sampling

Previous work (Laurent 2006) suggested that the most significant changes in the loch had taken place during the spring bloom which usually occurs towards the end of March. Therefore when setting up a sampling regime it was decided that greater emphasis should be placed on the months of March, April and May, with samples being taken once a week. During the rest of the year the intensity of the sampling decreased from two every three weeks during June, July and August to once per month during September, October and November. The sampling dates, locations and depths for both 2008 and 2009 can be found in appendix A.

In 2008 the research vessel RV Serpula, based on Loch Creran and owned by

Heriot-Watt University was chartered by Edinburgh Napier University (ENU) for two trips during the spring so that boundary conditions in the Lynn of Lorn could be determined and to allow temperature, depth, salinity and light penetration to be measured at several sites within Loch Creran. Samples were collected from four distinct sampling stations during each of two cruises which transected Loch Creran from the upper basin to the Greag Isles in the Lynn of Lorn. The location of the stations was chosen to match as closely as possible the stations used for sample collection during the 1970's. Measurements of fluorescence, dissolved oxygen, temperature, density, salinity and light attenuation were taken using an SBE 19plus SEACAT profiler supplied by Sea-Bird Electronics Inc. Washington 98005, USA and owned by ENU. At the same time discrete samples of water were obtained by attaching 5 litre Niskin bottles to the cable holding the profiler, from the lee side of the vessel while at rest, and remotely triggering them by a messenger. Samples were preserved in dissolved oxygen bottles, carefully ensuring that no air was trapped in the bottle, by adding 1ml of manganese sulfate followed by 1ml of potassium iodide and mixing well. These were then transported to ENU for later analysis of their dissolved oxygen content using the Winkler method.

Additionally, within six to eight hours of being collected two 0.5 litre aliquots, measured in a one litre measuring flask, were removed and filtered in a Nalgene 1 litre filtering unit, fitted with a Whatman GF/F 47 mm diameter filter, and utilising a vacuum of 150 mmHg induced by a Mityvac Silverline MV 4000 hand pump. After each sample was filtered the filter was carefully folded with a pair of tweezers and placed into the bottom of a 10 ml centrifuge tube and placed into a freezer at -9 degrees centigrade for storage until further analysis.

These samples allowed the results obtained by the Seacat profiler to be calibrated against observations. Further samples were stored in 250 ml glass bottles and treated by adding 1% by volume of 10% acidified Lugols iodine and gently shaking the bottles. These samples were then stored in the dark at 4^0C. This both preserved and stained the samples for later analysis on an inverted microscope.

In 2009 the research vessels RV Seol Mara and RV Calanus, both operated by the Scottish Association of Marine Science (SAMS), Dunstaffnage, were chartered for eight transects of the Lynn of Lorn and Loch Creran starting in March and ending in October. The same process of collecting water samples was used however as well as sampling at the sites originally used in 2008, the number of stations was increased to twelve and again the sites chosen matched those used during the 1970's. Four of these stations were located in the Lynn of Lorn and eight were located in Loch Creran (See figure 2.4 and table 2.1).

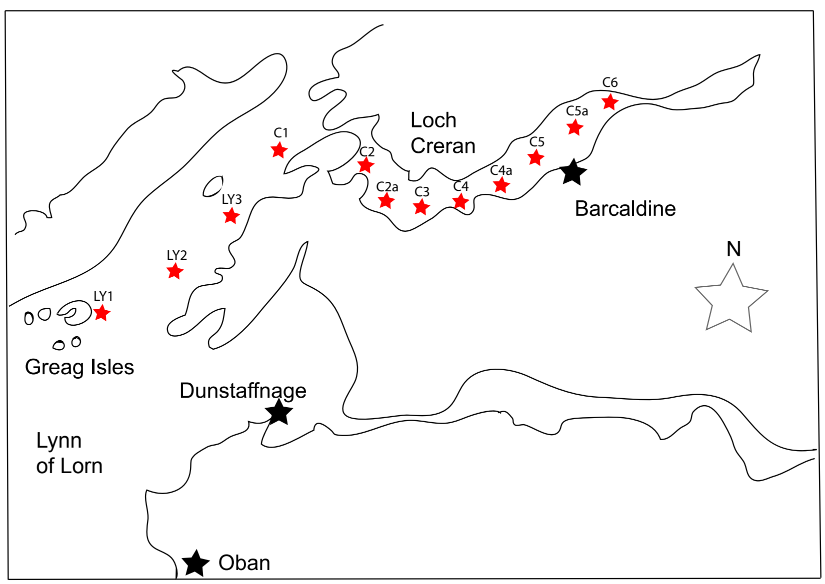


Figure 2.4: Sampling stations in the Lynn of Lorn and Loch Creran

Shore based water samples were also collected from Barcaldine pier, Barcaldine on Loch Creran approximately once a week during the spring falling to once every

Table 2.1: Location of sampling sites visited in Loch Creran and the Lynn of Lorn.

Name of Station	Location	Position: Northing	Position: Easting
LY1	Lynn of Lorn	56^0 29.013′ N	5^0 30.105′ W
LY2	Lynn of Lorn	56^0 30.241′ N	5^0 27.951′ W
LY3	Lynn of Lorn	56^0 31.459′ N	5^0 26.800′ W
C1	Lynn of Lorn	56^0 31.873′ N	5^0 26.102′ W
C2	Loch Creran	56^0 31.862′ N	5^0 23.913′ W
C2a	Loch Creran	56^0 31.313′ N	5^0 23.076′ W
C3	Loch Creran	56^0 31.109′ N	5^0 22.075′ W
C4	Loch Creran	56^0 31.549′ N	5^0 20.790′ W
C4a	Loch Creran	56^0 31.820′ N	5^0 20.143′ W
C5	Loch Creran	56^0 32.042′ N	5^0 19.751′ W
C5a	Loch Creran	56^0 32.447′ N	5^0 18.978′ W
C6	Loch Creran	56^0 32.867′ N	5^0 18.233′ W

three weeks during the summer. The samples were collected in a two litre Ruttner bottle from a depth of one meter. The water samples were immediately decanted into two, one litre vacuum flasks and three 250 ml glass medical bottles. Each of these was thoroughly rinsed with water from the sample before use. Two of the bottles were immediately sealed for later analysis of salinity and pH while 10% acidified Lugol's Iodine was added to the remaining bottle which was then gently shaken to preserve any phytoplankton present. The samples were subsequently transported to Edinburgh Napier University where they were stored in the dark awaiting examination. Within six to eight hours of being collected two 0.5 litre aliquots, measured in a one litre measuring flask, were removed and filtered in a Nalgene 1 litre filtering unit, fitted with a Whatman GF/F 47 mm diameter filter, and utilising a vacuum of 150 mmHg induced by a Mityvac Silverline MV 4000 hand pump. After each sample was filtered the filter was carefully folded with a pair of tweezers and placed into the bottom of a 10 ml centrifuge tube and placed into a freezer at -9 degrees centigrade for storage until further analysis.

2.4.2 Chlorophyll Analysis

Determination of Chlorophyll standard concentration

Before calibrating the fluorometer (the technical details are included below), it was necessary to establish the concentration of chlorophyll used as a standard. Following the methods outlined in Tett (1987), a one milligram sample of Chlorophyll *a*, extracted from spinach, batch number 038K5150, was obtained from Sigma Aldrich Co Ltd, Gillingham, Dorset. This was added to one litre of 90% acetone and kept in a darkened flask at 4 degrees centigrade for 24 hours to allow for 're-hydration' of the sample. Aliquots of the chlorophyll solution were placed into 4 cm path length cuvettes and analysed with a M550, double beam, scanning UV\visible light spectrophotometer supplied by Camspec-Spectronic Analytical Instruments, Tudor House, Garforth, Leeds, England, with a bandwidth of 1.8 nm. The optical density of the cuvette containing the chlorophyll standard was measured against a blank cuvette, containing 90% acetone, at approximately room temperature. Four drops of 2N 8% Hydrochloric acid were then added to each cuvette. The cuvettes were gently shaken for thirty seconds before being wiped clean and the optical densities were measured again. The absorbance at 750 nm was also recorded. the optical densities were corrected by first subtracting the value of the blank and then, to correct for turbidity, subtracting the optical density observed at 750 nm.

The red extinction peak for chlorophyll *a* in acetone is 663 nm, however the accuracy of spectrophotometers can vary and in this case as the optical bandwidth of the spectrophotometer was 1.8 nm the maximum observed extinction wavelength could be expected to lie anywhere between 661.2 nm and 664.8 nm. The actual wavelength, as determined by the spectrophotometer, corresponding to the red extinction peak for chlorophyll can be determined by finding the maximum optical density and observing the wavelength at that point.

The concentration of the chlorophyll standard was calculated from the equation:

$$\text{Chlorophyll concentration} = \frac{Absorbance\ at\ 663nm}{SEC \times\ path\ length}\ \mu\text{g ml}^{-1}$$

Where SEC = the Specific Extinction Coefficient of Chlorophyll *a* = 87.67 (Jeffrey and Humphrey, 1975) and the path length = 4 cm.

Fluorometer calibration

The Turner TD 700 Laboratory fluorometer, supplied by Turner designs, Sunnyvale, California, USA, was set up for chlorophyll analysis according to the instructions from the manufacturer, and calibration and subsequent measurements were made following the methods outlined in (Tett, 1987). In order to relate the fluorescence measurements, obtained in fluorescence standard units from the instrument, with the concentration of pigments in the samples the fluorometer had to be calibrated. A solid state standard was placed in the instrument and a reading of the fluorescence was taken. Aliquots were then taken from the chlorophyll standard which, had a concentration of 0.399 mg/ml^{-1} and various concentrations were made, ranging from 1:1 to 1:1000. Fluorescence readings were taken of each concentration before (f_o)(fluorometer units) and after (f_a)(fluorometer units) 2 drops of 2N 8% Hydrochloric acid were added. A blank containing only 90% acetone was also read before and after acidification. From these readings the following factors were calculated:

$$\text{Acidification Factor}\,(H_f) = \frac{F_c}{F_p}$$

Where F_c and F_p are the specific fluorescence coefficients for chlorophyll a and pheopigments respectively in 90% acetone at 663nm.

$$F_c = \frac{f_o}{S.S.S\,td \times\ concentration} \tag{2.1}$$

$$F_p = \frac{f_a}{S.S.S\,td \times\ concentration} \tag{2.2}$$

$$K_f = \frac{1}{1 - \dfrac{1}{H_f}}$$

Where units of K_f are given in (μg chl a) ml^{-1} (fluorometer unit)$^{-1}$.

$$\text{Chlorophyll Concentration} = K_f.(f_o^{'} - f_a^{'}).\frac{E}{V}$$

$$\text{Pheophytin Concentration} = K_f.(H_f \times\ (f_a^{'} - f_o^{'}).\frac{E}{V}$$

Where: the concentration of both chlorophyll and pheophytin is given in μg ml^{-1}, E = volume of the extract in ml and V = volume of the sample in litres. The terms f'_a and f'_o are given by:

$$f'_o = \frac{f_o - \text{blank}}{\text{S.S.Std}}$$

$$f'_a = \frac{f_a - \text{blank}}{\text{S.S.Std}}$$

To obtain the values of F_c and F_p used in the calculation of H_f and K_f the readings obtained for f_o and f_a, corrected for the blank, at different concentrations were divided by the value obtained from the Solid State Standard (S.S.Std) and the ratios were plotted onto a graph (See Figure 2.5). $\frac{F_c}{F_p}$ was calculated by taking the ratio of the slope of the two lines.

2.4.3 Fluorometrical analysis

Following the steps outlined in (Tett, 1987) the pigments were extracted from the filter by the following method, 10 ml of 90% acetone were pipetted into the centrifuge tube while the filter was still frozen. These centrifuge tubes were then placed in a refrigerator at 4 degrees centigrade for a minimum of 18 hours and a maximum of 72 hours. On removal the tubes were centrifuged for a couple of minutes to move the filter to the bottom of the tube then shaken to ensure the pigments were equally mixed throughout the tube. Finally the tubes were recentrifuged and the volume of the extract (E, ml) was recorded.

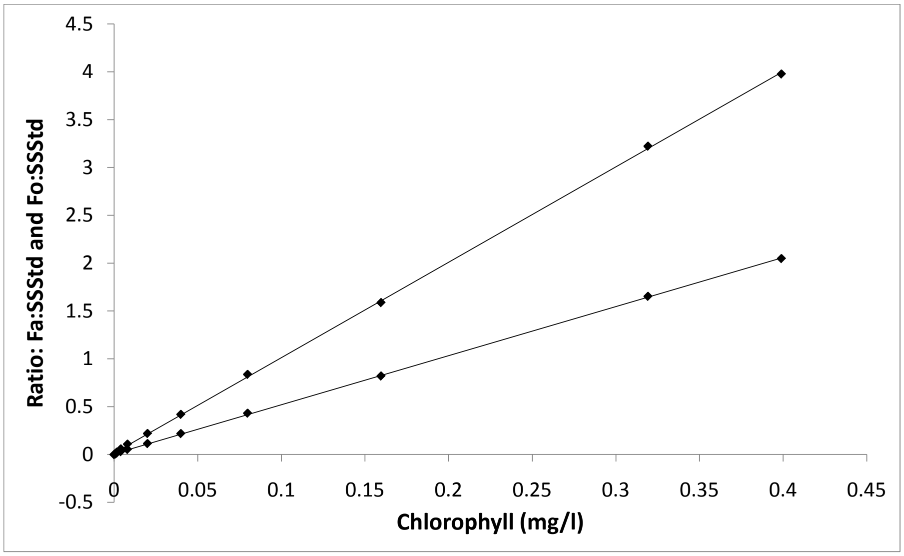


Figure 2.5: Diluted chlorophyll standards plotted against laboratory fluorometer readings used for calibration. The upper line represents the measurements made before acidification while the lower represents measurements made after acidification.

The fluorometer, was set up to use 25mm test tubes. Before taking a measurement the tube was rinsed thoroughly with 90% acetone then rinsed again twice with a small volume of the extract. The remaining extract was then added to the tube which was carefully wiped clean then placed in the fluorometer. Once the reading (f_o) was taken the tube was removed and two drops of 2N 8% Hydrochloric acid were added to the tube. the tube was gently shaken, wiped clean and placed back into the fluorometer and a final reading (f_a) was taken. These results were then substituted into equations (2.1) and (2.2) to calculate F_c and F_p respectively.

2.4.4 Phytoplankton Species Composition, Abundance and Morphology

Aliquots were removed from the preserved sample of loch water and placed into a 10 ml settling chamber where they remained in the dark for a minimum of 12 hours. Once settled the samples were examined on a Carl Zeiss Axiovert 25 inverted microscope supplied by The Microscope Company. Netherton House, Glasgow, U.K. fitted with 10x, 20x and 40x magnification objectives and 10x eyepieces. Samples were examined using both brightfield and phase contrast.

Each chamber was examined by counting the number of organisms present in a horizontal strip across the diameter of the chamber at 200x magnification. A count was also made of the ciliates and dinoflagellates in each sample. The chamber was then examined by counting the number of small flagellates present in a horizontal strip at 400x magnification, in this case no attempt was made to identify them to the level of species. In order to record those species which appear rarely the entire chamber was then examined at 100x magnification. During the spring bloom the number of organisms in the chamber could attain high enough numbers to make counting difficult. In this case only a few selected fields of view were counted. The various methods are summarized in figure 2.6.

Accurate identification of the different species present in the samples using a light microscope often proved difficult and the following guides were used extensively; *Identifying marine phytoplankton* (Tomas 1997), *Phytoplankton of Norwegian Coastal Waters* (Thronsden, Hasle & Tangen 2007) and *Marine Phytoplankton* (Hoppenrath, Elbrachter & Drebes 2009). When identifying a species of phytoplankter proved too difficult scaled drawings were made and photographs were taken, us-

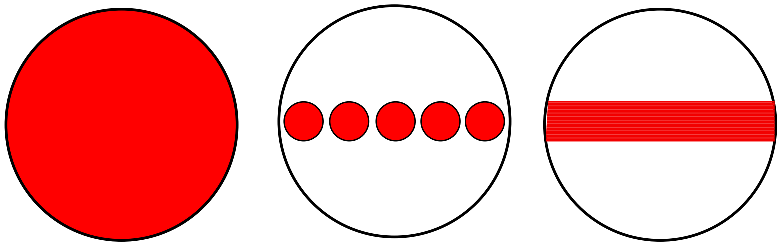


Figure 2.6: Various methods were used to count the number of organisms in a settling chamber. In diagram (A) the entire chamber was counted at 100x magnification. In diagram (B) several fields of view across the width of the settling chamber were counted - this method was generally used when the numbers of organisms in the sample were too numerous to count easily. In diagram (C) a horizontal strip at 200x and at 400x magnification across the width of the settling chamber was counted.

ing a Nikon D80 single lens reflex camera attached to the microscopes camera port, for later identification.

2.4.5 Calibration of Historic and Present Data

Phytoplankton taxonomy is an ever changing field and changes are regularly made to scientific equipment. As a comparison was being made between samples taken in the 1970's and samples taken today it was necessary to ensure that the sampling techniques used remained comparable. To minimize the possibility of species being misidentified or changes in the type of microscope being used, affecting the accuracy of the counting method, it was felt prudent to carry out regular calibration exercises between the different researchers examining the samples from Loch Creran. Fortunately Professor Paul Tett who carried out or oversaw much of the early sampling in Loch Creran also supervised the present study and this has allowed a high degree of continuity to be maintained. In addition a trip was made to the Agricultural Food and Biosciences Institute (AFBI), Northern Ireland, to take part in an inter-calibration exercise organized by Dr Richard Gowen during which several exercises were undertaken to identify and count various species of phytoplankton and to assess the accuracy both of counting methods and identification amongst a group of researchers.

2.5 Results

Due to the high heterogeneity of the medium in which they grow and the variability of their growth rate and succession, in both temporal and spatial terms, it can be difficult to make meaningful comparisons between samples of phytoplankton obtained from the field. One possible method is to plot the abundance of a species or a lifeform, such as *pelagic diatoms*, (Tett 2006) against the day of the year for large sets of data and use this data to draw an envelope encompassing the 5th and 95th percentiles and including the median. By creating such an envelope of historic data it is then possible to plot new observations onto the existing envelope and by means of a Chi Square test, determine if there has been any significant change. In this case the expectation is that the number of new points will be evenly distributed above and below the median i.e if 30 new points then the expected number would be 15, As there are only two categories a Yates correction, subtracting 0.5 from each calculated value of *Observed-Expected* was applied. This procedure can be carried out using data extraction software such as MATLAB (The Mathworks Inc.) All of The MATLAB scripts used in this thesis were written and developed by Paul Tett.

Figure 2.7 illustrates the changes between the historic observations made of pelagic diatoms present in Loch Creran in the 1970's with the observations made between 2006 and 2009. The black circles represent the observations made between 1970 and 1981 and these observations were used to calculate the 5th and 95th percentile envelope represented on the diagrams by the top and bottom dotted black lines. The line in the middle of the envelope represents the median. The red circles superimposed on this envelope represent the observations made between 2006 and 2009. The top diagram shows the number of cells $\log_{10}$ per litre plotted against the day of the year while the bottom diagram plots the biomass of the cell in mm^3 per litre against the day of the year.

Looking at the top diagram and the range of observations made during the 1970's it is evident that there is a clear pattern with a peak in abundance around the middle of March that then drops off during the summer months followed by a smaller peak around September before a fall in numbers during the winter months. Observations made during 2006 and 2009 do not show any significant change from this pattern during summer and autumn with new points fairly equally distributed above and below the median. However during the period encompassing the spring bloom the numbers of cells observed falls quite dramatically with all of the new observations falling below the median and in many cases falling outside the envelope entirely. Carrying out a Chi Square test reveals a value of 17.818, a significant change at the 1% level. An examination of the bottom diagram in figure 2.7 reveals a similar pattern in distribution throughout the year with a similar drop, in biomass, during the spring bloom. A Chi Square test results in a value of 13.091, again significant at the 1% level.

Figure 2.8 similarly illustrates the abundance and biomass of pelagic diatoms plotted against the day of the year, however it is constructed from data obtained in the Lynn of Lorn outside the loch. A fjordic sea loch, such as Loch Creran, usually exchanges water with the open sea or other adjoining water body, in this case the

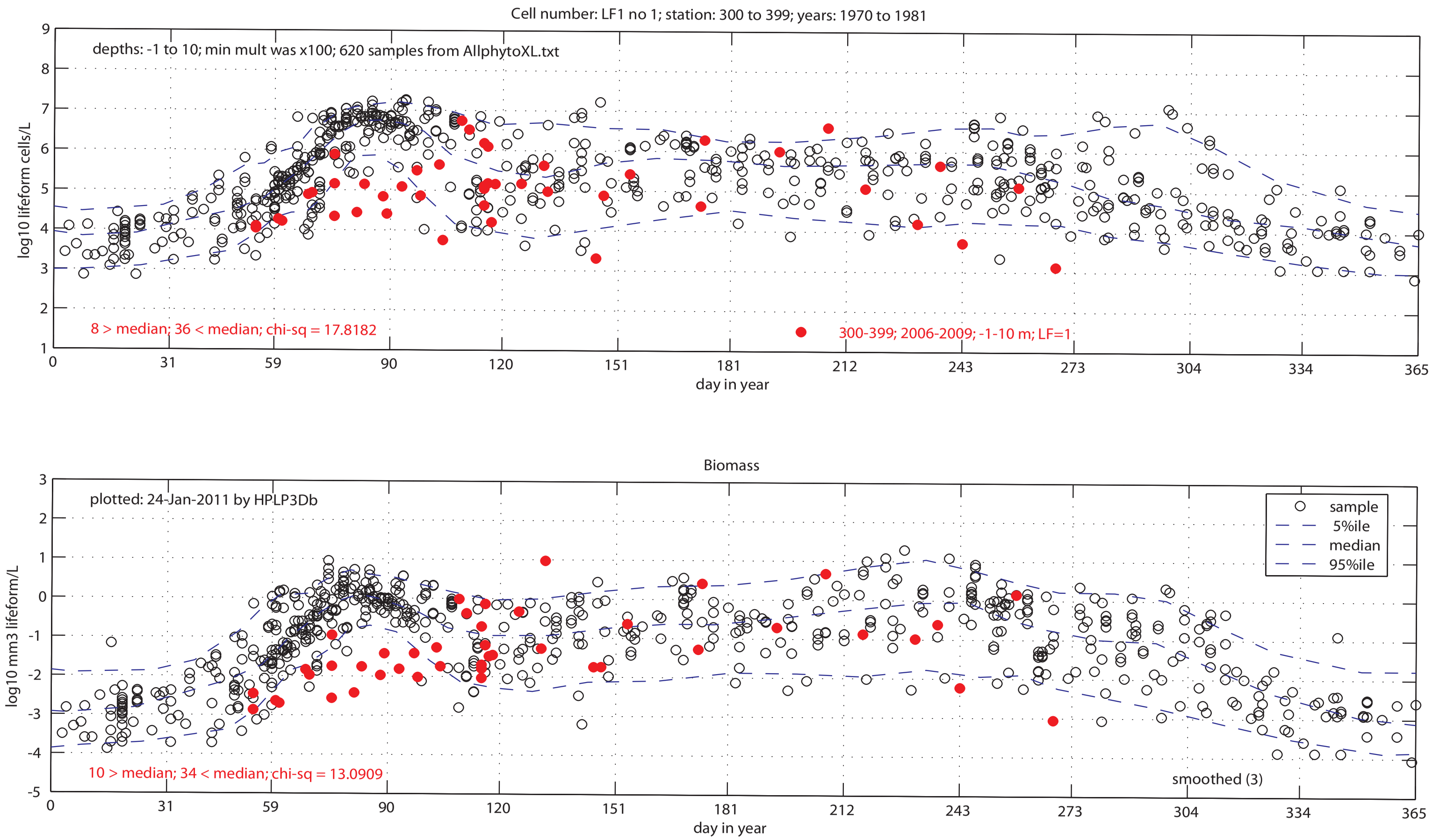


Figure 2.7: Abundance and biomass of pelagic diatoms observed in Loch Creran. The black circles shown on the above plots represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. Plot was produced using a MATLAB script written by Paul Tett.

much larger fjord the Lynn of Lorn. Through estuarine circulation patterns it will be strongly affected by the conditions, particularly the nutrient concentrations, found there. However while the nutrient concentrations in the sea loch will be affected by the outside concentrations, favourable conditions within the loch often mean that they can act as incubators for phytoplankton species (Tett and Wallis 1978).

The top diagram in figure 2.8 illustrates the number of cells per litre (note the log scale) plotted against the day of the year. The top and bottom dotted lines represent the 5th and 95th percentiles and the median is represented by the dotted line in the middle. The black circles represent the observations made between 1970 and 1978 in the Lynn of Lorn at sampling station LY1 (see figure 2.4) near the Greag Isles. the red circles superimposed onto this envelope represent the observations made at station LY1 between 2007 and 2009. It is evident that the more recent observations are equally distributed around the median and fall within the 5th and 95th percentile envelope. Carrying out a Chi Square on this data reveals a value of 0.4 suggesting that there has been no significant change in the abundance of pelagic diatoms in the Lynn of Lorn.

The bottom diagram in figure 2.8, while similar to the top, plots biomass in mm^3 per litre (again note the log scale) against the day of the year. Again all the recent observations are equally distributed around the median and mostly fall inside the envelope resulting in a Chi Square value of 0. In other words no significant change in the biomass of pelagic diatoms was found in the Lynn of Lorn.

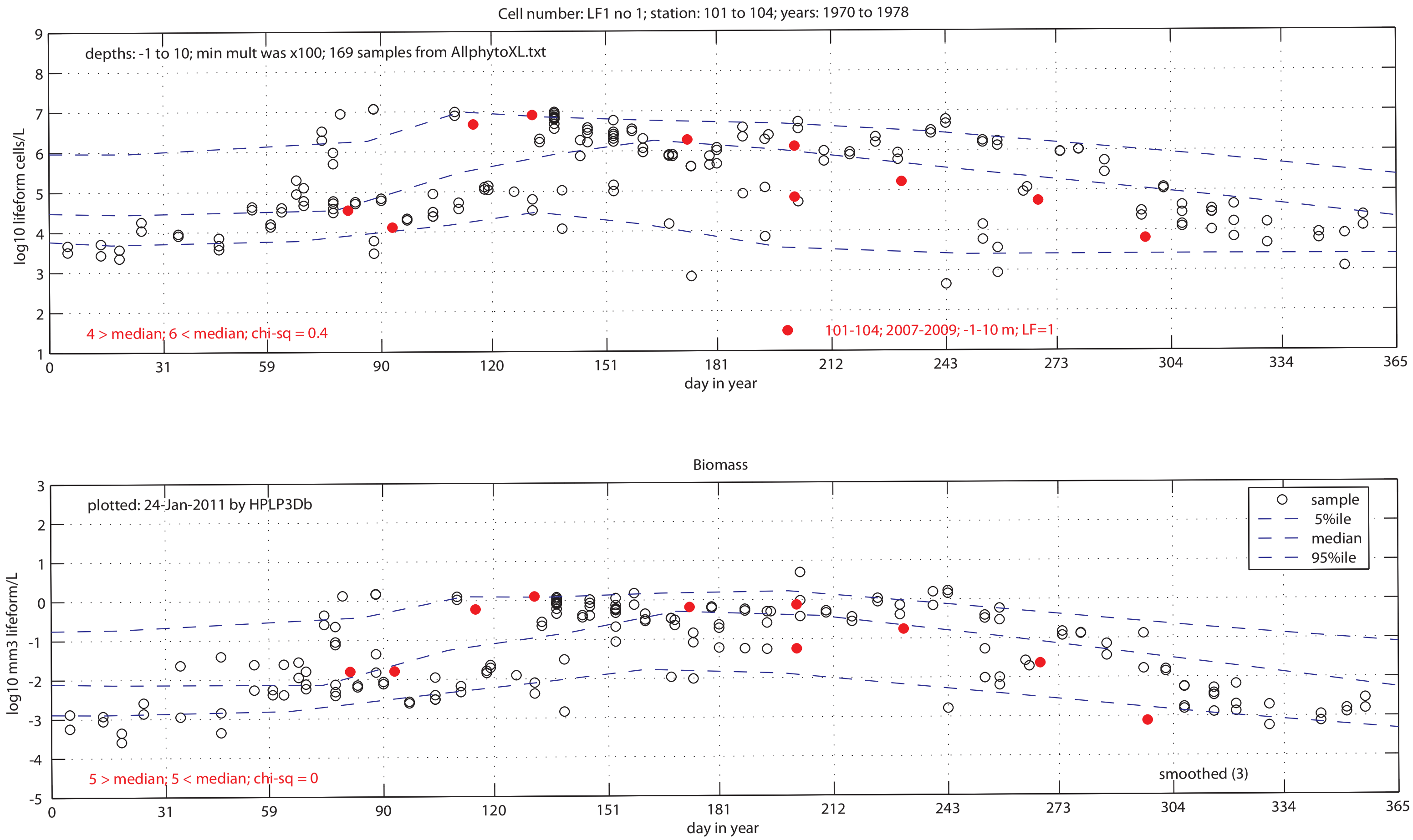


Figure 2.8: Abundance and biomass of pelagic diatoms observed in the Lynn of Lorn. The black circles shown on the above plots represent observations made between 1970 and 1978. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2007 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. Plot was produced using a MATLAB script written by Paul Tett.

2.5.1 *Skeletonema* spp

Historic records show that the dominant diatom during the spring bloom was *Skeletonema* spp. As figure 2.9 illustrates, this species made up a large part of the diatom abundance during the 1970's.

Figure 2.10 illustrates the changes that have occurred in the abundance of *Skeletonema* spp. in the loch. Again the top diagram shows the 5th and 95th percentile envelope and the median and the observations recorded between 1970 and 1981 are represented by black circles. The observations made between 2006 and 2009 are superimposed as red circles. While the abundance of *Skeletonema* spp. is reasonably well distributed throughout the summer it falls quite dramatically during the spring with many of the observations falling outside of the envelope. For clarity the bottom diagram in figure 2.10 plots the deviation of the 2006 to 2009 observations from the 5th and 95th percentile envelope. It is clear that the majority of the new observations fall below the median and indeed a Chi Square test carried out on this data reveals a value of 11.919, a decrease significant at the 1% level.

Figure 2.11 allows a comparison of the change in *Skeletonema* spp. numbers inside the loch with the larger Lynn of Lorn. Samples of *Skeletonema* spp. collected from the Lynn of Lorn are not as numerous as those collected within Loch Creran however there are enough to draw a 5th and 95th percentile envelope. It is apparent that the spring bloom, although present, is much less pronounced than that found within the loch. Again observations made between 1970 and 1978 are indicated by black circles and observations made between 2007 and 2009 are represented by red circles. While it appears from the top diagram in figure 2.11 that the numbers of *Skeletonema* spp. are lower during the summer months their abundance lies within the expected range during the spring. A Chi Square test carried out on this data gives

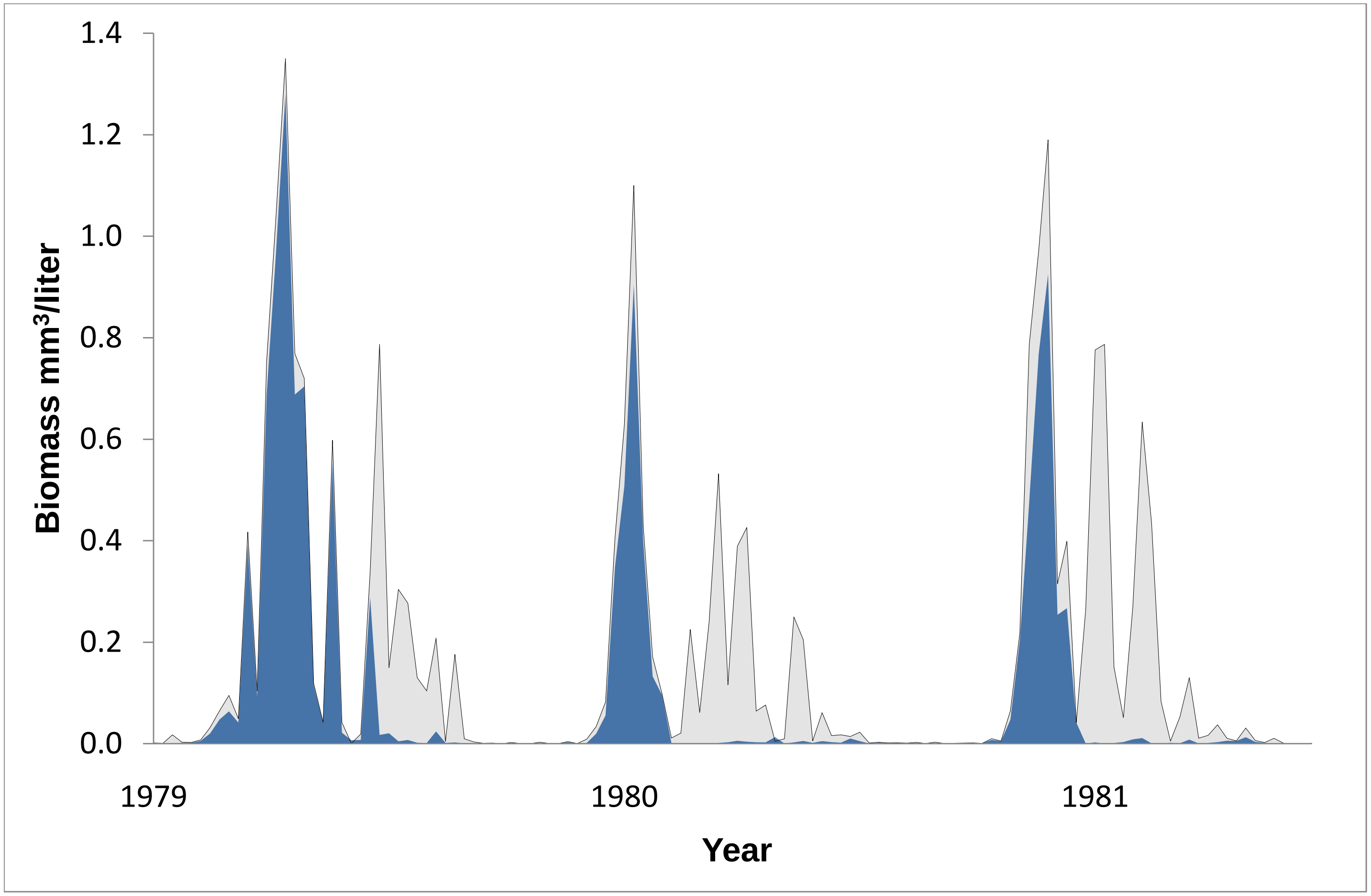


Figure 2.9: The abundance of *Skeletonema* spp. biomass plotted against the biomass of all diatom species recorded in Loch Creran between 1979 and 1981.

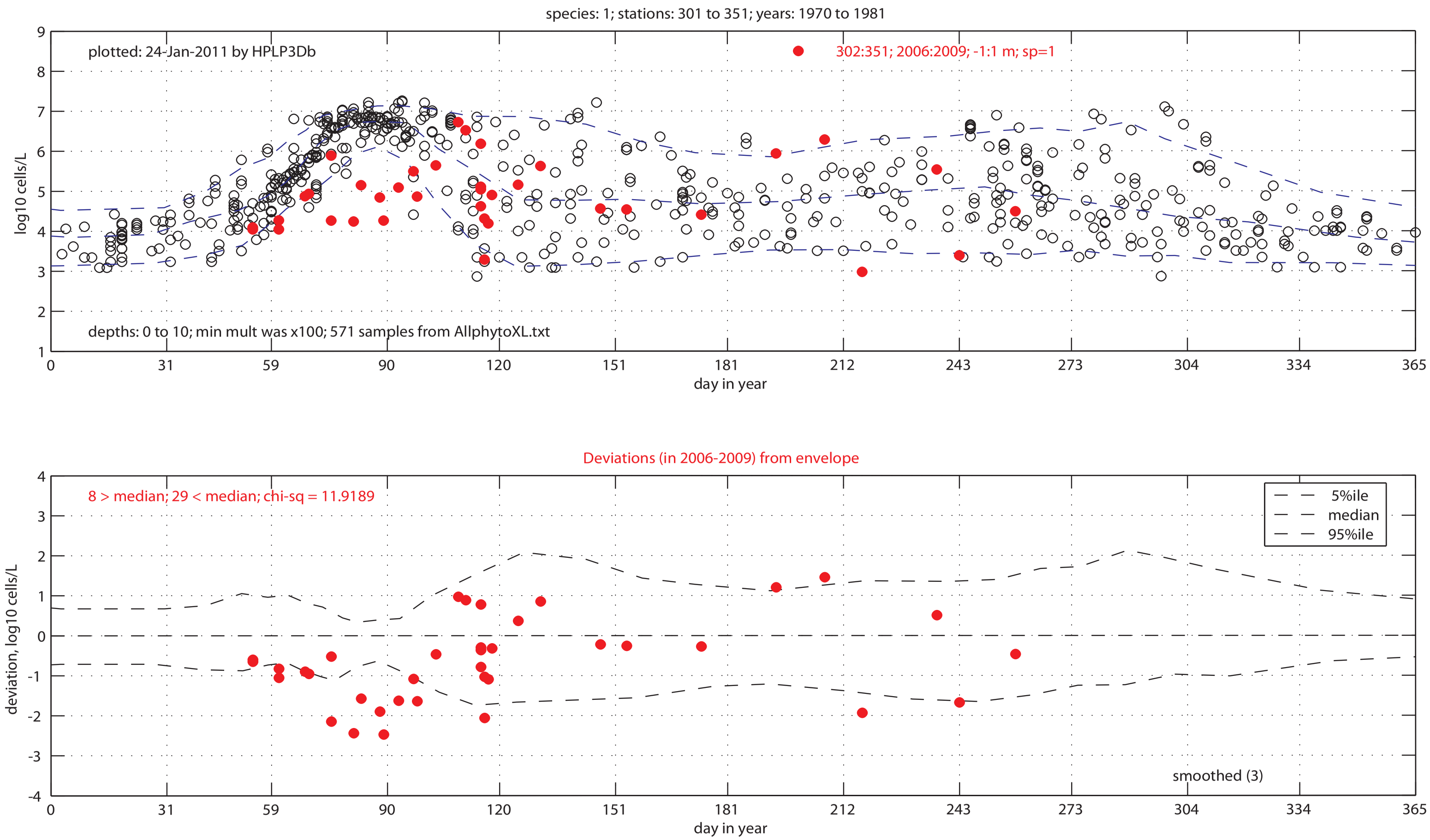


Figure 2.10: Abundance of *Skeletonema* spp. observed in Loch Creran. The black circles shown on the above plot represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. To clarify the distribution of recent observations around the median the bottom diagram plots the deviation of the 2006 to 2009 observations from the 5th and 95th percentile envelope against the day of the year. The plot was produced using a MATLAB script written by Paul Tett.

a value of 0.5 which is not significant. However given the lack of observations in the Lynn of Lorn it would be hasty to draw any firm conclusions from this particular analysis.

As mentioned earlier dinoflagellates are a lifeform that represent approximately 40% of the species recorded in marine microplankton assemblages. Whereas smaller diatoms such as *Skeletonema* spp. appear to thrive when conditions in the water column are still unstable, dinoflagellates generally prefer well stratified conditions. As changes to the mixing regime in the water column is likely to play a role in the phytoplankton community structure in the loch it will be useful to see if any changes have occurred in the abundance of dinoflagellates, particularly in the early part of the year. Figure 2.12 shows the 5th and 95th percentile envelope derived from plotting the observations made between 1970 and 1981 in Loch Creran while the red circles illustrate the observations made during 2008 and 2009. As dinoflagellates, particularly when stained with Lugol's iodine, are difficult to identify under a light microscope these results represent all of the dinoflagellates recorded in the loch during these periods, both heterotrophic and phototrophic. It is clear from figure 2.12 that both the abundance (top diagram) and the biomass (bottom diagram) of the dinoflagellates observed during 2008 and 2009 generally lie below the median, particularly during the early part of the year. A Chi Square test carried out on these observations yields a value of 9.8 for abundance and 12.8 for biomass, both results indicating a significant decrease at the 1% level in dinoflagellate numbers in the loch.

It has been estimated that ciliates can have a greater impact as grazers on phytoplankton production than macro-zooplankton (Sanders and Wickham 1993) and so they are an important group in a loch ecosystem. In a similar vein to figure 2.12,

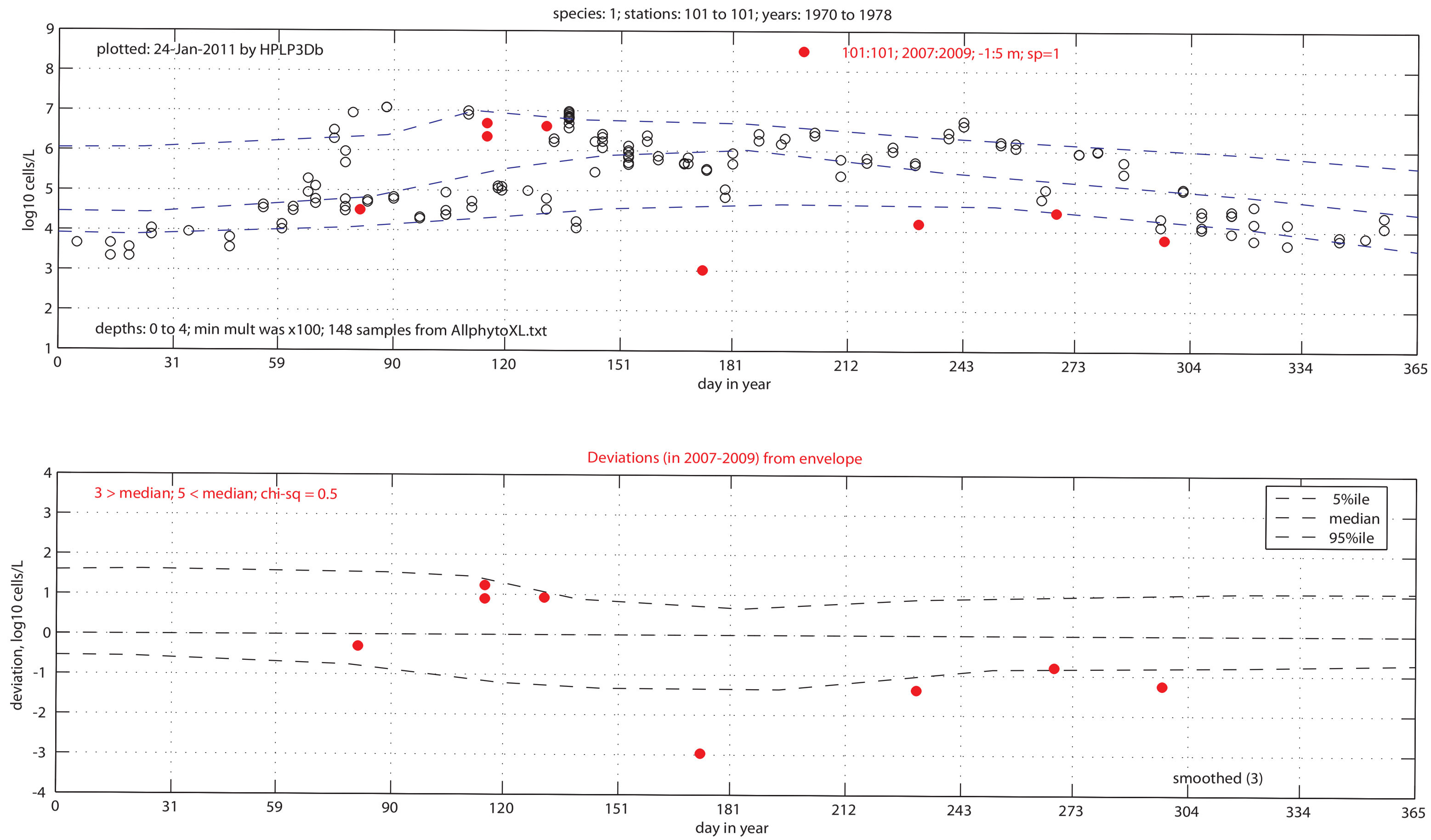


Figure 2.11: Abundance of *Skeletonema* spp. observed in the Lynn of Lorn. The black circles shown on the above plot represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. To clarify the distribution of recent observations around the median the bottom diagram plots the deviation of the 2006 to 2009 observations from the 5th and 95th percentile envelope against the day of the year. The plot was produced using a MATLAB script written by Paul Tett.

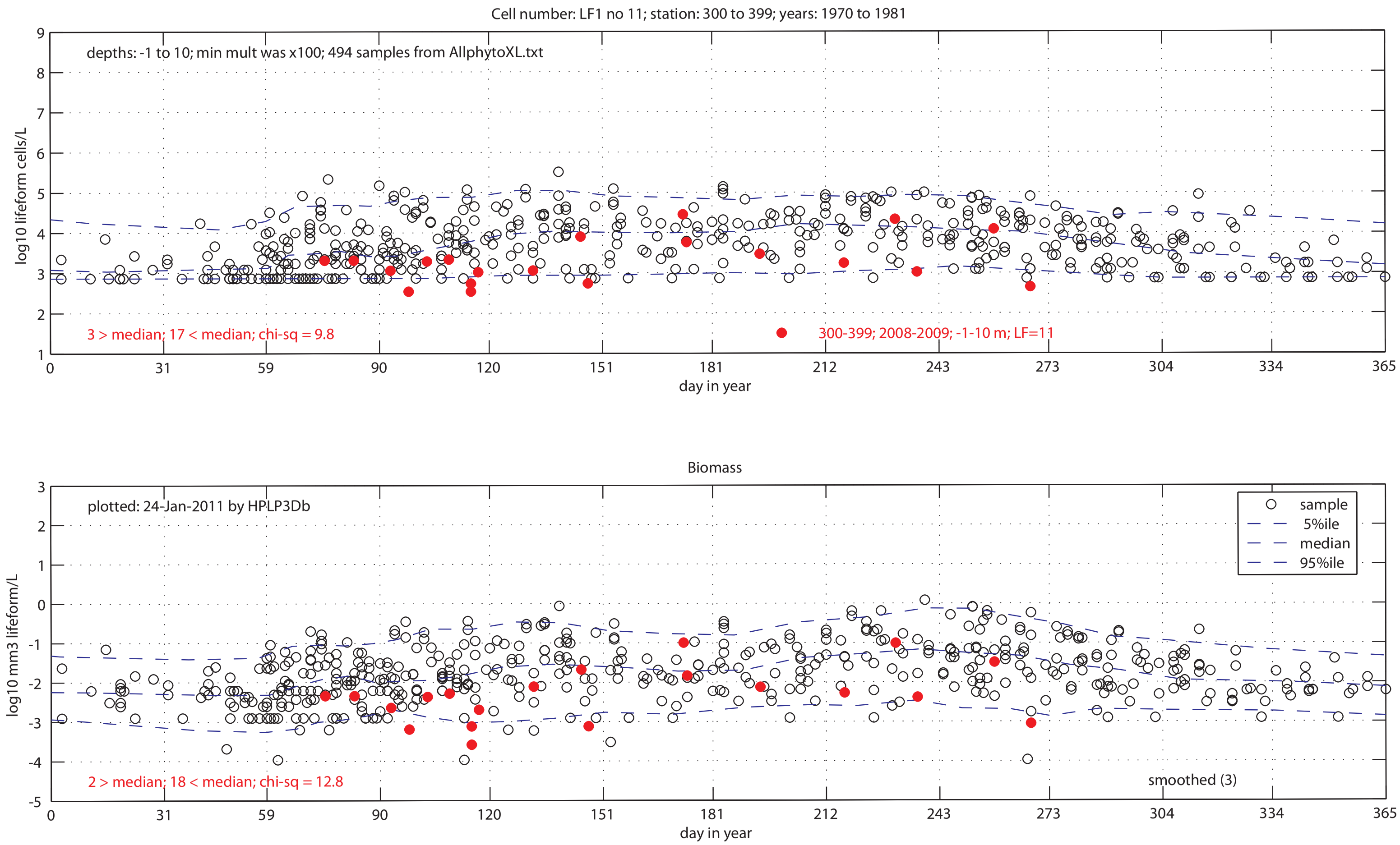


Figure 2.12: Abundance of Dinoflagellates observed in Loch Creran. The black circles shown on the above plot represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2008 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots the biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. The plot was produced using a MATLAB script written by Paul Tett.

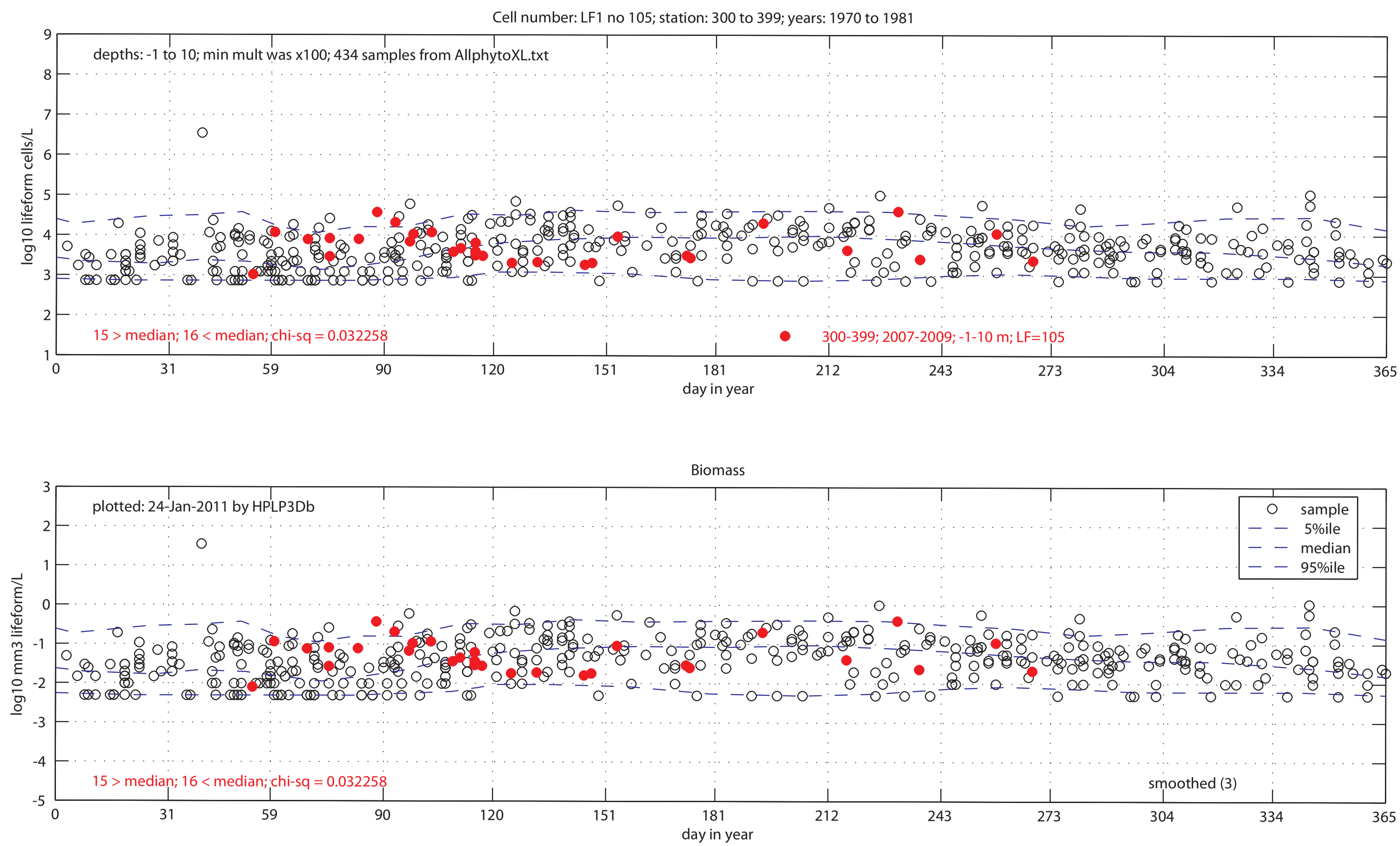


Figure 2.13: Abundance of Ciliates observed in Loch Creran. The black circles shown on the above plot represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots the biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. The plot was produced using a MATLAB script written by Paul Tett.

figure 2.13 illustrates the abundance (top diagram) and biomass (bottom graph) of ciliates in Loch Creran. Again due to difficulties in identification when stained with Lugol's iodine and the wide range of feeding strategies they employ, ciliates are treated as a life form rather than split into functional groups. Again most of the observations have been made during the earlier months of the year and it is apparent that for most of the year the data is fairly well distributed around the median. carrying out a Chi Square test on this data yields a value of 0.032. In other words no significant change in ciliate abundance throughout the year. If however we look more closely at figure 2.13 it appears that the majority of the observations of ciliates during the spring, particularly around the time of the spring bloom, are clustered above the median. Figure 2.14 plots the same data as figure 2.13 but in this case only the observations made during the spring months of 2006 to 2009 are plotted onto the envelope. While most of the new observations lie within the envelope they are predominantly greater than the median and indeed several values lie outside the envelope entirely. Carrying out a Chi Square test on this smaller set of data reveals a value of 5.26 which is significant at the 5% level. Nevertheless it has to be noted that this statistic is very sensitive to the time interval chosen. Including data from observations made only four days later, as the Spring bloom subsided, would reduce the significance of this increase to 10%.

John and Davidson (2001), Sherr and Sherr (2002), note that small flagellates can play a vitally important role in phytoplankton predation. Figure 2.15 plots the abundance (top diagram) and biomass (bottom diagram) of small flagellates observed in Loch Creran. Unfortunately small flagellates when treated with Lugol's iodine which, can cause many of them to lose their flagella, are very difficult to identify, particularly with a light microscope so no attempt has been made to differentiate between different trophic groups. Instead all small flagellates counted have been included. Unfortunately, given the proviso above, lack of flagella can lead to misidentification of the very smallest of the flagellates with the possibility that some may not be counted. As before the black circles represent observations made between 1970 and 1981 and are used to produce the reference 5th and 95th percentile envelope. The superimposed red circles represent more recent observations made between 2006 and 2009. It is apparent from the figure that while the abundance of small flagellates remains unchanged during the summer months there has been a major change during the earlier part of the year with the majority of observations lying below the median and in many cases lying outside the envelope entirely. A Chi Square test carried out on this data yields a value of 18.778. A significant decrease in numbers at the 1% level.

Table 2.2: Summary of results of comparing observations made between 1970 and 1981 with recent observations of the phytoplankton community in Loch Creran, df = degrees of freedom.

Lifeform or Genus	Test	df	Probability	Significant
Diatoms (Loch Creran)	χ^2	1	p = 0.001	Decrease
Diatoms(Lynn of Lorn)	χ^2	1	p = 0.700	No
Skeletonema spp. (Loch Creran)	χ^2	1	p = 0.001	Decrease
Skeletonema spp.(Lynn of Lorn	χ^2	1	p = 0.500	No
Dinoflagellates (Loch Creran)	χ^2	1	p = 0.010	Decrease
Ciliates (Annual)(Loch Creran)	χ^2	1	p = 0.900	No
Ciliates (Spring) (Loch Creran)	χ^2	1	p = 0.05	Increase
Small flagellates (Loch Creran)	χ^2	1	p = 0.001	Decrease

2.6 Discussion

The aim of this chapter was to compare data gathered for Loch Creran during the 1970's with data gathered between 2006 and 2009 and determine if there had been a change in the abundance of any of the groups of phytoplankton present. Rather

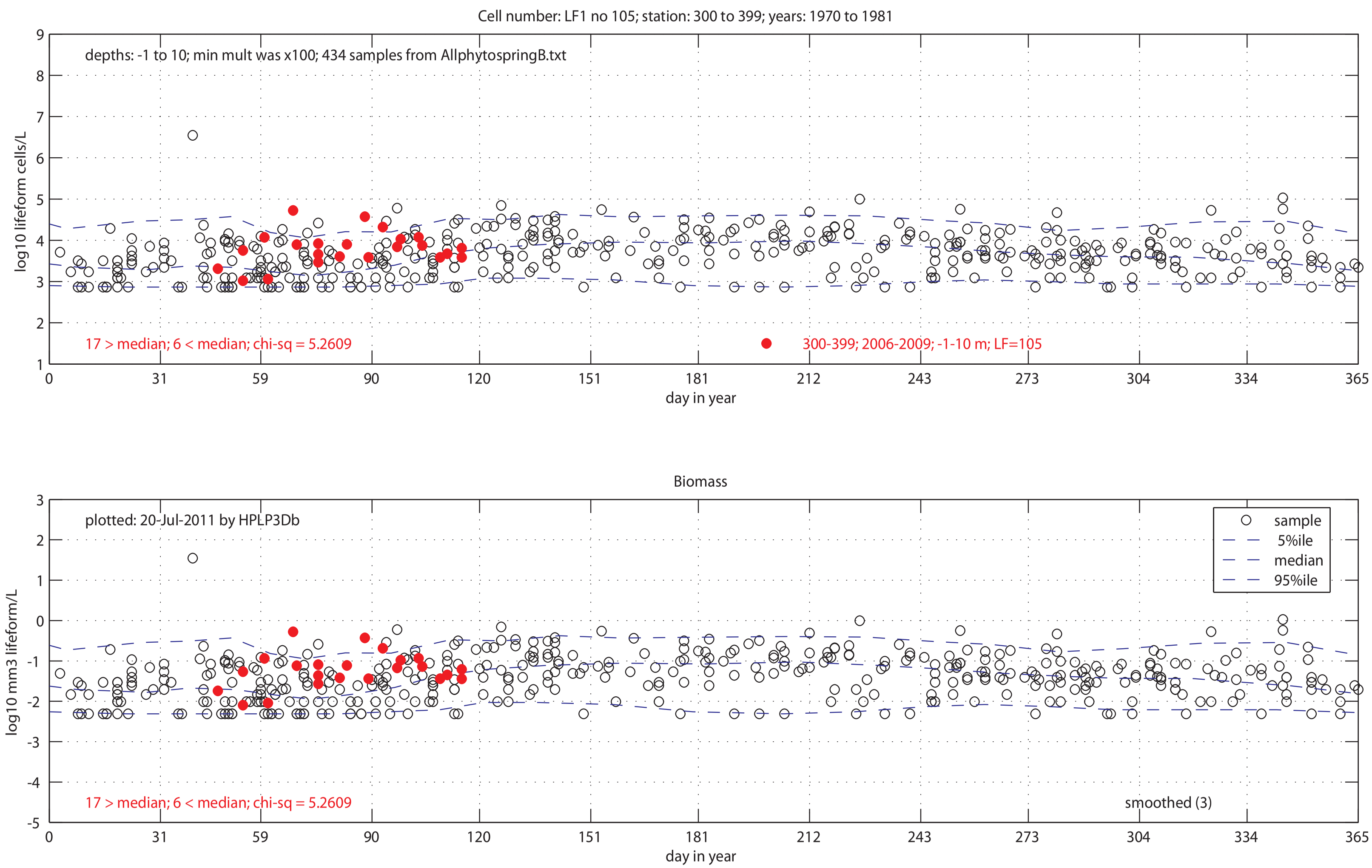


Figure 2.14: Abundance of Ciliates observed in Loch Creran. The black circles shown on the above plots represent observations made between 1970 and 1981 for the entire year. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made during the spring between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots the biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. The plot was produced using a MATLAB script written by Paul Tett.

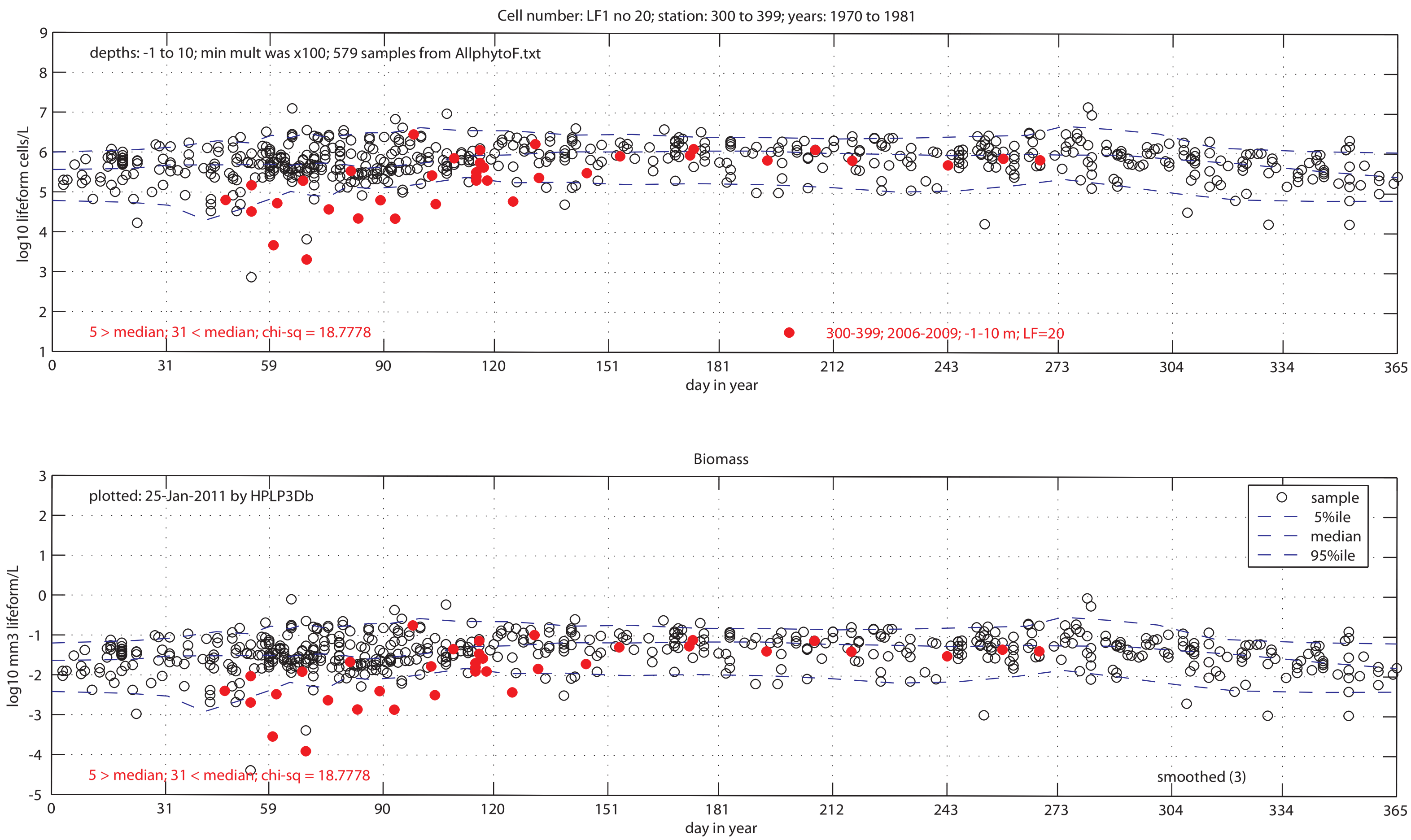


Figure 2.15: Abundance of small flagellates observed in Loch Creran. The black circles shown on the above plots represent observations made between 1970 and 1981. These historic observations were used to create the 5th and 95th percentile envelope represented by the black dotted lines and the median. The red circles represent observations made between 2006 and 2009. The top diagram plots cell numbers in $\log_{10}$ cells per litre against the day of the year. The bottom diagram plots the biomass in $\log_{10}$ mm^3 per litre against the day of the year. Biomass was calculated by using a mean cell volume derived from measurement of phytoplankton samples collected between 1970 and 1981. The plot was produced using a MATLAB script written by Paul Tett.

than consider each species separately the phytoplankton was looked at in terms of life form (Margalef 1978; Tett *et al*. 2008). In other words pelagic diatoms, dinoflagellates, ciliates and small flagellates. The exception was *Skeletonema* spp. a chain forming diatom that was so ubiquitous during the spring blooms of the 1970's that its presence or otherwise was worthy of special attention.

When studying phytoplankton assemblages in the field collecting data can be problematic. Changes in tidal levels, differences in weather, patchiness and succession that can vary from year to year can all affect the data collected. The method used in this chapter, whereby large sets of historic data are used to create an envelope which encompasses the large variability present in the system, allows trends in the behaviour of the phytoplankton community in the loch to be visualised and also compared with more recent observations. While calculating the median allows any apparent changes to be tested statistically. Suggestions made at the beginning of the study influenced the decision to increase the intensity of sampling during the spring and this has led to a bias in the weighting of the results obtained. However examination of the figures above generally reveal a good distribution of data around the median for each of the life forms considered throughout the year.

The results obtained so far suggest that the phytoplankton numbers in the loch have not changed significantly during the summer and autumn months. Although in the case of pelagic diatoms generally (Fig 2.9) and *Skeletonema* spp. in particular (Fig 2.10) there appears to be greater variability in numbers. However during the spring the changes appear to be significant (see table 2.2 for a summary of the results), particularly in the case of pelagic diatoms that show both a dramatic drop in numbers during the spring bloom and also a change in its timing which, appears to be delayed by approximately three weeks. Comparison with the Lynn of Lorn suggest that these changes are confined to the loch although lack of data from the Lynn of Lorn, (Fig 2.11) especially during the summer and autumn make it difficult to draw conclusions here.

Dinoflagellates also show a decline throughout the year although this is less marked than the pelagic diatoms. While the majority, but not all, of the new observations lie within the 5th and 95th percentile envelope most lie below the median (Fig 2.12). The data collected on dinoflagellates does not differentiate between different functional groups and so includes heterotrophic as well as photo-trophic species. It may be that the drop in dinoflagellate numbers partly reflects the drop in available prey species. Unfortunately it is not possible to draw any conclusions as dinoflagellates in their turn are preyed upon by groups such as the ciliates.

While the numbers of ciliates in the loch shows no significant annual change a closer look at the situation during the spring (Fig 2.13) does show elevated ciliate numbers although only significant at the 10% level (Fig 2.14). This significance is very much dependent on the actual cut off date chosen, however it certainly appears that the majority of values during March and April lie above the median while some actually lie above the 95th percentile.

The final group to be considered were the small flagellates. Again while the numbers throughout the summer and autumn months lie comfortably inside the envelope there is a significant decrease during the spring (Fig 2.15). The small flagellates proved difficult to identify under the light microscope and were considered collectively rather than attempting to split them into functional groups. It is generally accepted that small protists are responsible for a large part of the predation on primary producers in the sea. Their fast rates of growth allow them to keep pace with the exponential growth rates of small phytoplankton species. It could have been expected that the decline in pelagic diatoms during the spring was accompanied by an increase in the numbers of their predators such as small flagellates. However this is clearly not the case. It may be that the decline in diatoms has meant less food for small phagotrophic flagellates which have declined accordingly.

Several authors have noted a wide spread decline in phytoplankton biomass in recent years (Boyce 2010, Doney 2006, Jacobsen 1993). Of course, given the complexity of marine food webs, the decline of pelagic diatoms, ciliates and small flagellates may very well have its causes elsewhere and some of these possible causes will be examined in subsequent chapters.

Chapter 3

The Phytoplankton Community Index

3.1 Introduction

As has been seen in chapter 2, Loch Creran has experienced a decrease in the numbers of pelagic diatoms and dinoflagellates and this is especially noticeable during the early months of the year, particularly around the time of the spring bloom. This is a significant change and warrants further investigation. However whereas the gross numbers of phytoplankton in the Loch have decreased it is unclear whether or not there has also been a change in the composition of the phytoplankton community in the loch. It would be informative to compare the community observed in the loch during 2008/09 with that seen during the 1970's and try to determine if it has experienced any changes, apart from gross numbers, during the past three decades.

However determining the state of a phytoplankton community *in situ* is fraught with difficulty. Winds, tides and turbulence mean that phytoplankton are constantly in motion. Also, seasonal succession means that the composition of the population is steadily changing . Smayda (2001) has noted that the success and dominance of a phytoplankton species is as much due to stochastic processes i.e being in the right place at the right time and in sufficient number, as it is to species specific traits.

The ability to understand the state of a phytoplankton community, and by extension the ecological quality status of the water body where they reside, has increased in importance as a response to the need for methods to monitor the state of the pelagic ecosystem. This necessity has arisen with the advent of The Urban Waste Water Treatment Directive (CEC 1991) and OSPAR's Strategy To Combat Eutrophication (OSPAR 2003). These policies have been implemented to avoid, or ameliorate, any undesirable, environmental impacts caused, as a result of excessive nutrients (eutrophication), by the rapid growth of opportunistic primary producers.

The Urban Waste Water Treatment Directive (CEC 1991) gives the following definition of eutrophication:

"The enrichment of waters by nutrients, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality of the water concerned"

The European Water Framework Directive (WFD; 2000/60/EC) also proposes that phytoplankton be included as one of the indicators to be considered when determining the ecological status of a water body. This status combines both a measure of how well an ecosystem is functioning and an examination of its structure and can be determined by comparing the ecosystem, as it is now, with some previously determined reference conditions.

Methods for monitoring phytoplankton in the open sea have utilised several different indicators. These include:

- Bulk indicators such as measurements of chlorophyll concentration (exemplified by the work of the Comprehensive Studies Task Team), water transparency and deep water oxygen concentration.
- Flux indicators that measure the flow of energy through the ecosystem and generally concentrate on primary production, although they also consider oxygen consumption rates and fluxes to the sediment.
- Taxonomic indicators. These require that the phytoplankton is identified and counted and include diversity indices, the use of phytoplankton and zooplankton indicator species and phytoplankton trophic or community indices (DEFRA 2004).

As this study has focussed on the identification and enumeration of phytoplankton species present in Loch Creran, it is one of the latter, the Phytoplankton Community Index (PCI) developed by Tett *et al* (2008) to illustrate the state of the pelagic ecosystem that seems the best choice to carry out a comparison of the phytoplankton community in the loch now with its state during the 1970's.

Tett *et al* (2008) note that the health of an ecosystem has components that include "vigour", a measure of the energy flowing through the system, "resilience", the ability of a community to recover from disturbance and the organisation of a community or "structure" and have developed the PCI as a measure of the latter.

Key to Tett and his colleagues method are two main assumptions. The first that groups of different species of phytoplankton can be collectively described as groups of *life-forms*, for example, pelagic diatoms or autotrophic dinoflagellates (Tett *et al*. 2008). The second that an ecosystem can be treated as a system that can be defined at different points in time by a set of ”state variables”, in the case of the PCI these variables are represented by the relative abundances of different life-forms.

Margalef was perhaps the first to put forward the idea that different species of phytoplankton could be categorised in terms of their functionality into ”life-forms” (Margalef 1978). Concentrating on the supply of nutrients and the effects of decaying turbulence he conceived ”life-forms” as an aggregation of adaptations of different organisms to these selective pressures.

Tett *et al.* (2003) suggests that a major advantage of the life-form theory is that it is not defined precisely. Phytoplankton, categorised by their particular morphology, biogeochemistry or life history can be considered as part of a particular life-form while belonging to different taxonomic groups.

Smayda and Reynolds (2001) looking at harmful algal blooms surmised that Margalef’s original mandala correlating the degree of mixing with the nutrient levels in a water column should be modified to include the many micro-niches that different levels of turbulence introduced. However they also concluded that life-forms take precedence over phylogenetic influences when considering succession in a phytoplankton community.

Tett *et al.* (2008) then treat the abundance of each life-form present as a state variable. In order to distinguish changes in the phytoplankton community from the noise generated by inter-annual variability, both in the abundance of phytoplankton and in the species present, they plot the abundance of one life-form against that of another into a two dimensional phase space. As the relative abundances change throughout the year and between years this generates a cloud of points. An envelope can then be drawn around this collection of points which represents the expected ”natural” reference conditions for a phytoplankton community.

Controversially, Tett *et al.* (2008) argue that populations of phytoplankton should be influenced by the competitive exclusion principle (Gause 1932) and so there should be an empty space at the centre of the envelope. In other words the reference envelope can be expected to assume the shape of a misshapen donut (see figure 3.1). While the exclusion principle is a reasonable assumption when considering different species, in the case of the PCI it is groups of lifeforms that are being considered. It seems reasonable then to assume that different lifeforms could co-exist at all points within the given phase space. However, although the inclusion of the hole in the donut makes the PCI more sensitive to any changes in the community it is not essential for the PCI to work.

To determine the present state of a pelagic community new observations can be plotted into this phase space. Providing the new points plot somewhere inside the envelope it can be assumed no significant change has taken place. If, however they lie outside the envelope it suggests a change in the state of the community.

3.2 Aims

The aim of this section is to utilise the PCI developed by Tett *et al.* (2008) to determine if there have been any significant changes in the phytoplankton community in Loch Creran between the 1970’s and the present and if possible see where those changes have occurred. The null hypothesis being that there has been no significant change in the structure of the community in the loch over the past four decades.

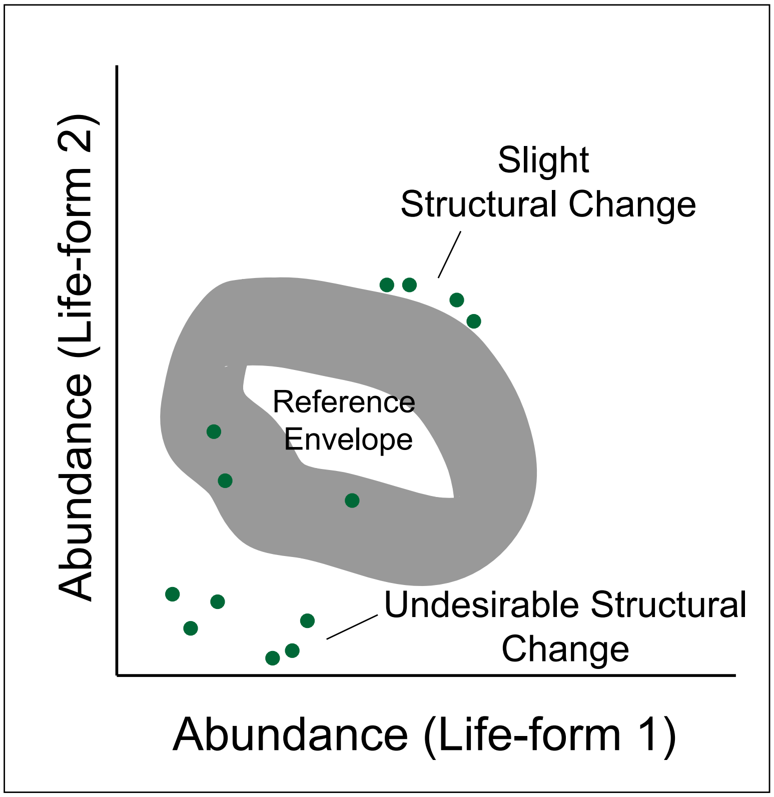


Figure 3.1: Diagram of the reference envelope representing the structure of a phytoplankton community under naturally fluctuating seasonal and annual succession. The small green dots represent new observations. Those lying inside the envelope indicate no change has occurred while those lying outside may indicate a slight or large change to the structure of the community. The diagram was redrawn with modifications from Tett *et al* (2008).

3.3 Methods

The methods used to collect and subsequently analyse the water samples taken from Loch Creran have previously been described in chapter 2. To calculate the PCI the data obtained from an analysis of the water samples was converted into a text file and read into a MATLAB script written by Dr Paul Tett. The script converted the data into cells/litre for the various life-form categories (see table F.1). The data was then converted by $\log_{10}(X + z)$ transformation, where X = life-form abundance, z =

$0.5 \cdot X_{min}$ and X_{min} = minimum abundance recorded for a particular life-form. The addition of z avoids the risk of errors when X = zero (Tett *et al* 2008).

The reference data was transformed in a similar fashion from data obtained between 1979 and 1981. The abundances for the two life-forms was combined to form pairs of coordinates, which were then plotted into a two dimensional phase space. To create the outer envelope a convex hull algorithm was used on this set of two dimensional data points (Weisstein 2011). Effectively the convex hull method, available as a function in MATLAB, finds the outermost points in a set of points and connects them. It achieves this by starting at the vertex furthest to the left of the set then makes the assumption that the next point is also a possible convex hull vertex. At each step three consecutive points are considered and the angles between them calculated, if the angle is found to be convex the new point is accepted and the entire set of three points is moved along one point and the procedure is repeated. The internal envelope was created in a similar way after inverting the data points around their centre (Tett *et al* 2008).

The PCI is given by:

$$PCI = 1 - \frac{\text{new points lying between inner and outer envelope}}{\text{total number of new points}}$$

A value of zero indicates that there has been no change while a value of one would indicate a complete change. The significance of the PCI can be calculated by using a binomial series to determine the probability of finding that number of points outside the reference envelope. If the number of new points exceeds 200 using the binomial becomes unwieldy and instead the PCI can be calculated by a Chi squared approximation. In both cases it is assumed that up to 5% of the new data points can fall outside the envelopes before assuming there has been a change (Tett 2006). It was found that due to the large amount of variation measured in phytoplankton communities, plotting weekly values could result in an excessively large reference envelope and reduce the sensitivity of the PCI. This was caused by relatively few, high values, which due to the convex hull method employed, greatly expanded the envelope (Tett *et al.* 2008). It was decided therefore to use monthly means.

3.4 Results

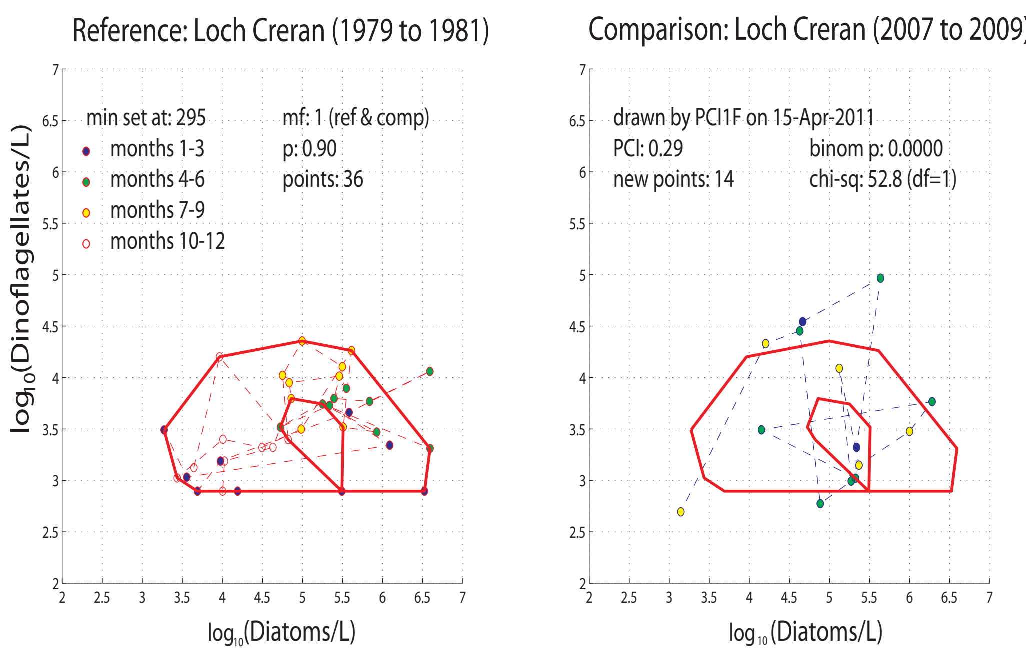


Figure 3.2: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of diatoms against the abundance of dinoflagellates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

Figure 3.2 illustrates a PCI plot of pairs of dinoflagellate and diatom abundances in Loch Creran. The left hand diagram is the reference envelope created from monthly mean values measured in the loch between 1979 and 1981. The diagram on the right shows the result of over-plotting the measurements made between 2007 and 2009. It is obvious from the right hand diagram that there have been significant changes in the relative abundances of diatoms and dinoflagellates in the loch, $p < 0.0001$, $X^2 = 52.8$ (df = 1). These changes appear to be particularly marked in the first 6 months of the year where the number of dinoflagellates has increased relative to the numbers of diatoms. This is to be expected since as we have seen in chapter 2 the abundance of diatoms in the loch has dropped dramatically during the spring. However, figure 2.12 indicates that dinoflagellate numbers in the loch have also fallen during the early months of the year. This suggests that the change in relative abundances between these two life-forms may be more noticeable than it appears from either figure 2.12 or figure 2.7. The flat bottom to the envelope reflects a lack of data most likely due to the sparse sampling that takes place during the winter months.

Figure 3.3 is a plot of the relative abundances of diatoms and ciliates measured in Loch Creran between 2007 and 2009 compared with the reference envelope created from data collected between 1979 and 1981. It is immediately obvious that significant changes have occurred between these two life-forms, $p < 0.0001$, $X^2 = 34.2$ (df = 1). The abundance of ciliates has increased relative to that of diatoms with most of this increase occurring in the first three months of the year and again between months 7 - 9. Again this could perhaps be anticipated from figure 2.13 which, while indicating that ciliate numbers had not changed significantly throughout the year, does show higher numbers of ciliates during the spring.

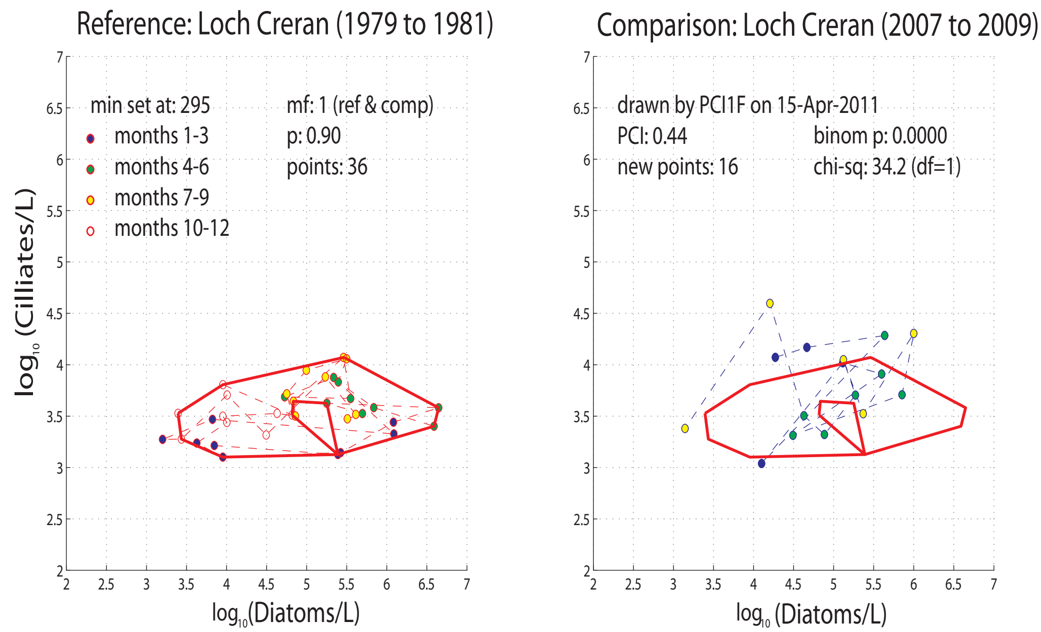


Figure 3.3: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of diatoms against the abundance of ciliates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

The reference plot comparing the relative abundances of diatoms and small flagellates (figure 3.4) is interesting in that while the abundance of diatoms varies widely that of the flagellates is restricted to a relatively narrow range. The plot comparing measurements made between 2007 and 2009 with the reference plot indicates that there has been a significant drop in the relative abundance of small flagellates particularly during the spring. Again this is not unexpected as referring to figure 2.15, plotting their abundance, it can be seen that there has been a drop in the numbers of flagellates observed in the loch and that this drop is concentrated around the time of the spring bloom.

Small flagellates are notoriously difficult to count particularly after preservation in lugol's iodine and it may be that this drop in numbers reflects counting error. How-

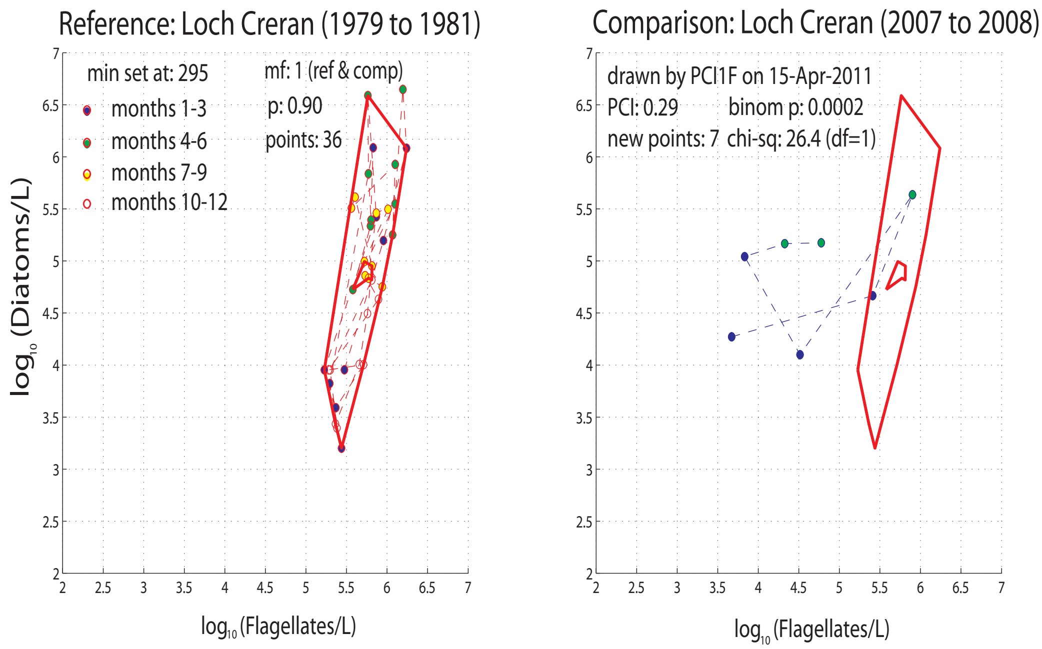


Figure 3.4: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of diatoms against the abundance of small flagellates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

ever it can be seen from figure 2.15 that the numbers of flagellates observed during the summer and autumn months lie comfortably in the expected range. Although a certain degree of under-counting has to be assumed, it would seem reasonable, given the perceived accuracy during the latter part of the year, to accept this drop in small flagellate numbers as a true reflection of their abundance in the loch.

Figure 3.5 illustrates the relative abundances of ciliates and dinoflagellates in the loch. The small reference envelope in the left hand diagram indicates that the ratio between these two life-forms in Loch Creran has lain within a relatively narrow range. This suggests that their relative numbers do not change substantially over the course of a year. Comparing this reference envelope with the results from 2007-

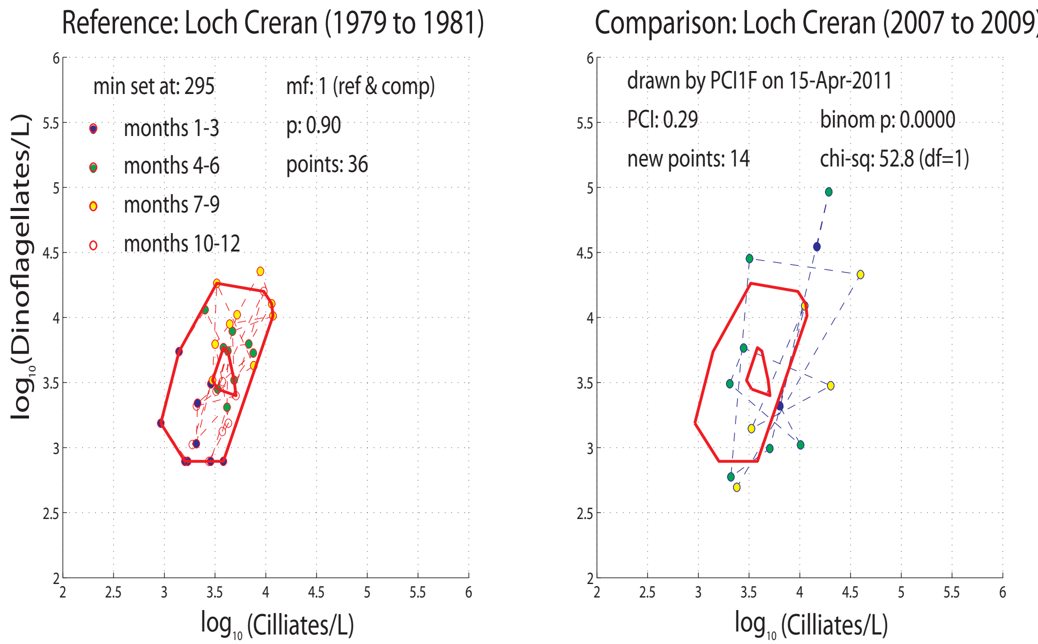


Figure 3.5: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of ciliates against the abundance of dinoflagellates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

2009 it is evident that there has been a significant change in the abundances of both ciliates and dinoflagellates in the loch, $p < 0.0001$, $X^2 = 52.8$ (df = 1). This change appears to be due to an increase in the relative number of ciliates compared to that of dinoflagellates. Again this change is most apparent during the first six months of the year although this may reflect the paucity of observations made during the winter months.

The small reference envelope in figure 3.6 , plotting the abundance of flagellates against ciliates, again indicates that the relative abundances of these two lifeforms varied little during the course of a year. The right hand diagram, over-plotting the measurements made between 2007 and 2009, however shows a dramatic shift

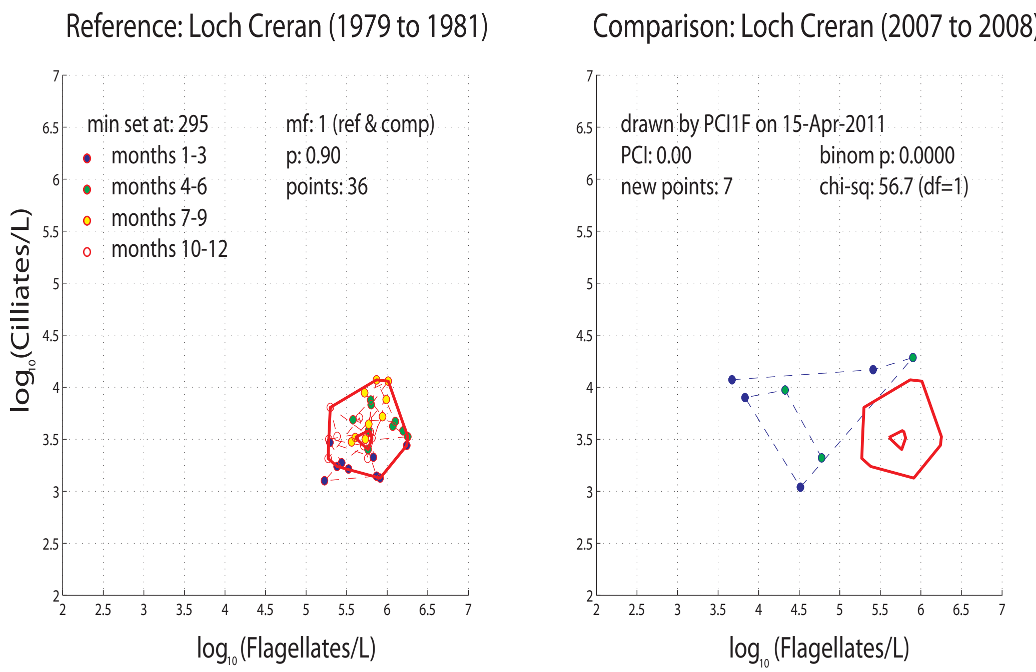


Figure 3.6: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of ciliates against the abundance of flagellates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

in their relative numbers. The numbers of flagellates in the loch have dropped significantly, $p < 0.0001$, $X^2 = 56.7$ (df = 1), when compared with the numbers of ciliates. It is evident that this change has occurred during the first few months of the year although once again this is most likely due to the lack of measurements during the autumn and winter months.

Finally figure 3.7 is a comparison of the abundances of small flagellates and dinoflagellates in Loch Creran. Again it is clear that there has been a significant change in the relative abundances of these two life-forms, $p < 0.0001$, $X^2 = 32.3$ (df = 1). Although there is a lack of data for the later part of the year, particularly during the winter, it is evident that the abundance of flagellates has declined

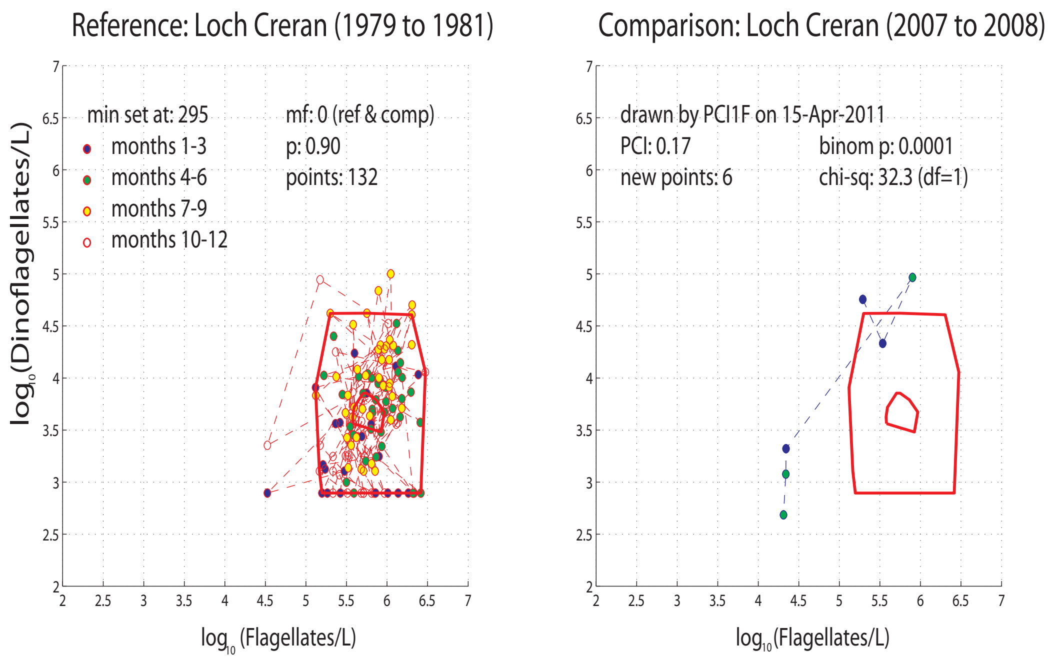


Figure 3.7: A PCI plot. The points represent vectors in two dimensional phase space. Here representing the abundance of dinoflagellates against the abundance of flagellates in Loch Creran. The plot on the left illustrates the reference envelope created from observations made between 1979 and 1981. The plot on the right represents the observations made between 2007 and 2009. The values used in both plots are monthly means. The different colours represent measurements made at different times of the year. The plot was created on a Matlab script written by Dr Paul Tett.

with respect to the abundance of dinoflagellates during the first six months of the year.

3.5 Discussion

The Phytoplankton Community Index developed by Tett *et al.* (2008) is a relatively new method that opens a window onto the state of the pelagic marine environment. By comparing the results obtained from the PCI with those in chapter 2, where individual species or life-forms were compared with reference conditions for that species/life-form, it can be seen that it highlights many of the changes already observed.

Comparing the numbers of a particular phytoplankton species present in the loch now with those recorded in the past allows a straight forward measurement of gain or loss. The PCI also provides a metric of change but goes further in allowing a glimpse of the state of the phytoplankton community as it is now compared to some reference condition. At the moment the PCI compares the relative abundances of two life-forms plotting them into a two dimensional phase space. Its usefulness would only be increased if it was developed further, allowing the possibility to plot several different lifeforms into a multi dimensional space.

From the results obtained above it is clear that the phytoplankton community in Loch Creran has undergone significant changes in its structure, changes that are somewhat difficult to explain. Seasonal succession in Scottish sea lochs generally follows an annual pattern of a spring bloom, typically dominated by diatoms that, as they become starved of nutrients, is succeeded by dinoflagellates and flagellates (Tett and Wallis 1978). The ability of diatoms to grow is very sensitive to the concentrations of nitrogen and silicon available to them. Silicon is of particular importance as it is needed to construct the diatom frustule. If this nutrient is in too low a concentration in the loch this could explain the drop in diatom numbers.

A major source of silicon comes from the rivers feeding into Loch Creran. However Jacobson *et al.* (1994), Justice *et al.* (1995) note that over the last twenty years the concentration of silicon in rivers has gradually declined. Officer and Ryther (1980) also point out differences in the recycling rates of silicon, nitrogen and phosphorus observing that unlike nitrogen or phosphorus which, tend to be recycled very quickly in the water column, silicon is recycled as the frustules of dead diatoms are re-mineralised on the sea bed, a much slower process. In a somewhat related process Ragueneau *et al.* (2005) studying the biogeochemical cycle of silicon found that an increase in bivalve suspension feeders led to significant amounts of silicon being bio-deposited into the underlying sediments. Could a lack of silicon be an explanation for the drop in the abundance of diatoms in the loch?

Figure 4.1 in chapter 4 shows that the concentration of silicon measured in the loch during 2009 was well within the expected range. Indeed compared to the reference conditions in the 1970's the concentrations in the loch were actually elevated. A further look at figure 4.1 shows that nitrate concentrations during the spring were also higher than expected with regards to the reference conditions. Nevertheless a comparison with the concentrations recorded in 1975 (Jones 1979), indicate that the increase was not significant. Indeed only phosphorus seemed to be significantly lower, (see chapter 4).

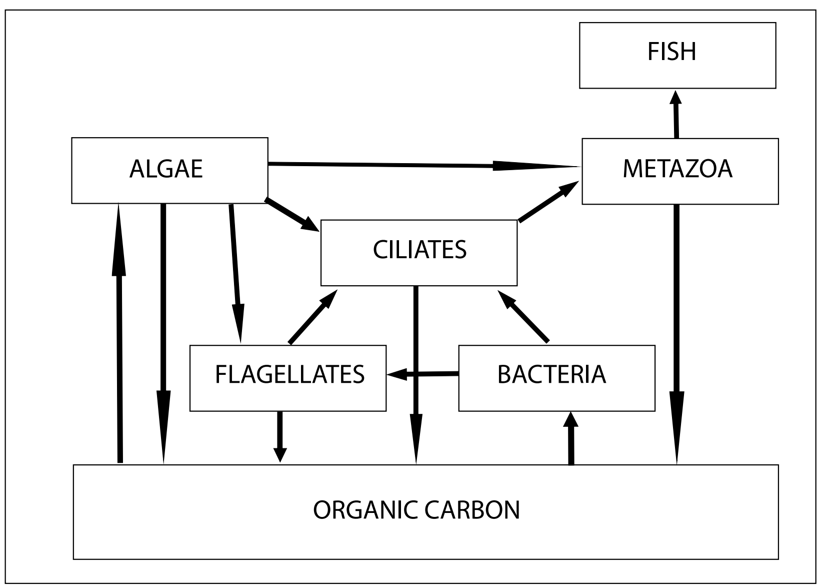


Figure 3.8: Diagram illustrating the major fluxes and functional pools in the marine food web. Redrawn with modifications from Ingrid *et al.* (1996).

Interestingly Ingrid *et al.* (1996) mapping the major fluxes and functional pools in the marine food web (see figure 3.8) showed the connection between abiotic organic carbon and bacteria. With the closure of the alginate factory in Loch Creran in 1996 (UK Marine SACs Project 2011) it is interesting to speculate whether or not the reduction in organic carbon to the loch, estimated to be between 30% and 50% (see section 7), has led to a reduction in the abundance of bacteria in the loch? Certainly Moore (1996) found that the seabed for 1km centred on the outflow from the alginate factory extending outwards from the shore for 200 metres and down to a maximum depth of 18 metres was covered in a white bacterial mat which he believed to be comprised of the genus *Beggiatoa*. These bacteria generally inhabit areas rich in sulfur which they oxidise as an energy source (Schmidt *et al.* 1987).

Low phosphate concentrations and relatively high nitrate concentrations are also often related to inputs of fresh water (European Environment Agency 2010). The measurements of nutrient concentrations were taken from samples collected in the top ten metres of the water column. It may be that the nutrient levels found are indicative of higher levels of rainfall in the lochs catchment area. This is a possibility that will be examined in greater detail in chapter 9.

In conclusion it is evident that not only have there been changes in the overall numbers of phytoplankton in the loch but, worryingly, that these changes are having an affect on the actual composition or structure of the phytoplankton community in the loch.

Nevertheless, interpreting these changes is more problematic. Elevated numbers of ciliates could partly explain a drop in both flagellate and diatom numbers which, they exploit as a food source. However small flagellates are also a major consumer of diatoms (Fileman 2011), it could be expected that as numbers of small flagellates decrease, thereby removing some of the pressure from grazing, the abundance of diatoms in the loch would increase, but this is evidently not the case. This suggests that the reasons behind the drop in biomass may have other causes and these will be discussed in the following chapters.

Chapter 4

Nutrient Concentrations in Loch Creran

4.1 Introduction

In order to grow, phytoplankton require a wide range of nutrients in varying amounts. Some, for example, hydrogen, oxygen and sulfur are readily available while others such as calcium, magnesium, sodium, potassium and chloride are usually abundant in terms of the requirements of the cell. Barium, cobalt, copper, manganese, molybdenum zinc and vanadium are found, but only required, in trace amounts. The lack however of any of the four elements; Nitrogen, phosphorus, silicon and iron can have severe consequences (Reynolds 2006) for the growth of phytoplankton.

Regardless of how abundant any of these elements are in sea water they are orders of magnitude more dilute than the concentrations found, and needed, in the phytoplankton cell. Phytoplankton have therefore devised sophisticated membrane transport mechanisms to assimilate the required molecules from their surroundings (Reynolds 2006). Although these ligand specific receptors pump the needed molecules into the cell using ATP phosphorylation, the cell is still dependent on diffusive and advective nutrient concentrations in the surrounding water and molecular diffusion dominates any transport within the viscous layer. At scales of a few centimetres, turbulence in the water column generally ensures that nutrient concentrations are homogeneous. However given the small size of most diatom cells the nutrient concentration around the cell can quickly become depleted (Pahlow *et al*. 1997).

It is generally accepted that run-off from the land ensures that concentrations of iron found in coastal waters exceed the usual requirements for phytoplankton growth (Valiela *et al*. 1999). However once the water column has become stratified, reducing the amount of nutrients mixing from deeper layers into surface waters, the supply of nitrates, phosphates and silicates can quickly become limiting. The concentrations of these nutrients is therefore of great importance when judging the growth potential of a body of water.

With the establishment of a fish farm in Loch Creran in the early 1990's a certain amount of nutrient enrichment, both from waste food and faeces, could have been expected. Nevertheless in earlier studies Laurent (2006) did not find any significant changes in the concentrations of nitrate, phosphate or silicate in the loch. As it was originally felt that the causes behind the change in phytoplankton abundance lay elsewhere, no attempt was made to measure these nutrients during 2008. However, with the increased level of sampling carried out from the research vessels RV Calanus and RV Seol Mara (both operated by the Scottish Association for Marine Science, Dunstaffnage) in 2009 it was decided to measure the levels present in the loch.

4.2 Methods

During the 1970s measuring the concentration of dissolved inorganic nitrogen (DIN) in Loch Creran followed the method determined by Mullin and Riley (1955) and modified by Strickland and Parsons (1960). This method reduced nitrate to nitrite by first passing the sample through a tube filled with cadmium filings. A similar method developed by Wood, Armstrong and Richards (1967) was rejected as, at the time, it was deemed too labour intensive (Laurent 2006).

Dissolved inorganic phosphorus (DIP) was determined by reacting a solution of ammonium molybdate containing ascorbic acid and antimony with the phosphate ions in the sample which, produces a blue purple compound (Murphy and Riley 1962). According to Laurent (2006) this method was further modified according to Strickland and Parsons (1972) and was chosen as it was felt that it was more reliable than other contemporary methods such as that proposed by Murphy and Riley (1958).

During 2009 water samples were collected using two litre Niskin bottles attached to a metal winch cable deployed from one of the above research vessels. They were lowered over the lee side while the vessel was stationary and fired by a messenger once the required depth had been reached. Once on deck the bottles were emptied into a nalgene container which had first been rinsed twice with seawater from the sample. Aliquots were removed with a 60 ml syringe fitted with a Sartorius 25mm polycarbonate syringe filter holder, (Catalogue number VWR 611-0689), with a Luer lock and fitted with a Whatman 25mm GF/C circular glass microfibre filter (Whatman catalogue number 1822-025). The water was then injected into a small acid washed bottle and kept in a cool-box for transportation to Edinburgh Napier

University where it was stored in a freezer at -9 ^{0}C until ready for analysis. The filters were disassembled, acid washed and then rinsed in de-ionised water after each use.

Once defrosted the samples were analysed on an AQ2+ Automated discrete analyser supplied by Seal Analytical Ltd. Hampshire, U.K. to determine the concentrations of nitrates, phosphates and silicates present in the loch. The method used to analyse each nutrient is summarized below.

4.2.1 Nitrate

Nitrate was analysed using the United States Environmental Protection Agency (USEPA) method 353.2. In this procedure nitrate is reduced to nitrite by copperised cadmium. This reacts with sulfanilamide to form a compound of diazonium. This compound is then added to dilute phosphoric acid whereby it couples with N-(1-napthyl)-ethylene diamine dihydrochloride forming a reddish-purple azo dye. This dye was then measured spectrophotometrically at 520 nm (Seal Analytical (a)).

4.2.2 Phosphate

To analyze phosphate the USEPA method 365.1 was used. In this case phosphate reacts with acidic molybdate in the presence of antimony to form an antimony phospho-molybdate complex. This is reduced by ascorbic acid to form the blue complex phosphomolybdenum blue. This complex was then measured spectrophotometrically at 880 nm (Seal Analytical (b)).

4.2.3 Silicate

Silicate was measured using the United Kingdom Accreditation Service (UKAS) method number 514-A Rev. 1. In this method reactive silicon combines with ammonium molybdate under acidic conditions to form a yellow molybdosilicic acid complex. This was then measured spectrophotometrically at 820 nm (Seal Analytical (c)).

4.3 Results

Figure 4.1 illustrates the concentrations (μM) of the three nutrients measured in Loch Creran during 2009. The top diagram plots dissolved inorganic nitrogen (DIN) against day of the year, the middle diagram plots dissolved inorganic phosphorus (DIP) and the bottom plots dissolved silicon (DSi). The black circles represent the accumulated observations of nutrient levels made between 1973 and 1976 and this data has been used to generate the 5th and 95th percentile envelope depicted by the blue dotted lines on each of the diagrams. The central dotted line represents the median. Observations made during the eight transects of the Lynn of Lorn and Loch Creran in 2009 have been plotted as red circles.

The top diagram in figure 4.1 indicates the concentration of DIN and it can be seen that most of the 2009 measurements lie within the 5th and 95th percentile envelope and are equally distributed around the median. Indeed a chi square test carried out on this data reveals no significant change in nutrient concentrations. However it does appear that DIN levels were elevated during the early part of the year, i.e around the end of March and the beginning of April at a time when their levels would be expected to be quite low. Unfortunately the low number of observations

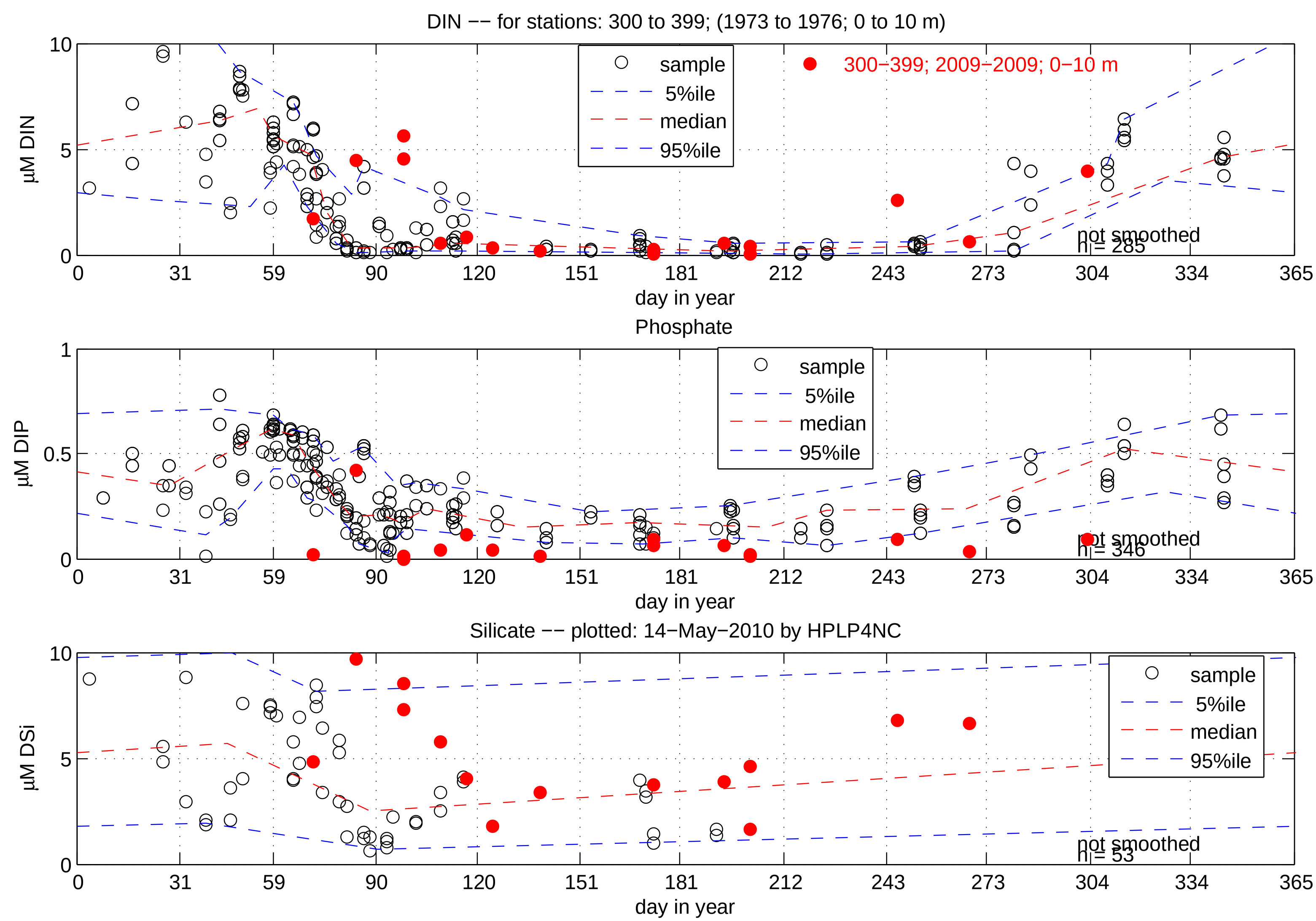


Figure 4.1: Dissolved inorganic nitrogen (top diagram), dissolved inorganic phosphorus (middle diagram) and dissolved silicon (bottom diagram) concentrations (μM) measured in loch Creran. The black circles represent the measurements made between 1973 and 1976 and were used to calculate the 5th and 95th percentile envelope displayed in the diagrams as a blue dotted line. The median is displayed as a red dotted line. The red superimposed circles represent the measurements made in 2009. The plot was made using a MATLAB script written by Dr P. Tett.

made during 2009 and the lack of any data from 2008 make it difficult to draw firm conclusions.

Figure 4.2 was made using data supplied by Dr Thom Nickell and the Scottish Association for Marine Science, Dunstaffnage (Personal communication). This data has been plotted in the same way as figure 4.1 and shows the measurements made between 2005 and 2006. Here we can see that while most of the observations are reasonably well distributed around the median during the summer months they are, similarly, also elevated during the early part of the year, particularly during March and April and again during November.

In the case of DIP plotted in the middle diagram of figure 4.1 most of the 2009 observations appear to lie below the median throughout the year. A Chi Square test carried out on this data reveals a value of 10.28, $p < 0.01$. This represents a significant decrease in the concentration of DIP. In comparison the observations made between 2005 and 2006 (see figure 4.2) show slightly elevated levels of DIP throughout most of the year.

The bottom diagram in figure 4.1 and in figure 4.2 represents the measurements of dissolved silicon in the loch. Here we can see a good agreement between the 2005-06 and the 2009 data, both showing elevated concentrations of DSi throughout the year, particularly during the spring and late autumn. A Chi Square test carried out on the 2009 data revealed a value of 7.14, $p < 0.01$. A significant increase over the 1973 to 1976 observations although it should be noted that apart from a few observations during March and April these observations still fall largely within the 5th and 95th percentile envelope. Unfortunately DSi has not been monitored as extensively as other nutrients, the assumption being that it is always present in concentrations that would make it unlikely to become growth limiting. This means

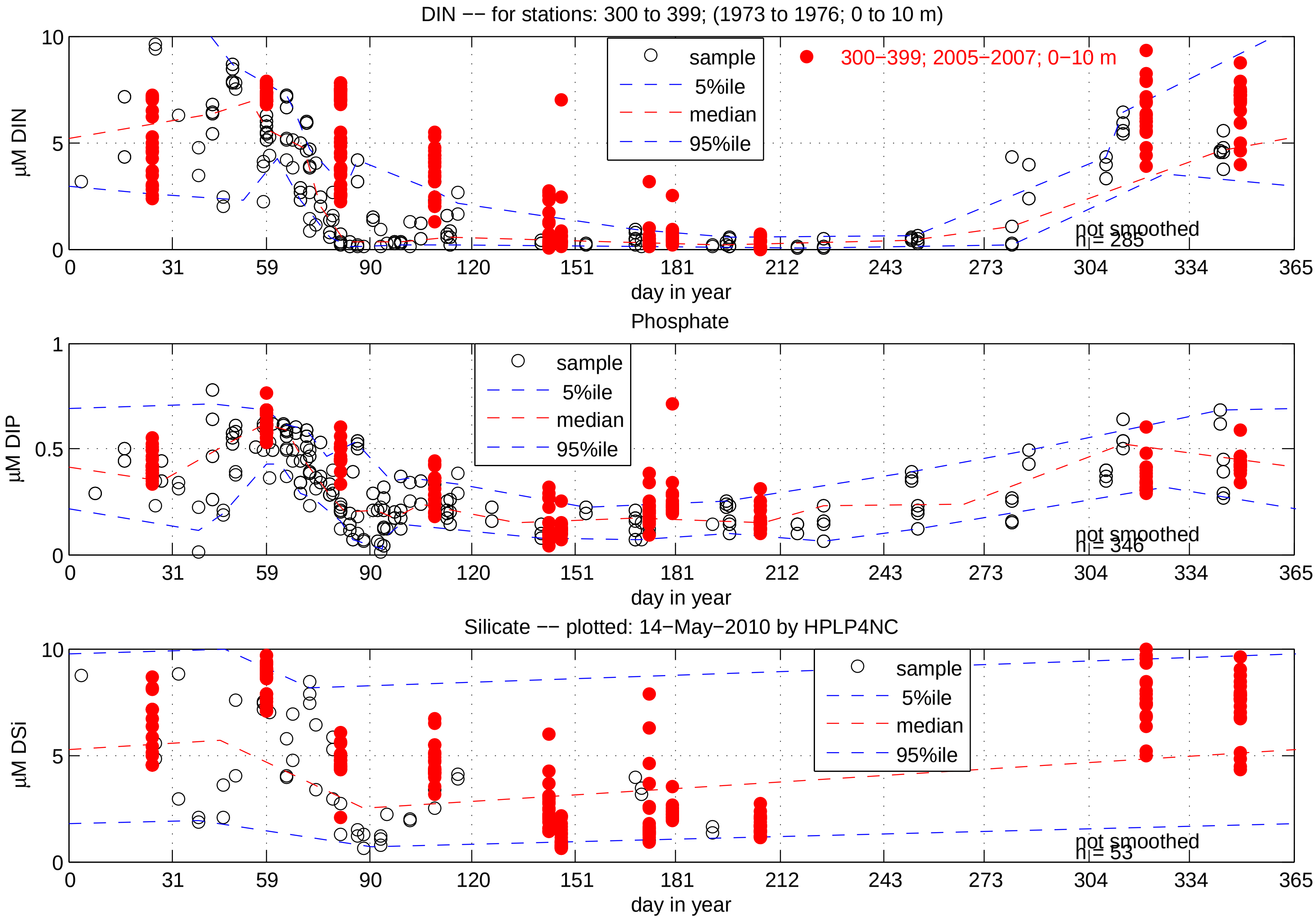


Figure 4.2: Dissolved inorganic nitrogen (top diagram), dissolved inorganic phosphorus (middle diagram) and dissolved silicon (bottom diagram) concentrations (μM) measured in loch Creran. The black circles represent the measurements made between 1973 and 1976 and were used to calculate the 5th and 95th percentile envelope displayed in the diagrams as a blue dotted line. The median is displayed as a red dotted line. The red superimposed circles represent the measurements made between 2005 and 2007. Data courtesy of Dr T Nickell and the Scottish Association for Marine Science, Dunstaffnage. The plot was made using a MATLAB script written by Dr P. Tett.

Table 4.1: Results of a Mann-Whitney U test Comparing concentrations of DIN in Loch Creran.

Year	N	Median	P value
1975	23	0.854	0.7780
2009	21	1.390	

Table 4.2: Results of a Mann-Whitney U test Comparing concentrations of DIP in Loch Creran.

Year	N	Median	P value
1975	35	0.2950	0.0001
2009	17	0.0626	

that the envelope created by the MATLAB script can be prone to errors associated with extrapolation especially during late summer and autumn. However it would seem unlikely that levels of silicate in the stratified surface layers found in the loch during summer would rise as most of the re-mineralized silicate would remain in the deeper layers of the loch until mixing of the water column took place during autumn and winter.

Jones (1979) measured the concentrations of DIN and DIP in Loch Creran during 1975. This data was compared with the measurements taken during 2005-06 and 2009 and the results have been plotted in figures 4.3 and 4.4 below. A non parametric Mann-Whitney U test was carried out on the 1975 and 2009 data sets (see table 4.2 and 4.1) revealing no significant difference for DIN between 1975 and 2009. DIP concentrations however were found to be significantly lower.

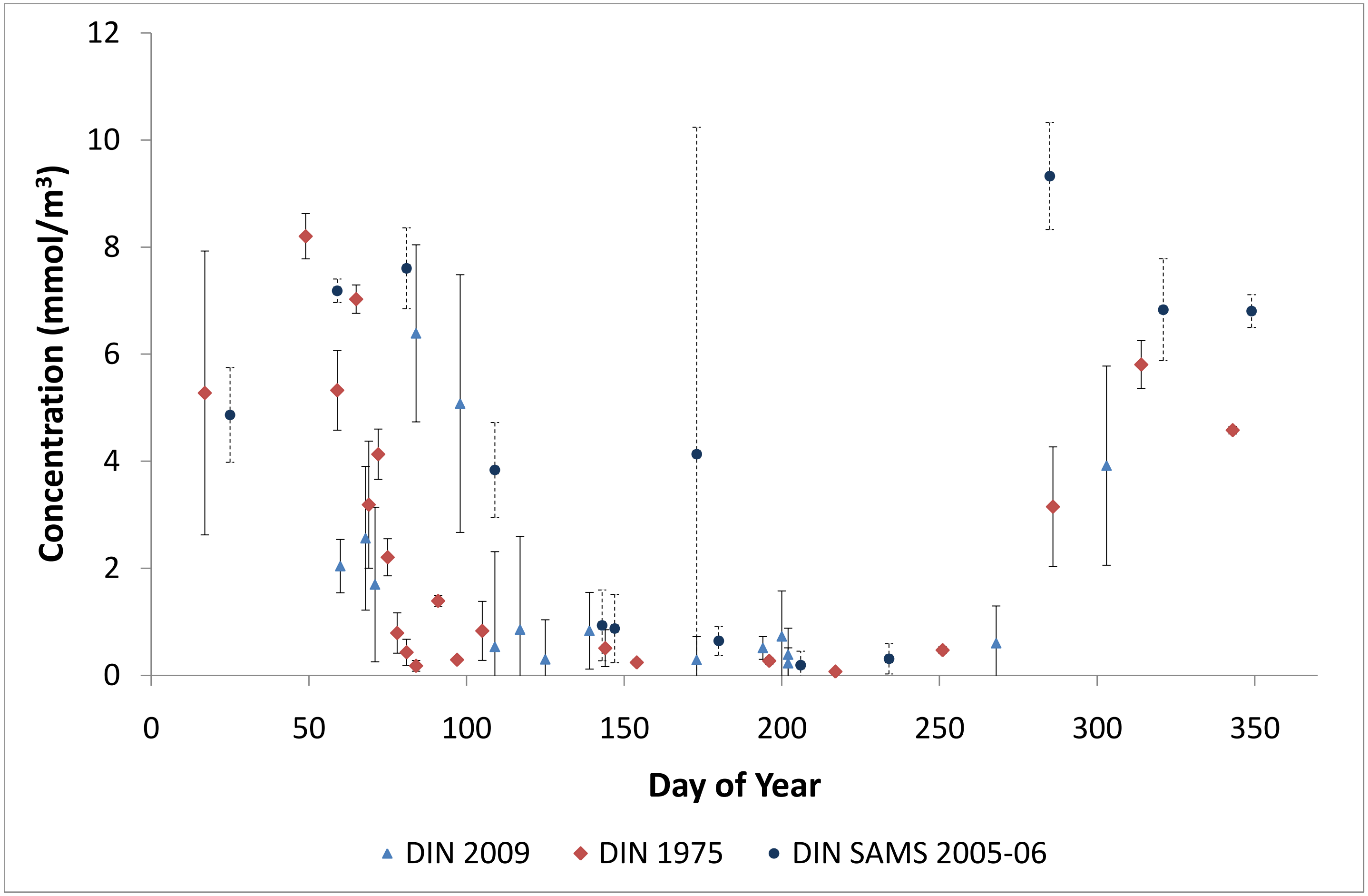


Figure 4.3: Plot of dissolved inorganic nitrogen (DIN) measured in Loch Creran in 1975 by Jones (1979) compared with measurements made in 2005-06 and in 2009. The data for 2005-06 was provided courtesy of Dr Thom Nickell, Scottish Association for Marine Science. The error bars represent one standard deviation. The data points represent mean values for the loch.

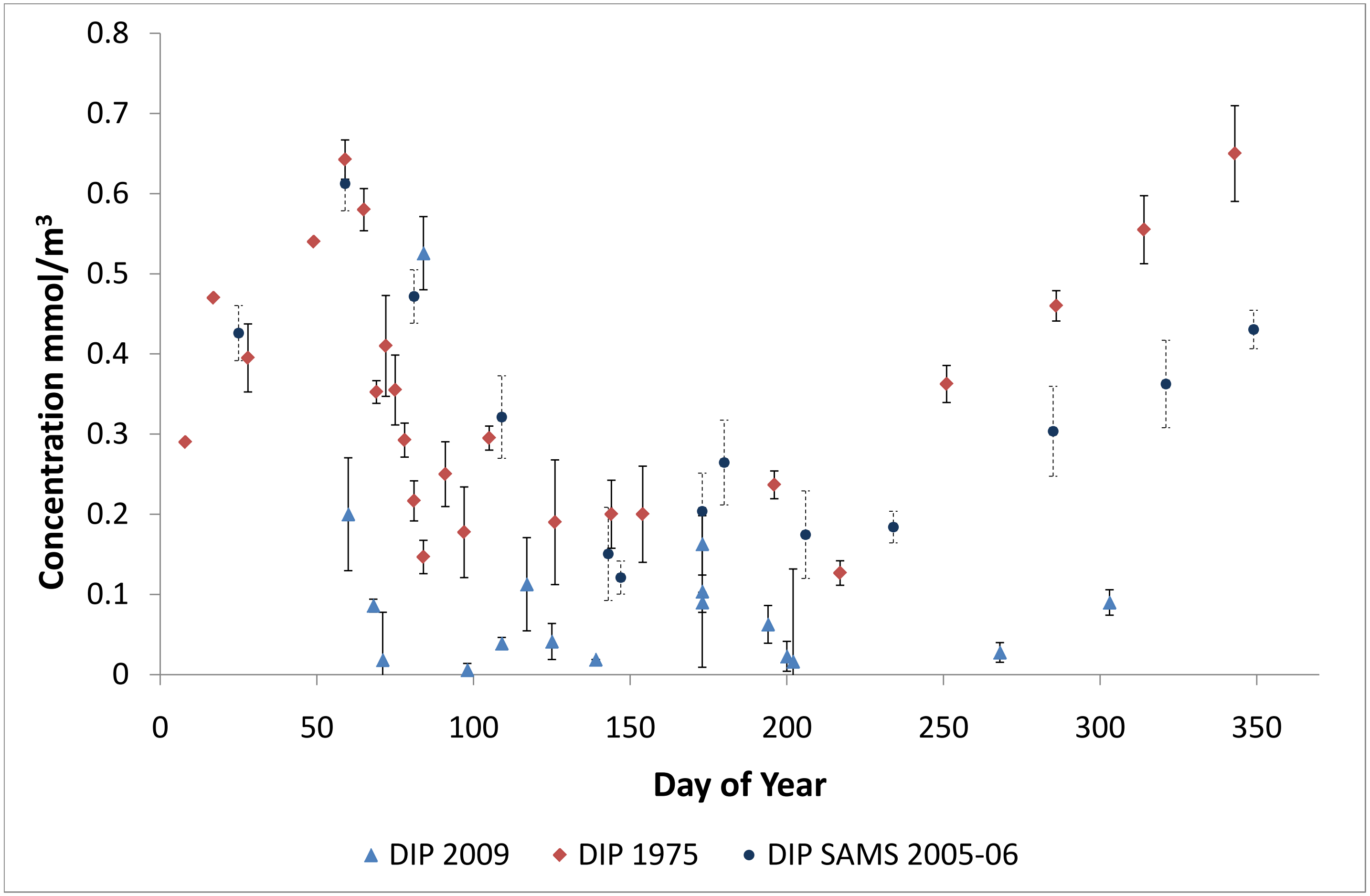


Figure 4.4: A comparison of dissolved inorganic phosphorus (DIP) measured in Loch Creran in 1975 (Jones 1979) and measurements made in 2005-06 and in 2009. The data for 2005-06 was provided courtesy of Dr Thom Nickell, Scottish Association for Marine Science. The error bars represent one standard deviation. The data points represent mean values for the loch.

4.4 Discussion

It would appear that there have been changes in the concentration of nutrients in the loch. Although there does not seem to be any significant annual change in the concentration of DIN the 2009 data appears to show slightly elevated levels of nitrates during the spring. The observations made by SAMS between 2005 and 2006 seem to confirm this with figure 4.2 showing higher levels in the spring as well as later in the year. Unfortunately the reasons for this change are not clear. The exceptionally high values measured on day 173 were only recorded in the top one metre of the water column adjacent to location C5 and C4. This may have been due to run-off containing high levels of nitrate but without further information it is impossible to say. The data obtained by SAMS was taken from observations made from sampling sites near to the location of one of the oyster farms which is situated in the loch and may show elevated levels of nutrients because of this. However the 2009 data was taken from several different locations along the length of the loch and so should not be influenced by any proximity to a fish farm.

There is a difference between the observations made between 2005 and 2006 and those made in 2009. The latter measurements indicate a significant decrease in annual DIP concentrations throughout the loch while those made earlier appear to show elevated levels particularly during spring, although they are lower than the 1975 values during late summer and winter. Again this difference may be explained due to the proximity of the earlier sampling sites to the fish farm, however without further study this cannot be determined.

The observations of DSi in the loch show good agreement between the data sets. Both show slightly elevated levels, particularly during the spring and again in the autumn. However while the concentrations are significantly higher they still generally fall within the 5th and 95th percentile envelope.

While the abundance of pelagic diatoms, dinoflagellates and small flagellates has decreased during the spring in the loch it is difficult to say if this is a result of the differences observed in the nutrient concentrations in the loch or if the decrease in the abundance of these organisms has led to an increase in nutrients that would normally be assimilated during the spring bloom. Unfortunately there is very little data from the Lynn of Lorn for 2009 and almost none for the 1970's so it is difficult to see if the changes within the loch are reflected in the larger water bodies outside the loch. While it would be expected that a large part of the nutrients within the loch would be introduced at an intermediate depth through tidal exchange these concentrations could be quickly altered through biological activity within the loch. The low levels of DIP measured during 2009 could also reflect changes in the amount of freshwater entering the loch (Rhee 1978). This could also account for the elevated levels of DIN observed during the spring and autumn. It is unfortunate that measurements of nutrients in the loch were confined to only one year. However even if observations had also been made in 2008 the short sampling time makes it difficult to draw any firm conclusions on the prevalent nutrient concentrations in the loch. The inclusion of the SAMS data obtained between 2005 and 2006 does suggest however that significant changes have occurred, at least during the last few years. Whether these changes are the result of long term changes to the loch or are part of a short term trend is difficult to say.

Chapter 5

Studying the physical structure of the loch

5.1 Introduction

Phytoplankton have few requirements; nutrients, trace elements, vitamins and light. In coastal regions the first three are generally available in varying but sufficient quantities in the surrounding water column to allow at least some growth throughout the year. The availability of the latter however depends very much on the position of the phytoplankter in relation to the well lit surface layers of the water column i.e. the photic zone.

This raises an interesting question. Given that many micro-phytoplankton (2-200μm), for example diatoms, are non-motile what prevents them from simply sinking out of the surface layers into deeper, less well illuminated layers where they die? After all, the forces that act on non-motile phytoplankton are the same as those regulating the settlement of any spherical object falling through a viscous fluid. These forces were defined by Stokes in 1851[1].

It is true that Stokes only considered spherical objects whereas phytoplankton exhibit a wide range of differing shapes. However since then other researchers have gone on to expand Stokes work. McNown and Malaika (1950) studying the sinking rates of several different shaped objects found that for small Reynolds numbers[2] < 0.1 the Stokes equation was still valid while for Reynolds numbers < 0.5 the error was only 10%, not enough to account for the extended residence times in the photic zone observed.

It could be surmised that phytoplankton may have evolved various mechanisms to stop or delay their sinking rate and indeed several different hypotheses have been put forward. Smayda (1966, 1970), Smetacek (1985), Sarthou *et al.* (2005) have found that live cells tend to sink more slowly than cells that have either been killed or anaesthetised. This suggests that there is some physiological mechanism controlling their sinking rates. Kahn and Swift (1978), Walsby and Reynolds (1980), Reynolds (2006) note that many marine diatoms are able to regulate the ionic composition of the sap inside their cells, replacing heavier divalent ions such as Ca^{2+} and Mg^{2+} with lighter Na^{+} and K^{+}, thereby reducing their density relative to the surrounding seawater.

Smayda (1974) however, points out that this mechanism may not be widespread amongst diatoms, and is perhaps restricted to only those genera containing larger cell vacuoles. Other studies have pointed to the presence of lipids in the cell. Smayda (1970), Reynolds (2006) note that fats make up between 2 and 20% of

[1]Stokes' law states that the final velocity (V) of a spherical particle of radius (r) and density (ρ) falling through a fluid of density (ρ') and viscosity (m) is: $V = 0.222 \cdot g \cdot r^2 \cdot (\rho - \rho')/m$, where g = acceleration due to gravity. (Margalef 1978).

[2]The Reynolds number has no dimensions but represents the ratio of inertial forces to viscous forces in a fluid. In terms of microplankton, although their low mass and the viscosity of the surrounding water ensures that they have a slow sinking speed it is not zero.

the ash-free dry mass of phytoplankton cells. As lipids are less dense than water these lipids and fats would also help to reduce the density of the cells. Nevertheless Boyd and Gradmann (2002) note that the quantity of lipids usually found in phytoplankton cells is not enough to allow them to achieve neutral bouyancy or even significantly lower their density.

Reynolds (2006) discussed the interesting possibility that some species of phytoplankton may make use of mucilage to lower their density however as he points out in some species the opposite appears to be true with mucilage apparently streamlining the phytoplankter cell. In the case of *Skeletonema spp.* a centric diatom whose cells are linked by silica rods, Smayda and Boleyn (1966) found that as the length of the chain increased, the sinking rate decreased. He surmised that the presence of connecting silica rods was an adaptation by *Skeletonema spp.* to aid flotation.

Micro-phytoplankton therefore live surrounded by water that is inherently viscous and through the interplay of such factors as; tides, currents, wind shear and solar heating, constantly in motion. Organisms living at such low Reynolds numbers face a unique set of difficulties. Purcell (1977) describes the dilemma faced by those species capable of some movement when trying to move through water. Reciprocating motions, such as those used by a frog when swimming, are virtually useless and the cell is restricted to using rotating motions such as those produced by a flagellum or corkscrewing through the water after the fashion of many ciliates and euglenoids.

Micro-plankton exist therefore, embedded within a spectrum of turbulent eddies, of decreasing size, albeit at a slightly larger scale, that are capable of transporting them through the water column, regardless of any inherent self propulsion that they may themselves be capable of (Reynolds 2006). As these eddies are not restricted to any particular direction it is just as probable that any algal cells embedded in them could be transported upwards, to the light, as downwards, through the water column.

It is likely then that the strategy employed by many species of phytoplankton is not to reduce their density until they become neutrally buoyant but, through different means, decrease their downwards motion through the water column and increase the probability that turbulence will lengthen their residence time in the photic zone (Sverdrup 1953, Smayda and Boleyn 1966, Reynolds 2006). Huisman *et al* (2002) hypothesised that there exists a *"turbulence window"* within which the conditions for sustained growth of a population of phytoplankton are met i.e. if the mixing depth is too great the phytoplankton will spend too long in regions where the light levels are insufficient to sustain growth. Conversely too little turbulence will allow the phytoplankton to sink out of the photic zone altogether. At intermediate mixing rates, although individual cells may continue to sink, the population as a whole will be maintained within the photic zone and will prosper.

Huisman *et al.* (2004) studied the impact on species composition as a result of changing the turbulence regime in Lake Nieuwe Meer. Physically changing the amount of mixing within the lake allowed them to compare actual observations with simulations. By increasing turbulence in the lake they found a significant change in the dominant species throughout the year. Although their experiment concentrated on the differences between buoyant and sinking species in the lake, similar changes to species composition can be observed in the open sea during El Nino events (Blanchot *et al*. (1992), Iriarte and Gonzalez (2004)), when changes to surface warming alter the mixing depth.

It is clear that turbulence and the extent of mixing in the water column are important factors affecting the successful growth of phytoplankton (Estrada *et al*. 1987). Given the observed changes in the abundance of the phytoplankton community in loch Creran (see chapter 2) it would be helpful to attempt to build a picture of the physical structure of the water column in the loch so that changes throughout the course of a year can be analysed. Unfortunately one of the problems often encountered in biological oceanography is finding the resources to thoroughly observe a water body both spatially and temporally and in this case it was only possible to survey the loch twice during 2008 and once every four weeks during the Spring, Summer and Autumn months of 2009. While not ideal, this does however provide a useful snapshot of the physical structure of the loch.

5.2 Aims

The aim is to create a picture of the physical and biological structure of Loch Creran. This will include salinity, temperature, density and the amount of chlorophyll present in the water column. As the physical and biological properties of the loch are also being modelled (see chapter 10) part of the Lynn of Lorn, representing a model boundary is also included.

5.3 Methods

During the spring of 2008 the research vessel RV Serpula operated by Heriot-Watt University, Edinburgh was chartered to make two transects of the Lynn of Lorn and Loch Creran. The following year the research vessels RV Seol Mara and RV Calanus, both operated by the Scottish Association for Marine Science, were chartered for a further eight transects of the loch. While the same sampling stations were used during both years, additional stations were introduced during 2009 (see figure 2.4 for their locations). The sampling stations were located by the Global Positioning System (GPS). The coordinates for these sampling stations have been listed in table 2.1. Apart from one occasion on the 2nd of April 2008 and again on the 19th of May 2009, when the transect was carried out during a rising tide, all other transects were carried out as the tide was falling.

At each station the vessel was brought to a stop and an SBE 19plus SEACAT Conductivity, temperature and depth (CTD) profiler, supplied by Sea-Bird Electronics (SBE) Inc. Washington 98005, USA and owned by Edinburgh Napier University, was lowered by a winch cable from the lee side of the vessel. The profiler was kept at a depth of two metres for a period of one minute to allow the sensors to equilibrate. It was then raised to within a few centimetres of the surface before being lowered to approximately five metres from the sea bed. Measurements of salinity, temperature, depth and fluorescence were recorded at 0.25 second intervals. Raw data was analysed with SBE data processing software. The profiler takes measurements during the time it is lowered to the sea bed (downcast) and as it is being raised to the surface (upcast). There is always a possibility that the water column will be disturbed by the downwards passage of the profiler so to avoid this only data obtained from the downcast was used. For clarity, measurements were averaged into one metre depth bins.

To allow the measurements made by the profiler to be calibrated, water sampling bottles were attached to the cable at several of the sampling stations and samples were collected for later analysis at Edinburgh Napier University. The methods used for this analysis have previously been described in chapter 2.

Contour diagrams of the loch were created using the software package *Surfer for Windows version 9* (Golden Software, Inc.). The gridding method chosen was "Kriging" employing a linear variogram, an anisotropic ratio of 2 and an angle of 0^0. Essentially this weights the interpolation, putting more emphasis on values lying in a plane horizontal to the observations. As water of different densities is subject to gravitational force this seemed a reasonable assumption to make.

Named after the South African D. Krige, kriging is a very flexible statistical technique that predicts the missing values in a series of spatially distributed variables (Stein and Corsten 1991). It attempts to predict trends that are suggested by the data essentially by giving more weight to neighbouring observations (Beers and Kleijnen 2003). The predictor in any location being a linear combination of actual observations and a certain amount of weighting. Amongst the different prediction methods, Stein and Corsten (1991) found it to be the technique with the smallest prediction variance and with the least systematic prediction error.

It must be stressed however, that the package is still relying on interpolated values to create the various contour maps included below. This inevitably leads to a certain amount of uncertainty towards the accuracy of the diagrams created. While the surface layers have a sufficient number of observations to allow an accurate picture to be created some of the deeper areas of the loch may rely more on interpolation and less on hard data. However as the interest in the loch, at this time, is focussed more towards the surface layers of the water column this uncertainty seems acceptable.

Creating a series of plots, such as these, of the structure of the water column in the loch allows a better understanding of the physical processes at work. While this gives valuable insight it would also be helpful if a comparison could be made between the structure of the loch in 2008/09 and as it was during the 1970's. To do this in a meaningful way it would be necessary to collate the data gained from a series of transects of the loch over several years but unfortunately this data is not available. Nevertheless Tyler (1983) made a series of measurements of temperature and salinity at various depths during 1978 and these have been converted by Enrique Portilla (personal communication) to sigma-t values.

Rather than use this data to create a series of contour plots for the different years which, it was felt, would have limited use as a comparison, it was decided to adopt the method put forward by Simpson and Bowers (1981) in which they calculated the energy needed to cause an immediate turnover of the water column thus gaining a way of judging the potential of a water column to stratify. Shonting and Cook (1970) surmised that changes in the water column due to continual seasonal alterations in the density were linked to changes in the potential energy contained within the water column. They found that as density varies with depth, each point, assuming that the water column can be treated as a series of point masses, in the column will have a certain amount of gravitational potential energy and this can be calculated from the sigma-t profiles. This potential energy varies with the density and the depth of the water column and by summing these different values an estimation of the potential energy needed to achieve an equilibrium within the column can be found by the equation derived by Simpson et al (1990):

$$\phi = \frac{1}{h} \cdot \int_{-h}^{0} (\rho_{mean} - \rho_z) g \cdot z \cdot dz \tag{5.1}$$

where ϕ (jm^{-3}) = work needed to completely mix the water column, h = the depth of the water column in metres, g = gravitational acceleration = 9.81 ms^{-2}, ρ =

the water density and ρ (z) = the density profile of a water column of depth z in metres.

5.4 Results

Each of the following contour plots has a vertical scale of -1 to -46 metres and a horizontal scale of 18.25 kilometres starting on the left at the Greag Isles in the Lynn of Lorn (station LY1) and extending to the head of the main basin of Loch Creran on the far right (station C6). High values are represented by dark green and red and lower values are depicted in light blue.

Figure 5.1 (a) illustrates the sigma-t values measured during a transect of the Lynn of Lorn to the top of the main basin in Loch Creran carried out on the 2nd of April 2008. A layer of relatively low density water can be seen originating at the top of the main basin and extending several kilometres seawards. Mixing at the sill decreases the depth of this layer although it is still visible. An area of low density water is also visible lying in the Lynn of Lorn, adjacent to the Greag Isles. It is unclear where this water originates however it is most likely to be the result of water flowing out of Loch Etive approximately 20 kilometres to the South of Loch Creran.

Figure 5.1 (c) is a plot of the chlorophyll concentration measured during the same transect of the loch on the 2nd April, 2008. The concentrations ranged from zero to 3.0 mg/m^3. Interestingly the greatest concentrations lay below the stratified surface layer. The ”patch” of chlorophyll indicated in the Lynn of Lorn appears to have been associated with the low density water possibly originating from Loch Etive. As these appear to be two separate water masses the presence of chlorophyll, albeit in low concentrations, lying beneath a stratified surface layer may indicate that the

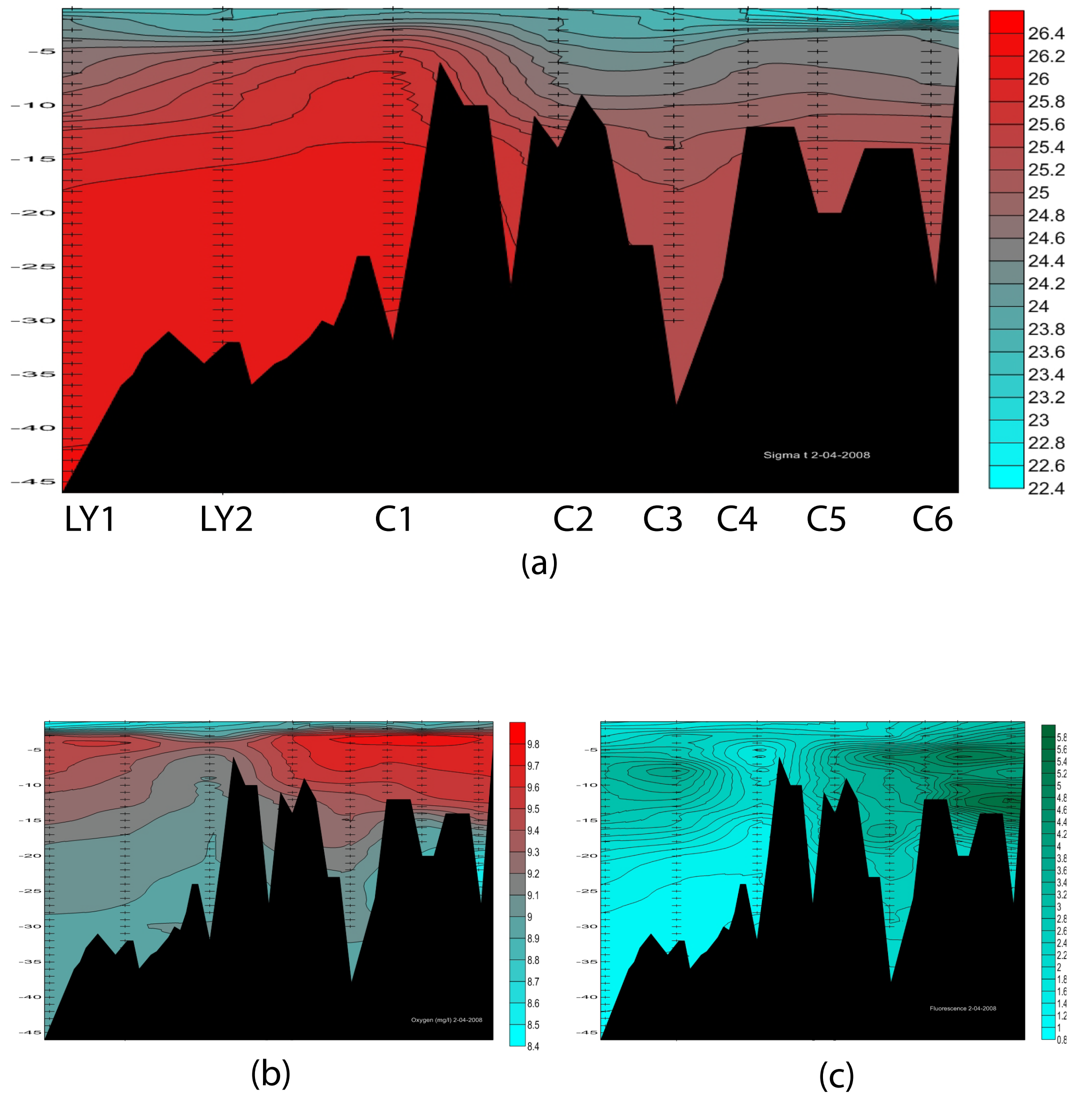


Figure 5.1: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 2nd of April 2008. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

surface layer had formed quite recently, perhaps as a result of heavy rainfall or run-off.

Figure 5.1 (b) indicates the dissolved oxygen levels in the loch during the transect of the loch on the 2nd of April. It is interesting to note that the highest concentrations of oxygen were associated with the same sub-surface layer where the greatest concentrations of chlorophyll was found. Again this would suggest that the surface layer had formed quite recently.

Figure 5.2 (a) represents the sigma t measurements made three weeks later on the 24th of April. While there was a large area of low density water lying in the Lynn of Lorn, the water column within Loch Creran was relatively well mixed. The patch of low density water possibly originates in Loch Etive although given its extent it may have been water flowing Southwards from Loch Linhe. As this transect was carried out towards the end of April it could be expected that the water column in Loch Creran would have exhibited a higher degree of stratification. Unfortunately only two transects of the loch were carried out in 2008 so it is impossible to gauge the duration of this mixing.

It is apparent from figure 5.2 (c) that the chlorophyll measured in the Lynn of Lorn (a maximum of 21 mg/m^3) was associated with the large area of low density water there. However it would appear that there was virtually no chlorophyll throughout the main basin of Loch Creran. Dissolved oxygen levels in the loch (see figure 5.2 (c)) also showed well mixed conditions throughout the main basin with very high concentrations of dissolved oxygen associated with the area of low density water in the Lynn of Lorn.

Figure 5.3 (a) is a plot of sigma t values measured during the first cruise of 2009 on the 25th of March. It is evident that there was a well stratified layer extending

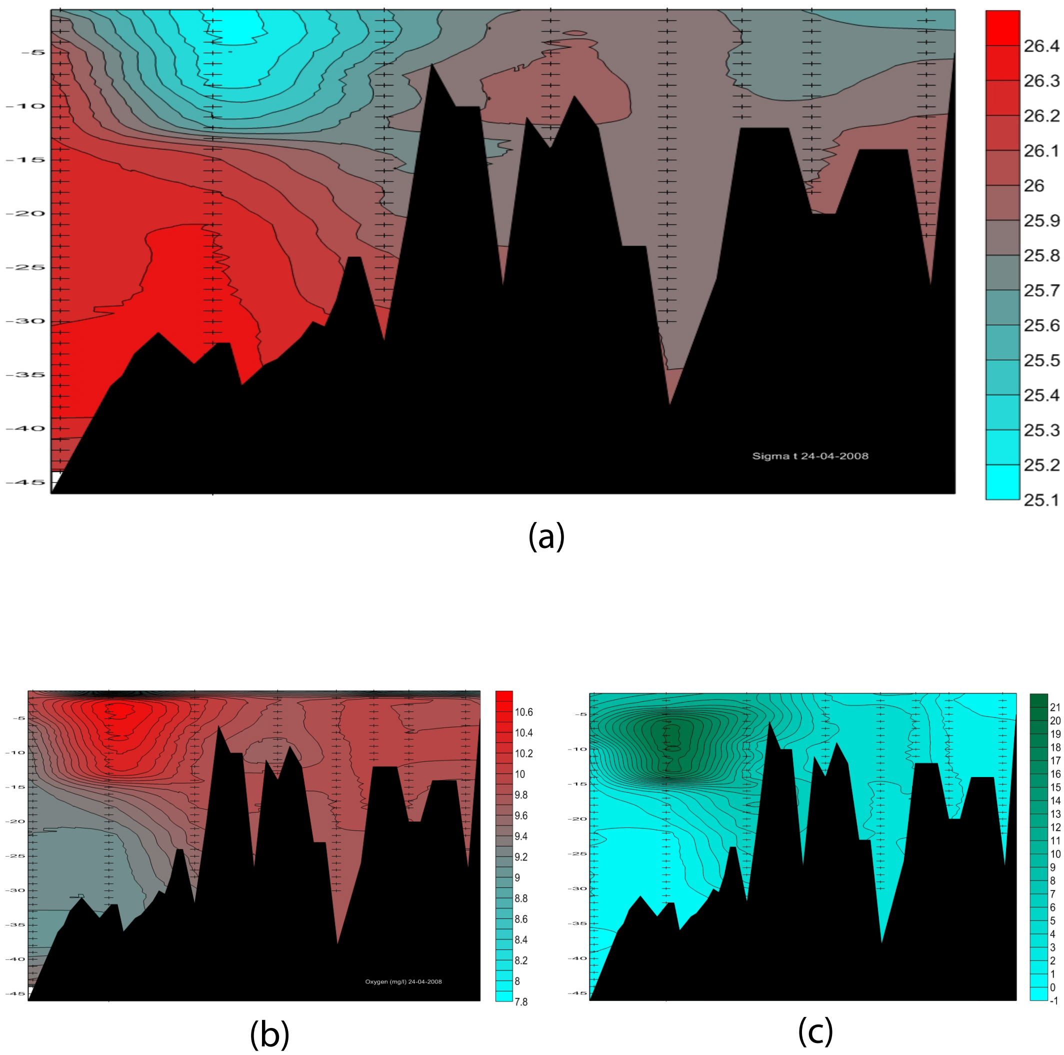


Figure 5.2: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 24th of April 2008. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

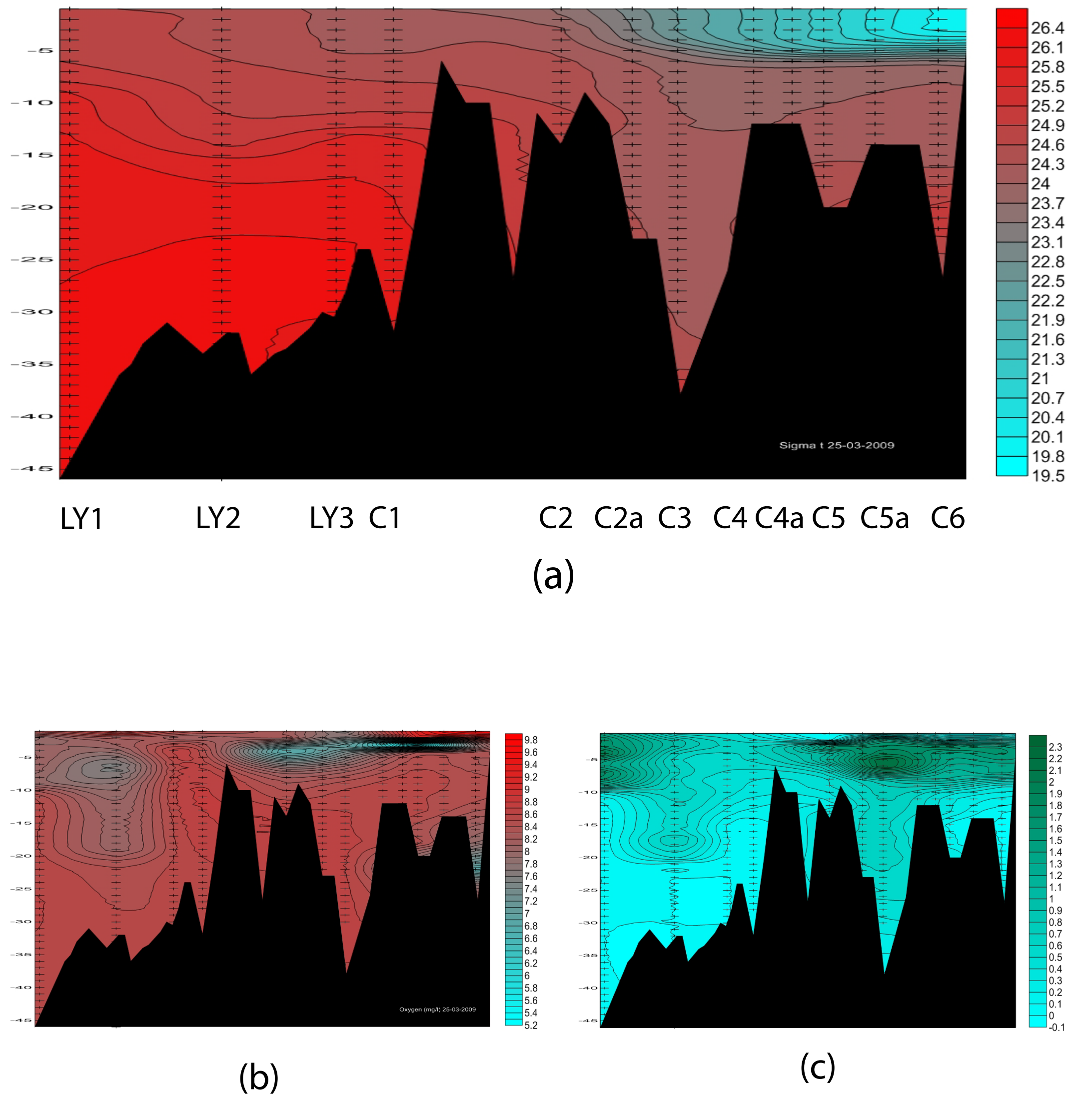


Figure 5.3: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 25th of March 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

through a large part of the middle basin. This stratified region contains small concentrations of chlorophyll (see figure 5.3 (c)) which, from figure 5.3 (b), appears to be associated with a subsurface layer with slightly reduced levels of dissolved oxygen. Another area with reduced oxygen levels can be seen at location C6 (see figure 5.3 (b)). This sampling station is located at the top of the main basin in Loch Creran in one of the deeper areas of the loch. This suggests that recent mixing events had not been extensive enough to replenish the water this far into the loch. Chlorophyll was also evident in the Lynn of Lorn and again this is associated with slightly reduced levels of dissolved oxygen. While this may be evidence of enhanced bacterial activity it is possibly the result of increased grazing levels.

Two weeks later on the 8th of April, 2009 the loch again showed a well stratified layer of water extending seawards along a significant part of the main basin (see figure 5.4 (a)). However while chlorophyll concentrations reached 3.2 mg/m^3 in the Lynn of Lorn, the maximum levels in the loch were between 1.4 and 1.8 mg/m^3 (see figure 5.4 (c)). The dissolved oxygen levels were high throughout the water column (see figure 5.4 (b)) with particularly high concentrations associated with the stratified surface layer.

Figure 5.5 (a) illustrates the measurements of sigma-t taken on the 19th of May 2009. It is apparent that there was a significant degree of stratification in the Lynn of Lorn at this time, although again it is difficult to say if this water is representative of water flowing out from Loch Etive or moving southwards from Loch Linhe. Loch Creran also appeared to be stratified although there is evidence of mixing extending down through the water column within the loch. The transect carried out on the 19th of May was one of two that were conducted on a rising, rather than a falling, tide. It may be that the high degree of mixing observed in the loch was associated

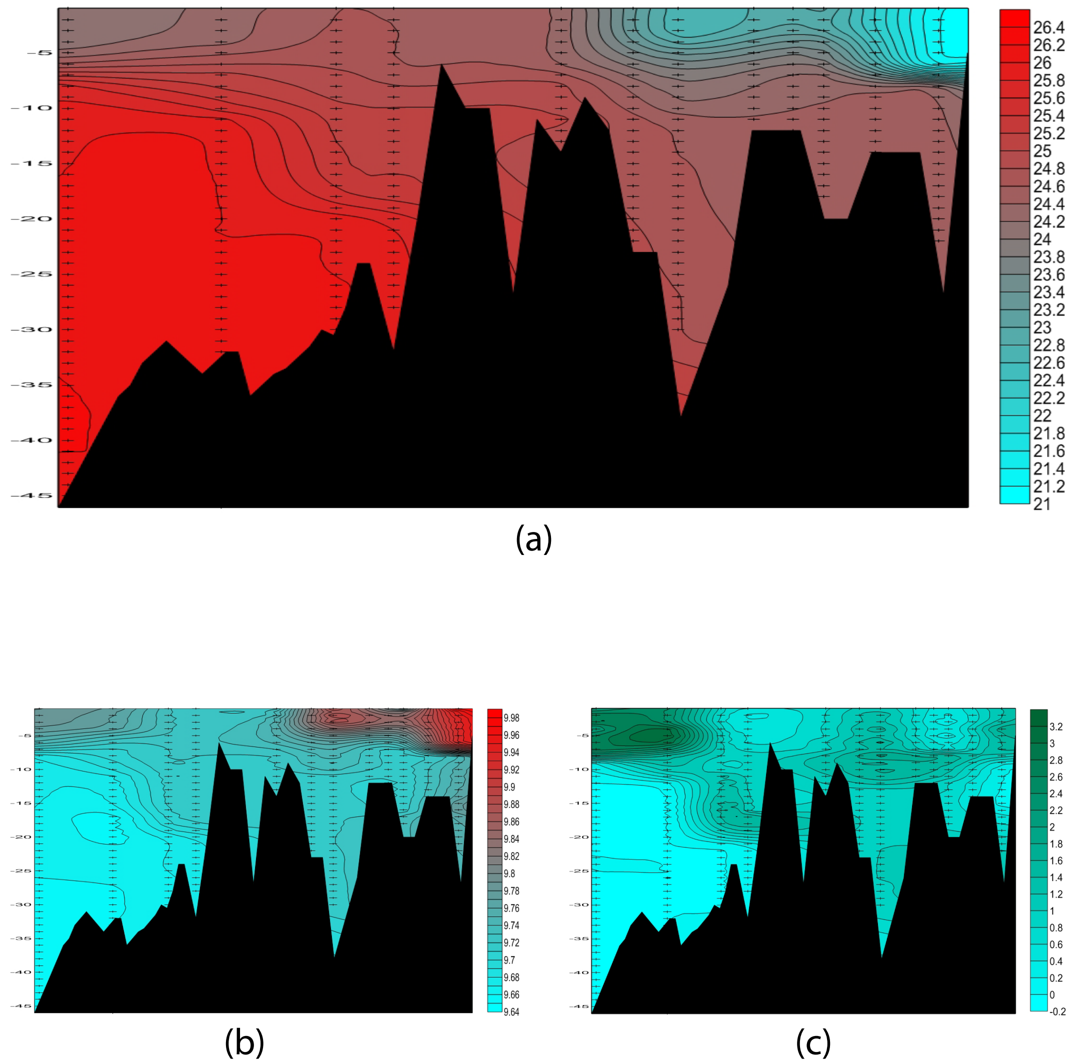


Figure 5.4: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 8th of April 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

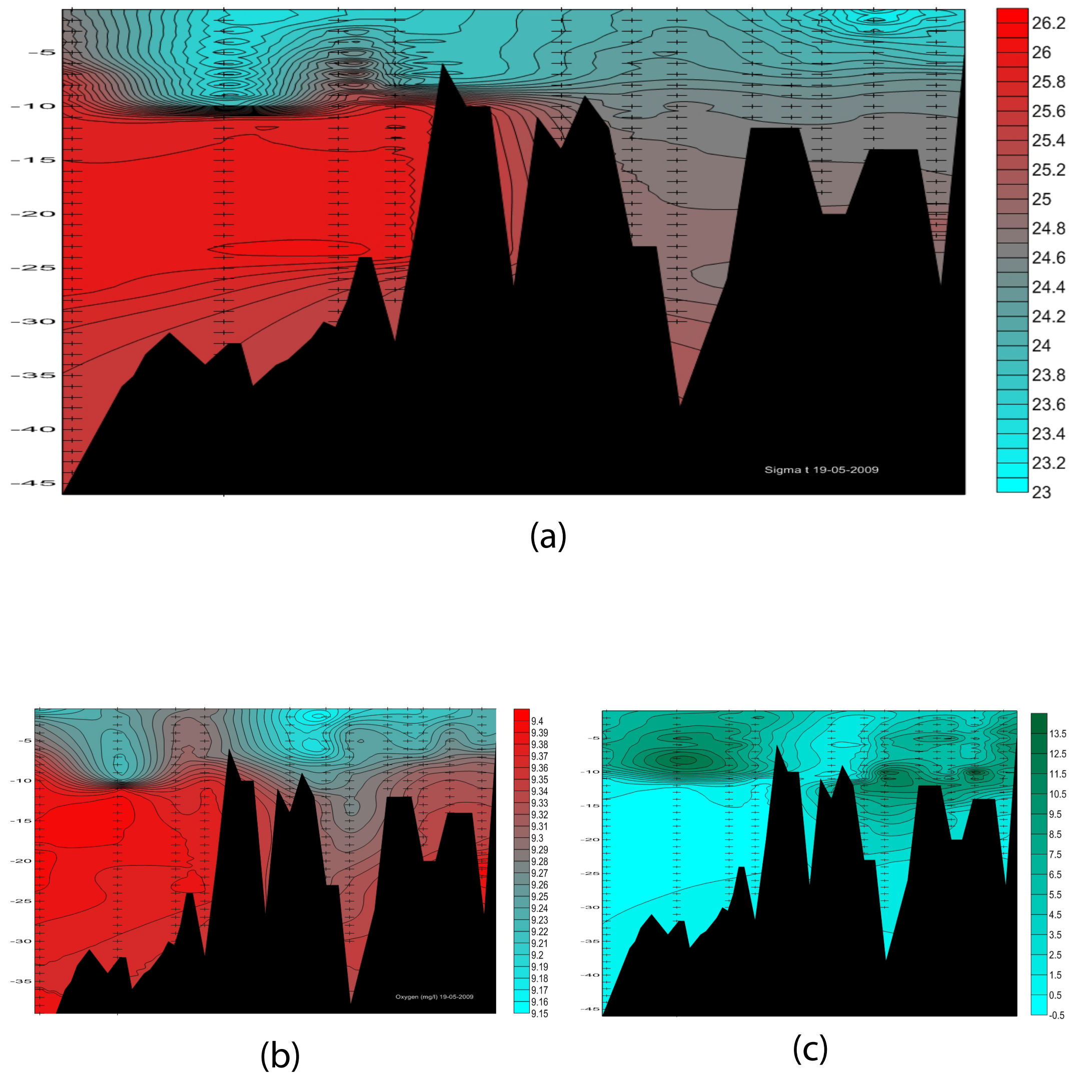


Figure 5.5: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 19th of May 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

with the inflow of tidal water. The stratified layer in the Lynn of Lorn is associated with concentrations of chlorophyll of around 13 mg/m^3. Similar levels were found in Loch Creran but at a slightly lower depth (see figure 5.5(c)). It may be that this is evidence of phytoplankton sinking through the water column as the mixing depth increases, however it may possibly be associated with water flowing into the loch at an intermediate level from the Lynn of Lorn. Figure 5.5(b) shows that the water column, both in the Lynn of Lorn and Loch Creran, was well oxygenated although levels at the surface were slightly lower than at depth.

The transect on the 22nd of June (see figure 5.6 (a)) also indicated that surface levels of dissolved oxygen were slightly lower than those at depth and this was echoed in the Lynn of Lorn. Chlorophyll concentrations in the loch (see figure 5.6 (c)) were associated with the surface stratified layer, reaching a maximum of 7.4 mg/m^3. However in the Lynn of Lorn the chlorophyll extended to a much deeper level. This may indicate the presence of two different water masses; a slightly de-oxygenated surface layer representing water flowing from Loch Etive lying over a layer of well oxygenated water moving northwards into the Lynn of Lorn. Figure 5.6 (a) shows a well stratified layer throughout Loch Creran, underlain with relatively well mixed deep water.

In contrast to June the transect carried out on July the 9th (figure 5.7 (a)) found a well mixed water column both in the Lynn of Lorn and Loch Creran. A shallow, stratified surface layer was present in the loch but it can be seen from figure 5.7(c) this was devoid of chlorophyll. The chlorophyll present below this layer reached a higher concentration (10.3 mg/m^3) in the loch than in the Lynn of Lorn. Apart from one or two days of heavy rain at the beginning of June (see chapter 9) there had been virtually no rainfall in the two weeks preceding this transect. As much of the

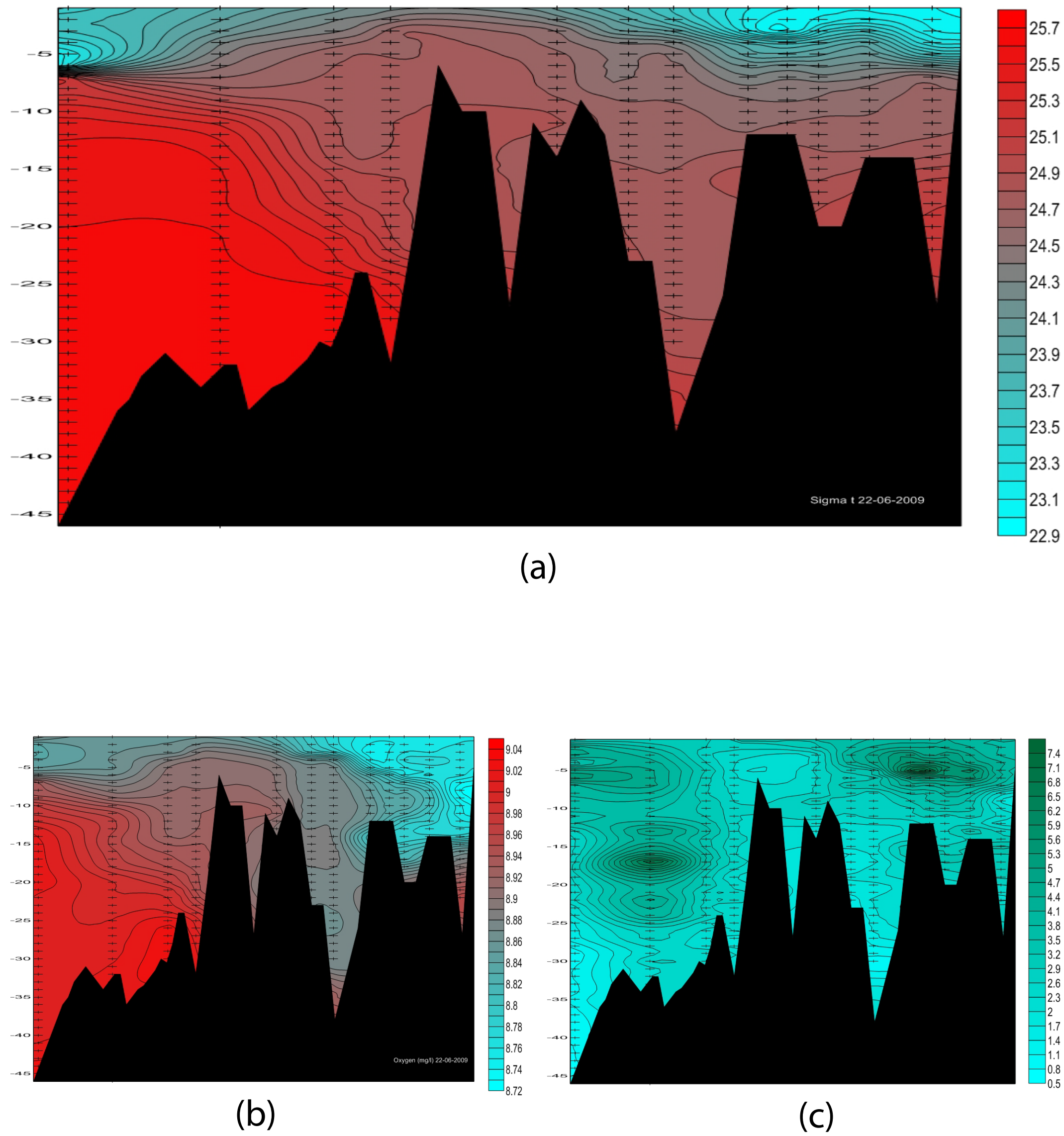
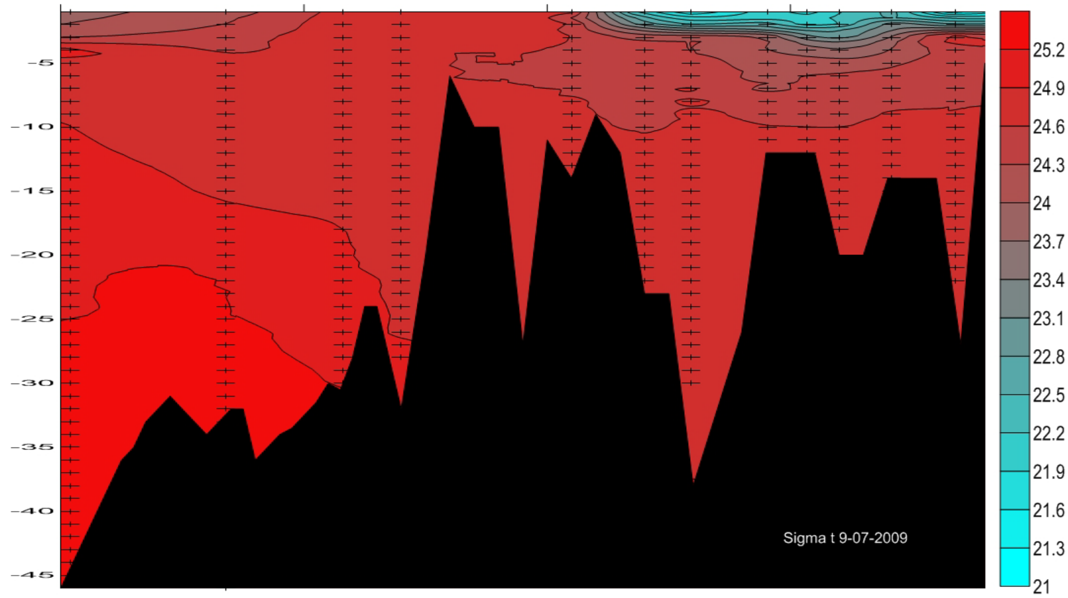
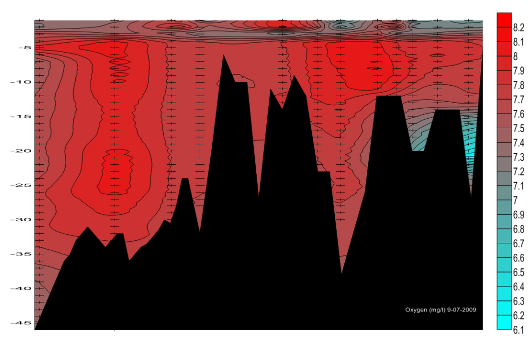


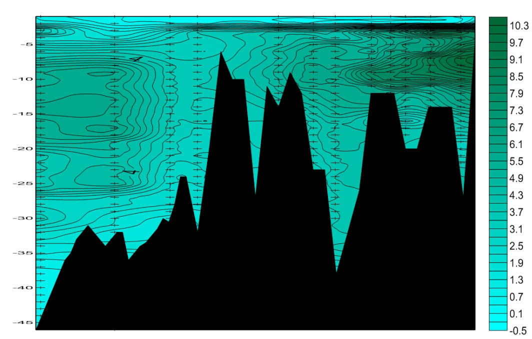
Figure 5.6: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 22nd of June 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.



(a)



(b)



(c)

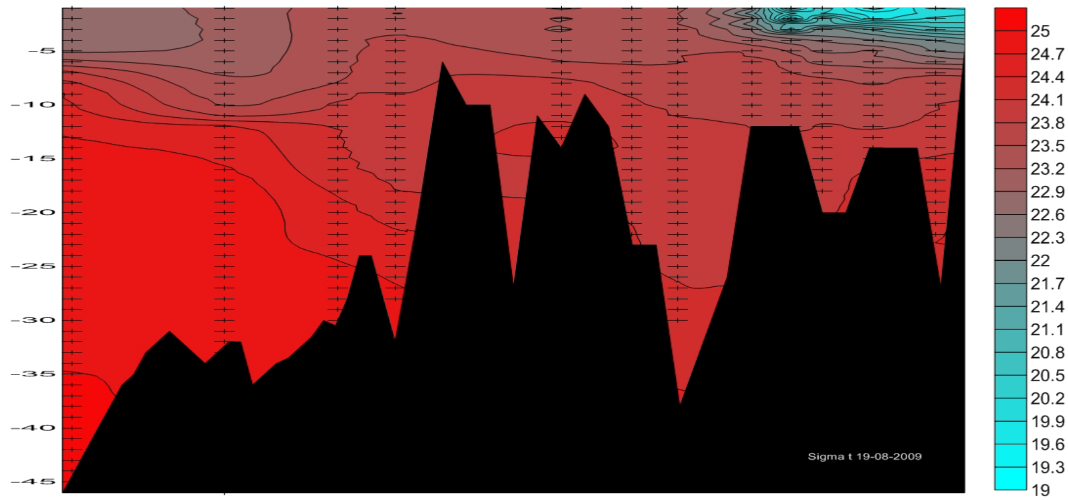
Figure 5.7: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 9th of July 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

stratification in the loch is probably due to the inflow of freshwater this may explain the very shallow surface layer observed. The areas with the lowest dissolved oxygen levels were generally associated with the highest concentrations of chlorophyll. However there was a deep layer of relatively de-oxygenated water found at station C6 near the head of the main basin. This suggests that any preceding mixing events had been insufficient to replenish this deeper water.

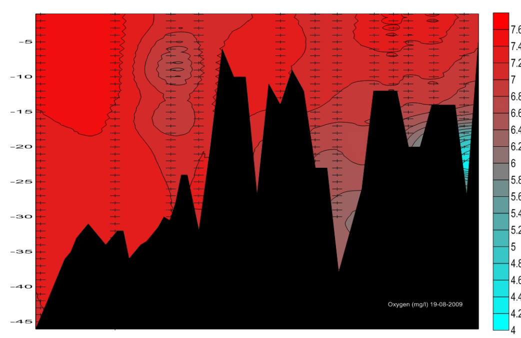
Figure 5.8 (a) illustrates the sigma-t levels measured on the 19th of August. Similarly to the transect of July the 9th the Lynn of Lorn and the deeper and intermediate layers of Loch Creran show well mixed conditions. A surface layer of stratified water extended a relatively short way (between stations C4 and C6) along the main basin. From figure 5.8 (c) it can be seen that there was an area of chlorophyll reaching a maximum concentration of 9.7 mg/m^3 associated with this stratified layer. However there was very little chlorophyll observed in the Lynn of Lorn. Figure 5.8 (b) shows that dissolved oxygen concentrations were high throughout the water column although once again it can be seen that the deeper areas around station C6 had relatively lower concentrations.

Stratified conditions were again noticeable (figure 5.9 (a)) in the loch, during the transect on the 25th of September. The stratified layer extended along most of the main basin overlying a well mixed water column. Chlorophyll concentrations in this layer reached 9.1 mg/m^3 (figure 5.9 (c)). No chlorophyll and very little stratification was observed in the Lynn of Lorn. Dissolved oxygen concentrations in the loch were however surprisingly low. The highest concentrations were associated with the surface layers.

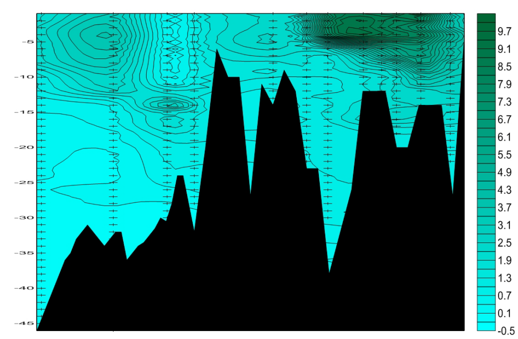
The final transect of Loch Creran was carried out on the 30th of October in quite windy conditions. Figure 5.10 (a) shows that there was a stratified layer extending



(a)



(b)



(c)

Figure 5.8: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 19th of August 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

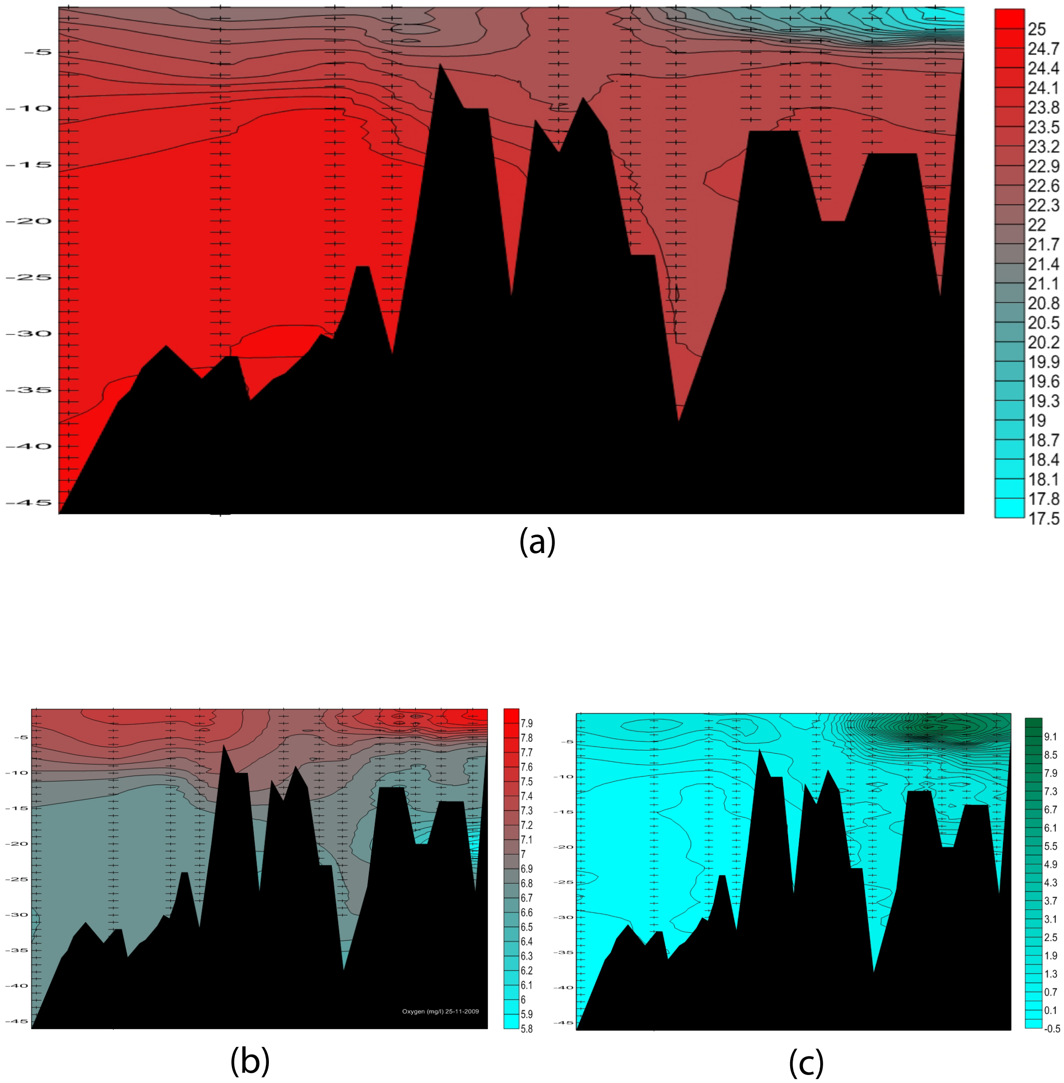


Figure 5.9: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 25th of September 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

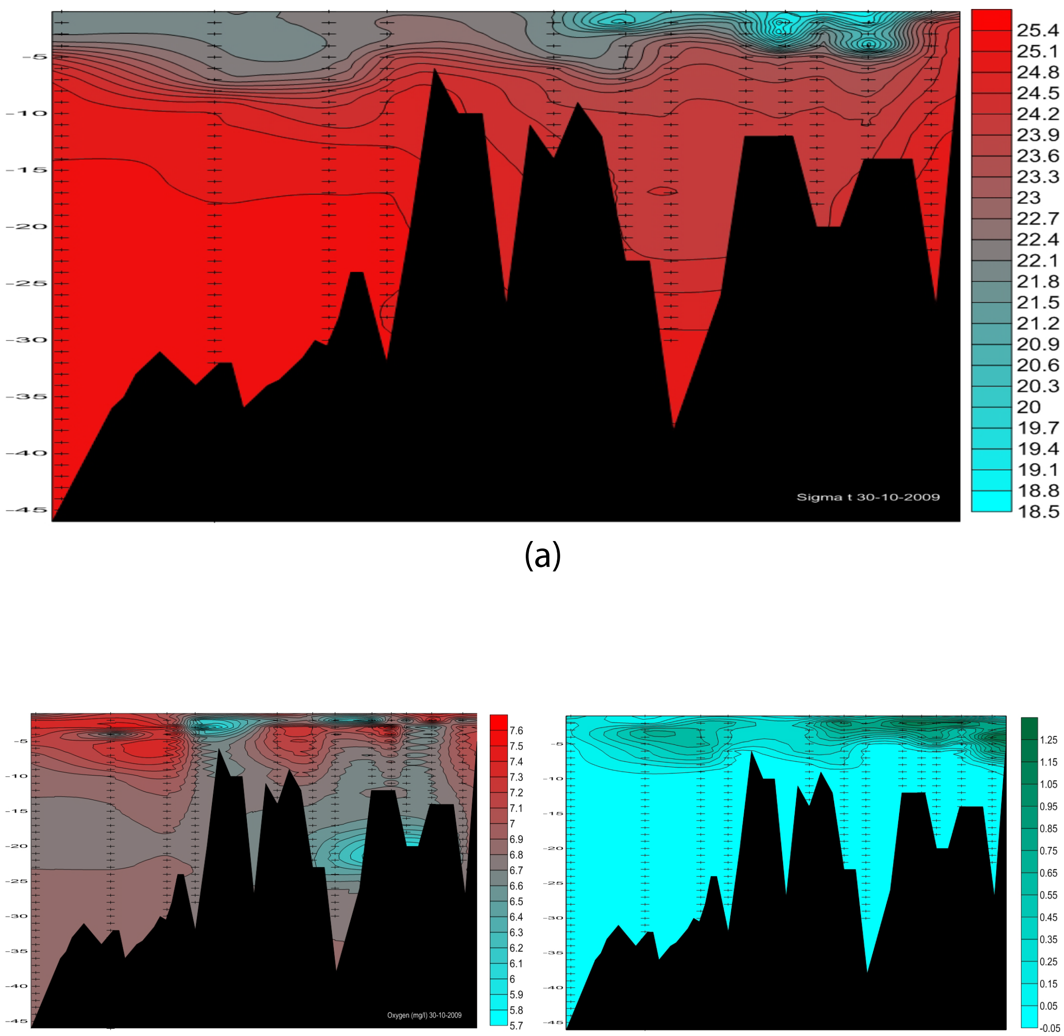


Figure 5.10: Plot of sigma t (a), dissolved oxygen concentration ((mg/m^3) (b) and chlorophyll concentration ((mg/m^3) (c), measured during a transect of the Lynn of Lorn and Loch Creran on the 30th of October 2009. The plot was created using the software package Surfer 9 (Golden Software Inc.) The left hand axis depicts the depth in metres. The horizontal scale is 18.25 kilometres. LY1 is located adjacent to the Greag Isles in the Lynn of Lorn, C1 is located just outside the loch, C2-C6 are located within the main basin of Loch Creran.

along the length of the loch and into the Lynn of Lorn.

Chlorophyll was present in this layer although in small concentrations (maximum of 1.7 mg/m^3) (see figure 5.10 (c))in both the loch and in the Lynn of Lorn. Again levels of dissolved oxygen were relatively low throughout the water column reaching a maximum immediately below the surface layer. A large area of deeper water (figure 5.10 (b)), lying between stations C2 and C5, also exhibited reduced levels of dissolved oxygen.

Creating a series of plots, such as these, of the structure of the water column in the loch allows a better understanding of the physical processes at work. While this gives valuable insight it would be helpful if a comparison could be made between the structure of the loch now and as it was during the 1970's. To do this in a meaningful way it would be necessary to collate the data gained from a series of transects of the loch over several years. While this data was, unfortunately, not available the series of measurements of temperature and salinity made during 1978 (Tyler 1983) allowed sigma-t values for the loch to be calculated.

Figure 5.11 illustrates the result of plotting the potential energy anomalies recorded during transects of the loch during 1978 and during 2008-09. The mean values for the 1978 transects are plotted as a blue line and the 5th and 95th percentile of the values recorded have been plotted as the dotted black lines. The observations made during 2008 and 2009 have been plotted as a red line. To indicate the large amount of variability in density found throughout the loch, error bars have been included representing one standard deviation. The Y axis represents the energy required in Jm^3 to immediately mix the water column. In other words the higher the value shown on the Y axis the more likely it is that the water column will be stratified.

Again this is a comparison of only two years of data so any analysis must be treated with a high degree of caution. Interestingly the only time when the 2008/09 data differs greatly from the 1978 data is during April/May and August. August appears to have been weakly stratified during 1978 compared to 2008/09. However the opposite appears to be the case for May 2009 during which the water column appears to have been well mixed. This mixing is also apparent in figure 5.5. It is unfortunate that the earliest transect carried out in 2008/09 was on the 25th of March. The mean value for the potential energy anomaly measured on the 25th of March 2009 lies out with the 5th and 95th percentile envelope created from the 1978 data suggesting that there was a greater level of stratification in 2009 than in 1978.

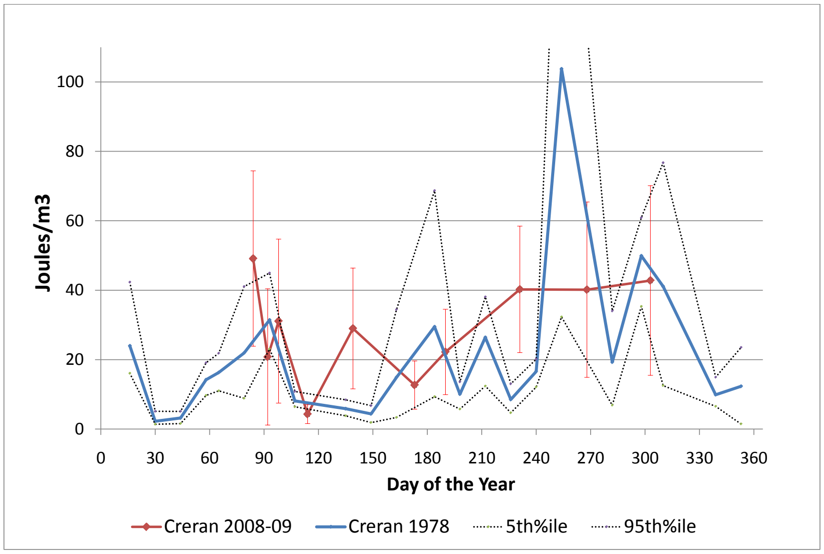


Figure 5.11: Plot of the potential energy anomaly measured in the loch for transects of Loch Creran made during 1978 (blue line) compared with similar transects carried out in 2008/09 (red line). The points represent the mean PEA for the loch on a particular day of the year, calculated by averaging the PEA values measured at locations C2 to C6 during the transect. The black dotted lines represent the 5th and 95th percentiles of the data obtained during 1978. The error bars represent one standard deviation of the values measured during 2008/09 and illustrate the large variation in PEA calculated along the length of the loch.

5.5 Discussion

It is unfortunate that the survey of the Lynn of Lorn and Loch Creran was restricted to the ten transects illustrated above. While the results are revealing, much of the fine variability in the structure of the water column is lacking. Nevertheless the information these plots provide does allow a general picture of the water structure in the loch to be built up.

Although it is not immediately evident from the plots, which present the transects as a linear cross section, the stations in the Lynn of Lorn actually lie to the South of Loch Creran the entrance of which lies at virtually 90^0 to the lynn of Lorn. Station LY1, located adjacent to the Greag Isles, lies almost opposite the entrance to Loch

Etive, a large loch to the south of Loch Creran and it is likely that the stratified layer and its associated chlorophyll seen around the first two sampling stations is evidence of water flowing out from this loch. It is clear that in general the chlorophyll measured is associated with the surface stratified layers in the loch and in the Lynn of Lorn, however it would be difficult to determine if the chlorophyll concentrations in the loch are dependent on the levels in the Lynn of Lorn. This point is of interest as the model (see chapter 10) indicated a high degree of sensitivity to chlorophyll levels as a boundary condition, suggesting that concentrations of chlorophyll outside the loch could have a large impact on levels inside.

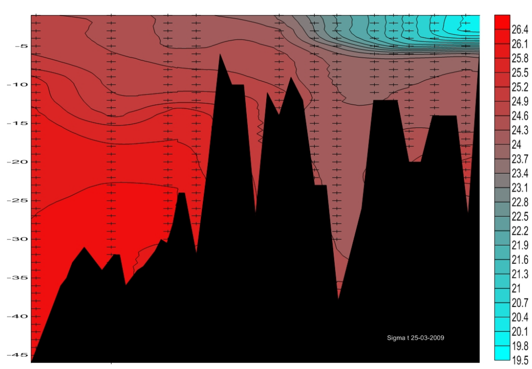
It seems apparent that the loch is stratified for much of the year and this is to be expected as Loch Creran is fed by several small rivers providing an ample supply of freshwater (Edwards and Sharples 1986, Gillibrand and Inall 2006). The amount of stratification also appears to vary seasonally with a shallow stratified layer during the summer months when rainfall is less. The plots for April and May however are a little surprising, particularly those for the 24th April 2008 and the 19th may 2009, which show a relatively well mixed water column and, in the case of the transect on the 24th April, no evidence of chlorophyll at all in the main basin of Loch Creran. Chlorophyll was found in the loch during March but the levels measured were very low, reaching a maximum of ≈ 2.3 mg/m^3 at a time when it could be expected that evidence of the spring bloom would be visible.

The plots of dissolved oxygen concentrations indicate that the water in both the Lynn of Lorn and Loch Creran is well oxygenated throughout the year although low levels, for example on the 19th May (figure 5.5(b)), are associated with relatively high concentrations of chlorophyll. It also seems that water in the deep area, located at station C6, at the head of the main basin is not refreshed as often as deeper areas closer to the mouth of the loch, evidenced by the lowered levels of dissolved oxygen in this area. The levels of dissolved oxygen measured on the 25th September and the 30th October are surprisingly low, both within the loch and in the Lynn of Lorn. This may indeed reflect actual levels in the water column however, given that the dissolved oxygen levels were quite consistent throughout the rest of the year, it is possible that the oxygen sensor had become impaired on a previous trip. Coming at the end of the sampling regime as it did this was not noticed and would not have been rectified until the sensor was recalibrated for a new season of sampling.

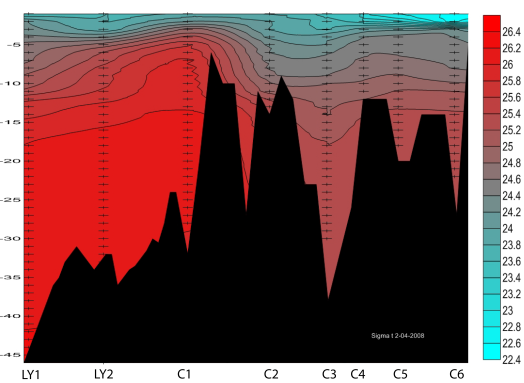
Although data was only available for two years, the results of plotting the potential energy anomaly (figure 5.11) are interesting. While for most of the year the potential energies recorded were comparable they did appear to diverge during the early part of the year. Diatoms, such as *Skeletonema* spp. favour a slightly mixed water column with ample nutrients (Reynolds 2006). However if the stratified surface layer in which a population of diatoms was growing experienced mixing, severe enough to redistribute the cells throughout the water column, any cells lying below a newly stratified surface layer would be very unlikely to survive. It is interesting to speculate whether changes in the pattern of mixing and stratification in the loch, particularly during the early months of the year is playing a part in the observed reduction in biomass in the loch. While some of the results from the early part of the year appear to show unusual amounts of mixing, unfortunately the frequency of sampling was not high enough to allow a definitive answer to this point. Chapter 9 will consider the possibility that there has been a change in the mixing depths in the loch by examining local weather patterns, particularly rainfall, to try and determine if it may be having an affect on stratification in the loch.

5.6 Contour plots of Density, Chlorophyll Concentration and Dissolved Oxygen concentration

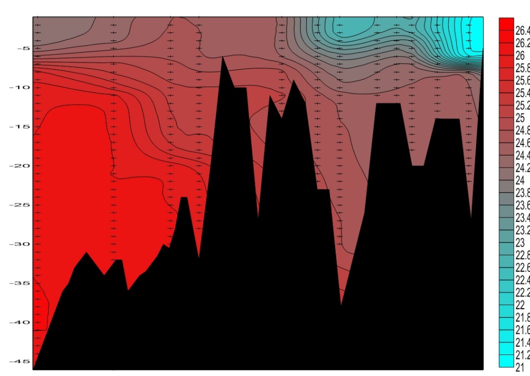
The following pages contain a summary of the contour plots created from transects of the Lynn of Lorn and Loch Creran during 2008 and 2009 and arranged from March through to October.



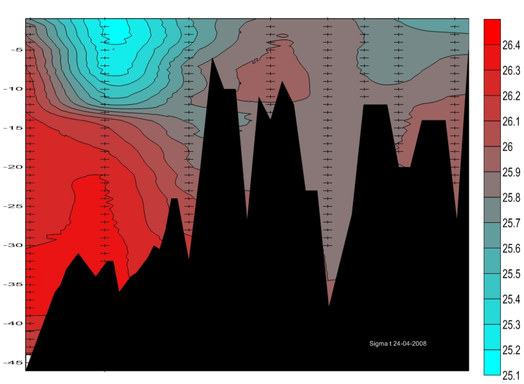
(a) 25th of March 2009



(b) 2nd of April 2008

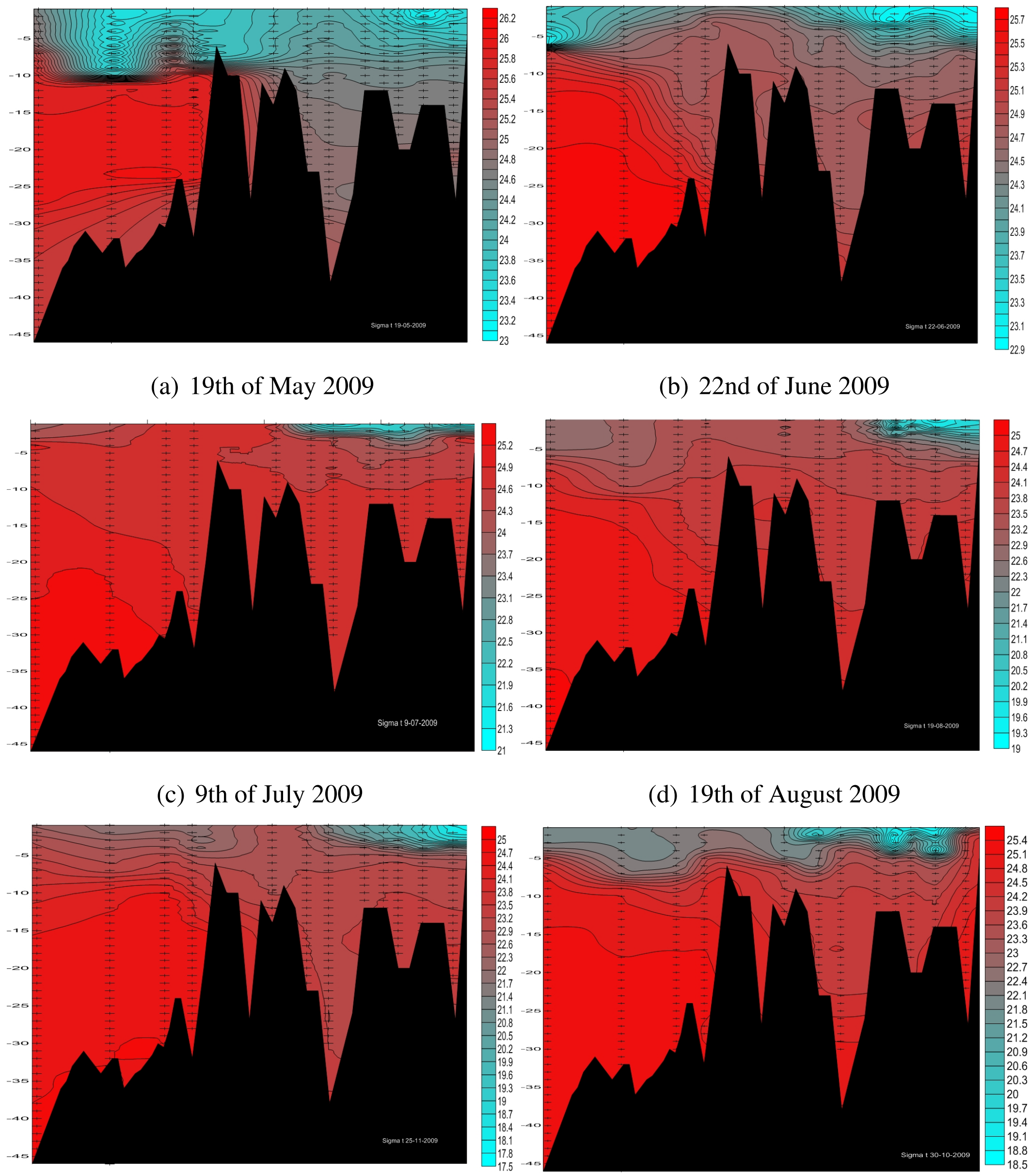


(c) 8th of April 2009



(d) 24th of April 2008

Figure 5.12: Contour plots of Sigma-t levels for transects of the Lynn of Lorn and the main basin of Loch Creran made during march, April, May and June of 2008 and 2009.



(a) 19th of May 2009

(b) 22nd of June 2009

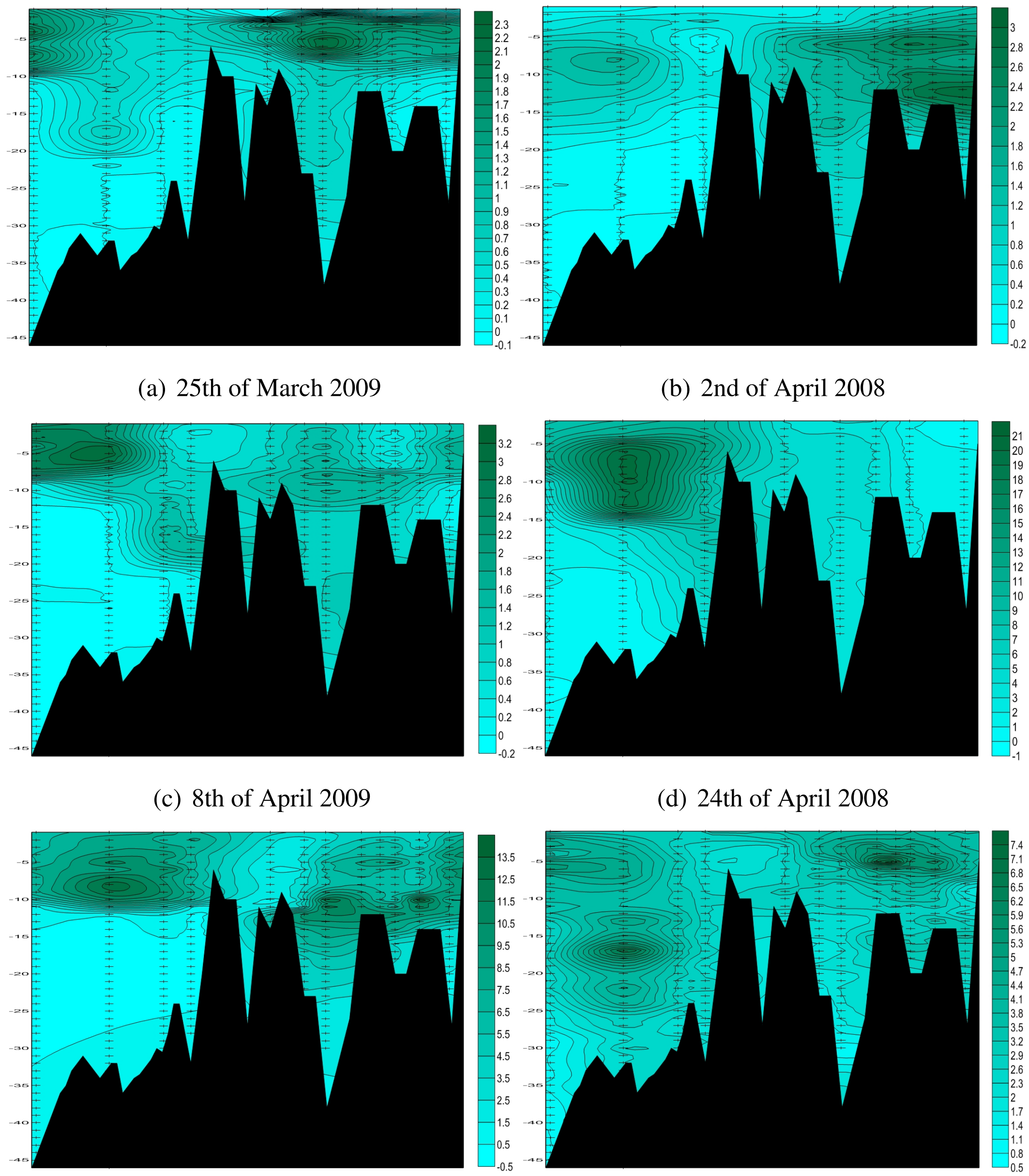
(c) 9th of July 2009

(d) 19th of August 2009

(e) 25th of September 2009

(f) 30th of October 2009

Figure 5.13: Contour plots of Sigma-t levels for transects of the Lynn of Lorn and the main basin of Loch Creran made during July, April, August, September and October of 2008 and 2009.



(a) 25th of March 2009

(b) 2nd of April 2008

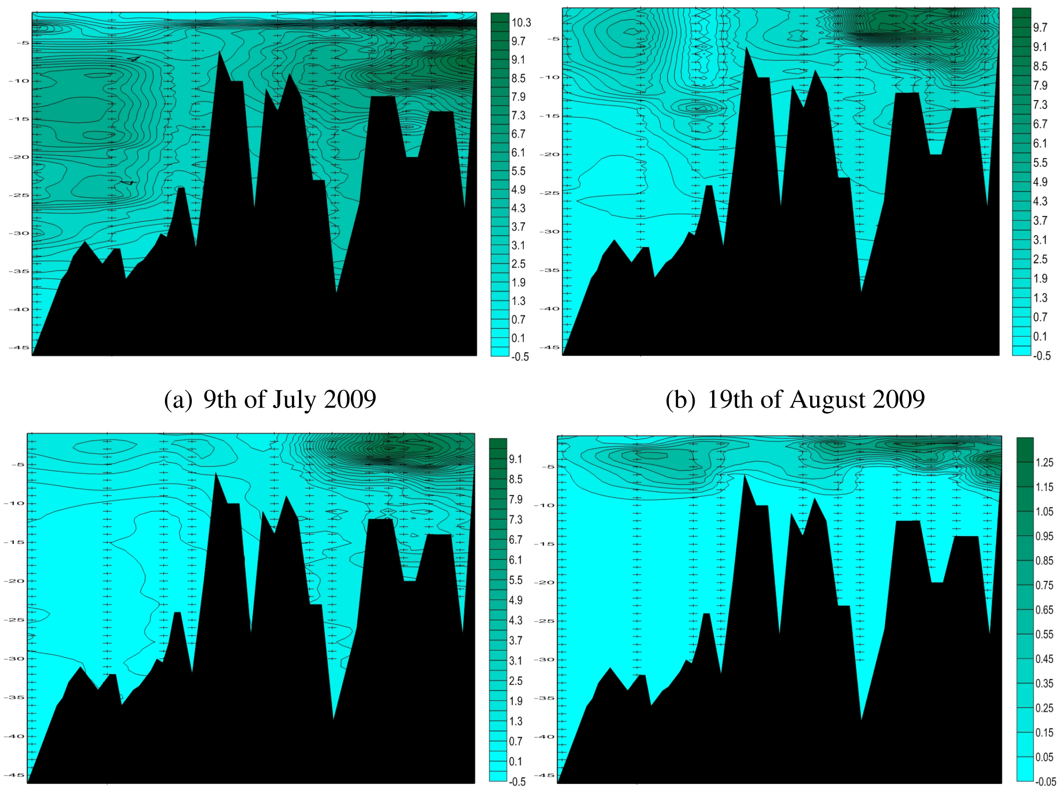
(c) 8th of April 2009

(d) 24th of April 2008

(e) 19th of May 2009

(f) 22nd of June 2009

Figure 5.14: Contour plots of Chlorophyll concentrations (mg/m^3) for transects of the Lynn of Lorn and the main basin of Loch Creran made during March, April, May and June of 2008 and 2009. Note the high chlorophyll concentrations recorded on the 24th April ranging from 0 to 21 mg/m^3.



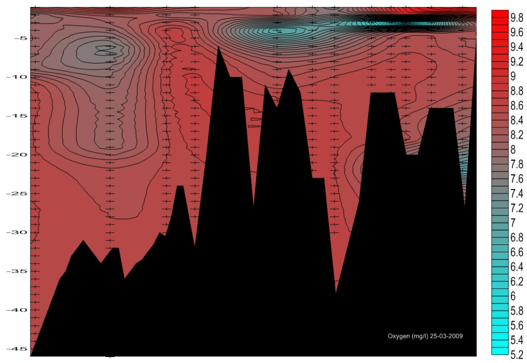
(a) 9th of July 2009

(b) 19th of August 2009

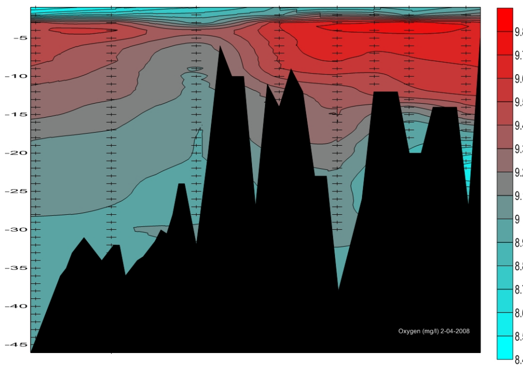
(c) 25th of September 2009

(d) 30th of October 2009

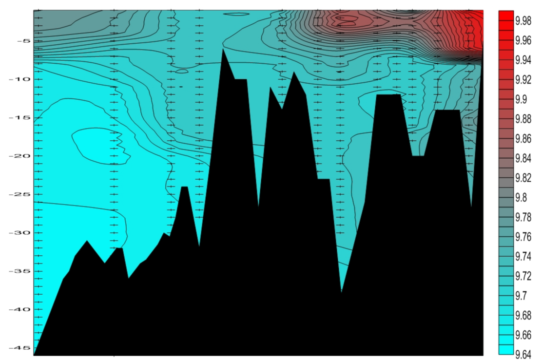
Figure 5.15: Contour plots of chlorophyll concentration for transects of the Lynn of Lorn and the main basin of Loch Creran made during July, August, September and October of 2008 and 2009.



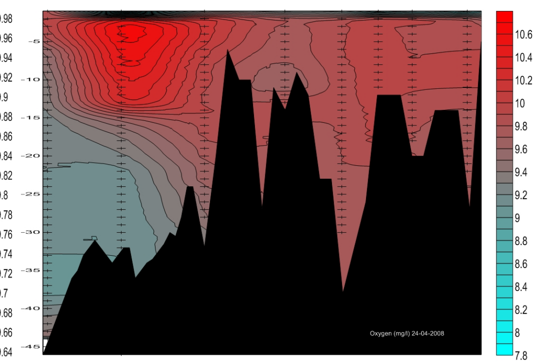
(a) 25th of March 2009



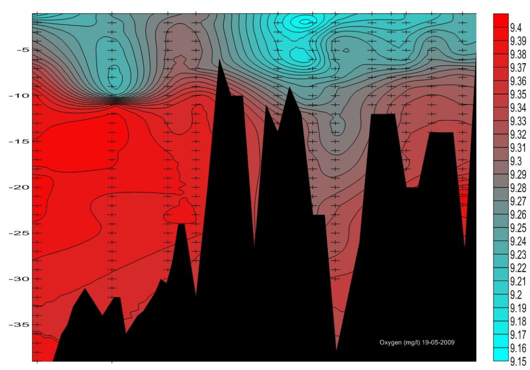
(b) 2nd of April 2008



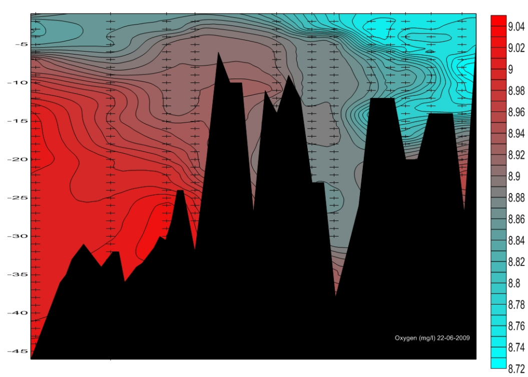
(c) 8th of April 2009



(d) 24th of April 2008

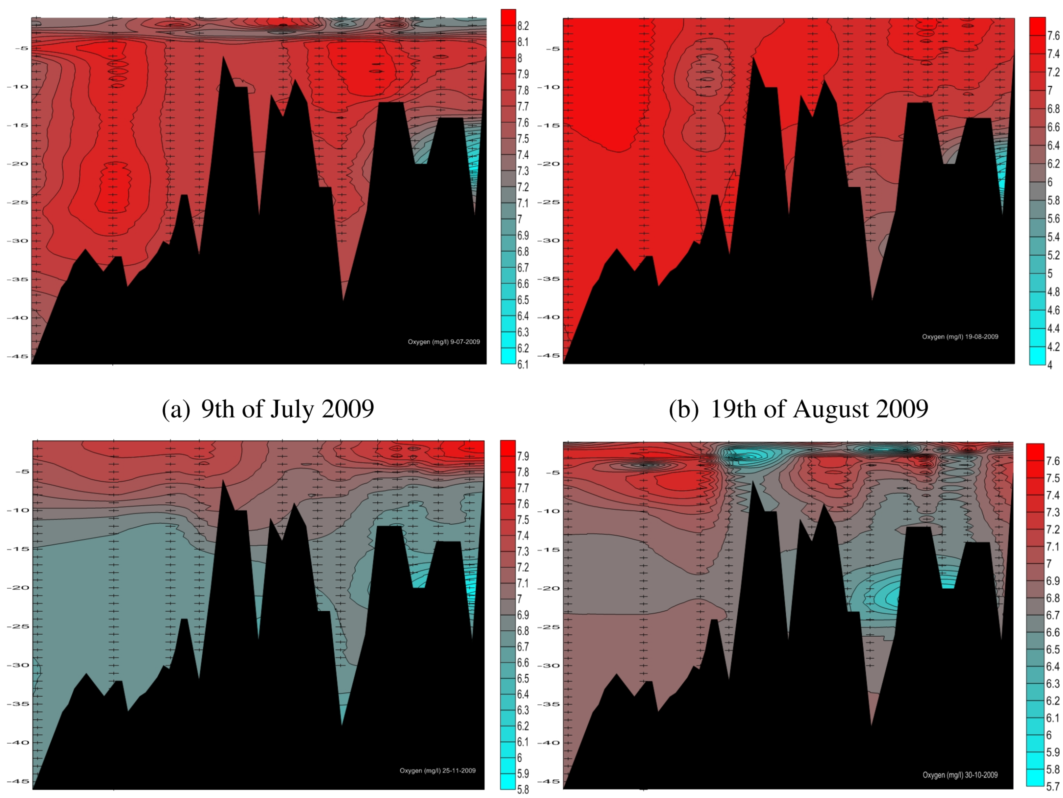


(e) 19th of May 2009



(f) 22nd of June 2009

Figure 5.16: Contour plots of dissolved oxygen concentrations (mg/m^3) for transects of the Lynn of Lorn and the main basin of Loch Creran made during March, April, May and June of 2008 and 2009.



(a) 9th of July 2009

(b) 19th of August 2009

(c) 25th of September 2009

(d) 30th of October 2009

Figure 5.17: Contour plots of dissolved oxygen concentrations (mg/m^3) for transects of the Lynn of Lorn and the main basin of Loch Creran made during July, August, September and October of 2008 and 2009.

Chapter 6

Antifouling Compounds

6.1 Introduction

The settlement and growth of algae, mussels, barnacles and other encrusting invertebrates onto submerged structures such as ships hulls, buoys, the legs of oil rigs, jetties and fish cages, detrimentally affecting their structural integrity and efficiency has long been recognised as a major problem in marine based industries. Historically chemicals including arsenic, lead, mercury and DDT were all used as anti-fouling compounds, (the use of copper as a constituent of an antifoulant was first mentioned in a patent from 1625, (Woods Hole Oceanographic Institute, 1952)). However by the early 1960's, as the risks they posed both to the environment and human health became ever more apparent, their use was voluntarily withdrawn (Evans *et al.* 2000).

Nonetheless marine industries still had a pressing need for effective antifoulants and in general this requirement was met by compounds containing tributyltin (TBT). Unfortunately TBT was found to be acutely toxic to a wide range of marine organisms including zooplankton (Huang *et al.* 2006), algae, (Sargian *et al.* 2005), (Beamont & Newman 1986), crustaceans (Ohji *et al.* 2003) and fish (Dimitriou *et al.* 2003) and was found to cause imposex and death (Lapota *et al.* 1993), in molluscs, a condition in which female gastropods develop male sex characteristics often resulting in sterility.

During the 1980's as concern grew over the effects of this product the UK government implemented a series of initiatives to control its use. In 1986 under the Control of Pollution Act (1974), retail sales of TBT were banned, followed a year later by a ban on its use in anti-fouling paints and aquaculture, and on all boats less than 25 metres in length. The government also set an Environmental Quality Standard (EQS) for TBT at 1ng/litre although this was later amended in 1997 to 2ng/litre.

By 1998 signatories to the Oslo-Paris (OSPAR) convention had included TBT in their list of priority chemicals and in 2001 the International Maritime Organisation (IMO) agreed to a complete ban on the application of TBT paints effective by 2003 and their complete elimination from boat hulls by 2008, (Evans *et al.* 2000).

With the ban on TBT manufacturers of anti- fouling coatings were forced to look for other alternatives and in the main TBT was replaced by various copper compounds. Unfortunately some algal species have a high tolerance to copper, (Karlsson *et al.* 2006) and so in order to achieve a level of protection against them "booster" biocides were combined with the copper. Chief among these are zinc pyrithione (ZnPT), Irgarol 1051, the trade name for Triazine, (2-methylthio -4-tert-butylamino-6-cyclopropylamino-s-triazine) and Diuron, (1-(3,4 dichlorophenyl)-3-3 dimethyl urea). Prior to the ban on TBT very little was known of any possible impact these compounds might have on the environment. Evans *et al.* (2000) however, raised concern that these new compounds could have serious environmental implications and was particularly troubled at the possibility that synergistic interactions between the different compounds could significantly increase their toxicity.

This concern was investigated by Fernandez-Alba *et al.* (2002). They considered the toxic effects of several antifoulant chemicals including Diuron, Irgarol, Dichlofluanid and TBT and several of their metabolites on *Vibrio fischeri, Daphnia magna* and *Selenastrum capricornotum*. They observed that when various compounds were mixed, only 33% of the toxicities were additive. However synergistic enhancements of toxicity were noted in 46% of the mixtures.

Gatidou and Thomaidis, (2007) looked at the synergistic effects of Irgarol 1051, Diuron and their breakdown products; M1 (2-methylthio-4-tert-butylamino-s-triazine); DCPMU (1-(3,4-dichlorophenyl)-3 methyl urea); DCPU (1-(3,4 dichlorophenyl urea) and DCA (3,4 dichloroaniline) and copper on two species of phytoplankton; *Dunaliella tertiolecta* and *Navicula forcipata*. While they found antagonistic effects between copper and Diuron, including its metabolites, all the other combinations resulted in additive synergistic effects.

Nagata *et al.* (2008), also looked at the possible antagonistic and synergistic effects of various combinations of anti-fouling chemicals. They carried out toxicity tests on forty five different combinations of two antifoulants each and did not find any antagonistic effects among them. However additive effects were observed in Diuron, TPBP (triphenylborane pyridine) and Sea Nine 211 (isothiazolone) when mixed with IPBC (3-iodo-2-propynylbutylcarbamate) and noticeable synergistic effects were observed for Irgarol, Ziram, Zn-pt (zinc 2-pyridinethiol 1-oxide) and Cu-pt (copper 2-pyridinethiol 1-oxide) in the presence of copper sulphate leading them to conclude that copper ions increase the toxicity of these chemicals in aquatic environments.

Interestingly Hernando *et al.* (2003), also found marked synergistic effects between antifoulant compounds such as Diuron, Sea Nine, Irgarol, Dichlofluanid and TBT with MTBE (Methyl-tert-butyl ether) which is a fuel oxygenate commonly added to petrol. In some cases these effects were quite significant, for example, combining MTBE with Diuron increased its toxicity by more than 50%.

These growing worries over their environmental impacts led in 2001 to the Health and Safety Executive's (HSE) Biocide and Pesticide Unit (BPU) revoking product approval for five of the eight approved "booster" biocides including, TCMTB, Diuron, Irgarol, Sea Nine and Chlorothalonil under the Control of Pesticides regulations (COPR) for vessels under 25 metres in length, leaving only Zineb, Dichlofluanid and Zinc pyrithione available for use (Cresswell *et al.* 2006).

6.1.1 Zineb

The first of these compounds Zineb (Zinc ethylene-Bis dithiocarbamate) has been in use since 1934 and is a member of the dithiocarbamates, a group of pesticides used to control insects. Unfortunately very little information on the toxicity of Zineb to marine organisms exists in the literature. Krishnakumari (1977), carried out toxicity tests on the freshwater alga *Scenedesmus acutus* and found that the growth rates of the alga were significantly reduced at concentrations as low as 500 parts per billion. In a similar study Ma *et al.*, (2002) looked at the sensitivity of two green freshwater algal species; *Scenedesmus obliqnus* and *Chlorella pyrenoidosa* to Zineb. Ma found EC50 levels of 0.5272 mg/l for *C. pyrenoidosa* and 0.5099 mg/l for *S. obliqnus*. They also made the observation that the level of sensitivity exhibited by different algal species to a pesticide could vary by as much as two orders of magnitude. This could certainly have implications for the species composition of different communities exposed to these chemicals.

6.1.2 Dichlofluanid

Studies on the toxicity of Dichlofluanid (1,1-Dichloro-N-((dimethylamino) sulfonyl)-1-fluoro-N-phenylmethane sulfenamide) to marine organisms are also limited. Bellas (2006), using worst case predicted environmental concentrations found that Dichlofluanid was toxic to the embryonic stages of the mussel *Mytilus edulis*, the sea-urchin *Paracentrotus lividus* and the ascidian *Ciona intestinalis*. Interestingly Bellas found Dichlofluanid to be more toxic to the organisms studied than Irgarol 1051. Fernandez-Alba *et al.*, (2002), looked at the bacterium *Vibrio fischeri*, the alga *Selenastrum capricornotum* and the crustacean *Daphnia magna* and found that while Dichlofluanid was toxic to all of the tested organisms *V. fischeri* and *D. magna* were also more sensitive to Dichlofluanid than to Irgarol 1051.

Although Dichlofluanid exhibits high toxicity to marine organisms it is highly unstable in seawater with a half life of 1.4 days, and is generally only found in the form of its far less toxic metabolite DMSA (N'-dimethyl-N-phenyl-sulphamide). Hamwijk *et al.* (2005) examined marina ”hotspots” in Greece including monitoring areas of sediment which had been ”spiked” with paint particles of Dichlofluanid but were unable to detect any of the compound in the water or in the sediment. Given its high degradation rate they also checked for the metabolite DMSA but again were unable to detect any traces of the compound.

6.1.3 Zinc Pyrithione

A survey of chandlers in the UK in 1998 indicated that paints containing zinc pyrithione (ZnPT), were the most commonly used anti-fouling products on boats under 25 metres in length as well as being widely used on yachts and larger vessels, (Thomas 1999). Boxall *et al.* (2000) estimate that the leaching rate for zinc pyrithione from small vessels lies between 4.64 and 13.54 microgrammes per cm^2 per day which suggests a large amount of zinc pyrithione is released into the marine environment in areas where the level of boating activity is high. The zinc salt of pyrithione (Omadine, 2-mercaptopyridine-N-oxide, 1 hydroxy-2(1H)-pyridinethione, 2-pyridinethiol-1(N) oxide), ZnPT appears to work by inhibiting membrane transport (Chandler and Segel 1978) and has long been used in anti-dandruff compounds such as Head and Shoulders shampoo. It is a lipophilic metal complex and can react with free metal ions in seawater, as well as forming new complexes with other ligands which may be present in the water column, (Turley *et al.* (2000), Grunnet & Dahllof (2005)).

The number of studies on the toxicity of ZnPT is rather limited nevertheless Konstantinou & Albanis (2004), found ZnPT to be more toxic than both Irgarol 1051 and Diuron. Initially although ZnPT was found to be toxic to marine organisms it was believed that it would pose very little environmental impact as it quickly photo-degrades to less harmful compounds (Turley *et al.* 2000). However Bellas (2005), studying the toxicity of ZnPT on the development of the ascidian *Ciona intestinalis* found that while the toxicity of ZnPT did indeed decrease in the presence of sunlight it did not entirely disappear and Grunnet & Dahllof (2005) noted that photo-degradation of ZnPT appeared to be low in natural waters and practically non existent below the top metre of the water column. Thomas *et al.* (2000) hypothesised that in low light waters where the degradation of ZnPT was limited; the pyrithione would form a stable manganese pyrithione complex and accumulate in the sediments. However a study by Nakajima *et al.* (1990) found that the pyrithione was much more stable when it formed a complex with copper. Bao *et al.* (2008), looked at the synergistic toxicity of ZnPT and copper on the diatom; *Thalassiosira pseudonana*. They found that at even low concentrations of copper (10 micrograms per litre) there was a synergistic effect between it and the ZnPT. They felt that this was due to the formation of copper pyrithione by trans-chelation of ZnPT with copper.

Mochida *et al.* (2006) in a study on sea bream (*Pagrus major*) and a crustacean (*Heptacarpus futilirostris*) also found that the toxicity of ZnPT was enhanced in the presence of copper and again felt that this was due to the conversion of ZnPT to the more toxic copper pyrithione. This tendency for ZnPT to form complexes with copper and other metals also means that the fate and consequently the effects of ZnPT in the environment will largely depend on the availability of other metals and may therefore vary widely with location and over time, (Hjorth *et al.* 2006).

Hjorth *et al.* (2006), carried out a mesocosm experiment attempting to mimic a small group of leisure boats, treated with ZnPT anti-fouling paint, anchoring in a shallow Danish fjord for three nights. They found that chlorophyll concentrations in the treated mesocosms were significantly lower than in the controls. In a similar experiment Maraldo *et al.* (2004), carried out a study on a phytoplankton community in Roskilde fjord, Denmark. While they found that the toxicity of ZnPT was as high as TBT and higher than either zinc or copper alone they also found a seasonal variation in the sensitivity of the phytoplankton to ZnPT. They surmised that this sensitivity was due to both the community structure of the phytoplankton and the amount of biomass present. They also found that the quantity of available nutrient had a significant effect on the toxicity of the ZnPT which was enhanced at low phosphate levels.

In conclusion, all of the three approved booster biocides for anti-fouling products appear to have a detrimental environmental impact on a wide range of non target marine organisms including phytoplankton. Unfortunately while their toxicity can be relatively easily established under laboratory conditions, ascertaining their presence in the field, particularly at the low levels in which they often appear, can be more problematic.

6.2 Aims

It has been hypothesised that the number of leisure boats frequenting Loch Creran has risen over the past few years and that this increase has led to a rise in the concentration of anti-fouling compounds, leaching from the boat hulls, entering the water column with detrimental affects on the phytoplankton community within the loch.

The aim of this chapter is to model the impact of anti-foulants on the phytoplankton in the loch to try and determine if they are having any observed affect on their growth. The null hypothesis being that they are not.

6.3 Methods

Given the difficulties, discussed above, of detecting the presence of anti-fouling compounds in the field it was decided that the most cost effective method to examine the possible effects of anti fouling compounds in Loch Creran was to use a mathematical model. To this end a single box model (a detailed description of the model can be found in chapter 10), of the loch was programmed to simulate phytoplankton growth, output as chlorophyll concentration (mg m^{-3}), when subjected to different levels of boating activity. Several scenarios could then be run, investigating the effects of changing the maximum number of boats moored in the loch and the anti-fouling compound used. As it was necessary to determine the concentrations of anti-fouling compound leaching from a boats hull into the water column it was decided to employ the use of an existing model developed by Van Hattum and his colleagues (Van Hattum *et al.* 2002) which, was designed to determine the chemical fate of a compound in the marine environment - the MAMPEC model.

The MAMPEC model, developed by Delft hydraulics and the Vrije Universiteit Amsterdam, is a well validated model (OECD 2005, EPA 2011) that predicts the environmental concentration of various anti-fouling compounds in the marine environment. In order to calculate this concentration the dimensions and properties of the environment, including information such as depth and current velocity, have to be input to the model. The model also requires the emission properties of the compound and information on its behaviour in the environment to be defined. In an effort, by the developers, to simplify setting it up the properties and behaviours of the most common anti-fouling compounds in use in the U.K. have already been predefined. The model also requires the number and different sizes (in terms of hull length) of the boats present in the defined environment. The model then predicts the environmental concentration of the defined compound in the immediate vicinity as well as in the surrounding area.

The predicted concentrations for three of the most common anti-fouling compounds in use in marinas around the UK i.e. Zinc Pyrithione, Zineb and Dichlofluanid were calculated for a set of moorings containing different numbers of boats of varying lengths. These results were entered into a database for later use in the single box model (see chapter 10).

Macedo *et al.* (2007), and Devilla *et al.* (2005) studied the effects of various anti-fouling compounds on phytoplankton. They found that they had a detrimental effect on the photosynthetic efficiency of the algae, impairing their ability to grow. The single box model uses the data obtained from the MAMPEC model to calculate the concentration of anti-fouling compounds found in the vicinity of a set of moorings in Loch Creran. This concentration varies throughout the year as the number of boats berthed changes with the season. The model treats this concentration as a ”hot spot” and using the exchange equation described in chapter 10 calculates the concentration of anti-foulant present throughout the main basin of the loch. It then takes this predicted environmental concentration (PEC) and divides it by the predicted no effect concentration (PNEC), obtained from the literature, to determine a risk quotient (RQ). If the value of RQ is found to be less than or equal to 1 no action will be taken. If however the RQ is found to be greater than 1 the parameter representing the photosynthetic efficiency (α) in the model will be reduced.

It is difficult to find relevant toxicological studies in the literature describing the effects of anti-foulants on phytoplankton and this introduces a large degree of uncertainty into the model. To address this the model provides a drop-down list of uncertainty factors (UF) ranging from 100 to 100,000. These values of UF are introduced into the calculation of RQ to give:

$$RQ = \frac{PEC}{PNEC \cdot UF} \tag{6.1}$$

Altering the type of anti-fouling compound, the number of boats at berth and the uncertainty factor, allowed various scenarios to be simulated in the loch.

6.4 Results

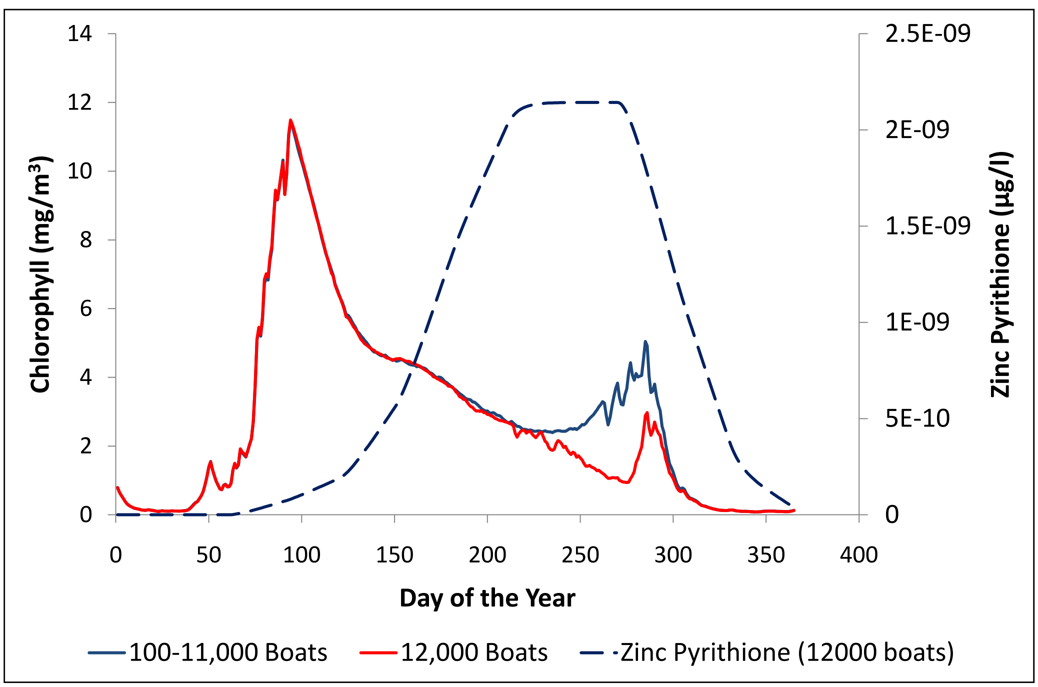


Figure 6.1: Plot illustrating the effect on chlorophyll concentration (mg m^{-3}) obtained by changing the number of boats berthed in Loch Creran. The anti-fouling compound simulated was Zinc Pyrithione and the uncertainty factor used was 10,000. The blue line represents normal phytoplankton growth during a single year, while the red line represents phytoplankton growth assuming 12,000 boats were moored in the loch. The dotted blue line plots the concentration of Zinc Pyrithione in the loch when 12,000 boats are present.

Figure 6.1 shows the effect of changing the number of boats berthed in the loch on phytoplankton growth. The number of boats used in the simulation varies throughout the year, peaking during the summer months and dropping to zero during the winter. It is apparent that the concentration of the anti-fouling compound Zinc Pyrithione does not reach a high enough concentration to retard phytoplankton growth until there are in excess of 11,000 boats moored in the loch. The maximum number of boats actually observed in the loch during 2008 and 2009 rarely exceeded 100.

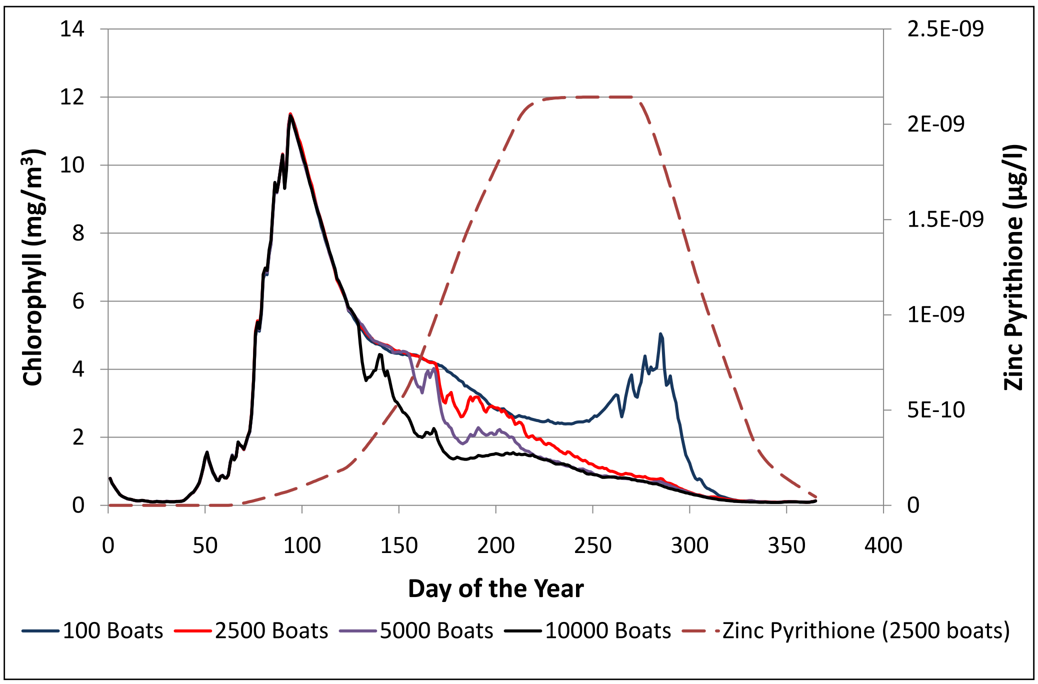


Figure 6.2: Plot illustrating the effect on chlorophyll concentration (mg m^{-3}) obtained by changing the number of boats berthed in Loch Creran. The anti-fouling compound simulated was Zinc Pyrithione and the uncertainty factor used was 100,000. The blue line represents normal simulated phytoplankton growth during a single year, while the red line represents phytoplankton growth assuming 2,500 boats were moored in the loch and the black line represents phytoplankton concentration when 10,000 boats are moored there. The dotted red line plots the concentration of Zinc Pyrithione in the loch when 2,500 boats are present.

Figure 6.2 again shows how the simulated phytoplankton concentration in the loch is affected by changes in the number of boats moored in the loch. In this case the uncertainty factor has been increased to 100,000. It is clear that this causes a decrease in the concentration of phytoplankton when the number of vessels exceeds 2,500 and continues to decrease as the number of boats rises. However as in figure 6.1 all of this decrease takes place during the summer months and late autumn. The spring bloom does not appear to be affected.

6.5 Discussion

As mentioned above, the single box model was based on the existing CSTT model (see chapter 10). This was originally formulated as an assimilative capacity model with the intention of creating a tool that would allow the processes underlying eutrophication to be examined. To this end the model made the assumption that all of the nutrients present in the water body would be made available for conversion into phytoplankton. While this assumption errs on the side of caution when considering eutrophication it may lead to an overestimation of chlorophyll concentration and subsequently undervalue the effects of anti-foulants when considering the real system.

Nevertheless, given the disparity between the number of boats observed mooring in Loch Creran, which rarely exceeded 150 relatively small sized yachts, and the number of boats needed to trip the model into lowering the photosynthetic efficiency - between 2,500 and 12,000 depending on the uncertainty factor used, it would seem reasonable to accept that this assumption has a relatively small influence on the phytoplankton growth in the loch.

The model also assumes a single water layer and so disregards the probability that some of the anti-fouling compounds are adsorbed by sediments thus making them available for re-suspension during mixing events. However as figures 6.1 and 6.2 show the concentration of anti-foulant in the loch increases when the moorings are highly utilised i.e. during the summer months and drops when they are virtually abandoned during the winter, as most of the boats are removed from the water. It could be surmised therefore that any anti-fouling compounds, re-suspended during winter storms, would have either re-settled or been washed out of the loch before stratification of the water column occurred in spring.

As previously pointed out, when the model was being implemented, it proved difficult to find suitable toxicity tests, in the literature, that had been carried out with regards to the effects of anti-fouling compounds on marine algae. The best documented was Zinc Pyrithione and as this was also deemed to be the most toxic in the environment it was the one used preferentially when running the model. Nevertheless There was a wide range of values reported amongst the different studies.

It is common in toxicology to make use of ”safety factors” for example if an LD_{50} value is available for one species of mammal it may be increased by a factor of 10 to account for differences between it and another species of mammal. It may be increased by a further factor of 10 if it was a different chordate class such as a fish and a mammal and a further factor of 10 if the difference was between an animal and a human.

As there was a great deal of uncertainty with regards to the toxic effects of the anti-fouling compounds it was decided to adopt the same approach and introduce a choice of uncertainty factors into the model. Because the model was a single box model constructed with the assumptions outlined above, it was deemed prudent to err on the side of caution and introduce a choice of uncertainty factors which ranged from a factor of 100 to a factor of 100,000. Indeed it was only when uncertainty factors of 10,000 and 100,000 were used that any appreciable drop in phytoplankton growth in Loch Creran was observed.

To conclude, while a degree of uncertainty regarding the toxicity of anti-fouling compounds such as Zinc Pyrithione to marine algae remains, the introduction of large uncertainty factors into the model should be more than adequate to ensure that the simulated results can be accepted with a certain degree of confidence. It would seem then that the null hypothesis that the phytoplankton community in Loch Creran is not being affected by an increase in leisure boating can be accepted and that the causes of the observed drop in their numbers must lie elsewhere.

Chapter 7

Dissolved Organic Matter

7.1 Introduction

Since the 1970's there have been several changes in the way Loch Creran has been utilised by various interests. These include the introduction of two mussel farms, three oyster farms and a salmon farm, (see chapter 8). The installation of approximately 150 moorings for leisure craft, and the closing down of the alginate processing plant at Barcaldine.

Originally established as a private enterprise under the name of Cefoil the company initially carried out research into extracting alginates from seaweeds. With the outbreak of the Second World War the company entered into an agreement with the government and the factory at Barcaldine was opened to extract fibres from seaweeds for the production of camouflage netting, (Le Quesne, 1979). However by the end of the war these products were no longer in demand and so after buying back its interest from the government, the company reformed as Alginate Industries and building on its initial research, turned to producing high grade alginate products for the food and pharmaceutical industries.

As a by product of this process small, macerated, fibrous particles of seaweed, along with various chemicals and acid were periodically pumped as effluent into the loch through two pipes which, extended beyond the low water mark approximately 200 metres from the shore. This fibrous waste built up around the outfall, eventually becoming visible at low tide and was accompanied by a bad smell, Clyde River Purification Board (CRPB) (1975). This led to complaints from local residents. Several studies into the impacts of the effluent on the loch were carried out by the Scottish Marine Biological Station at Dunstaffnage. Unfortunately for the company, cheap alginate imports from China drove down prices forcing them to gradually cut production until, unable to compete, it finally closed in 1996.

For the duration of its operation it has been calculated that the annual organic carbon content of the effluent which the factory pumped into the loch was approximately 3,250 tonnes, (Tyler, 1983). Of this 2500 tonnes was particulate matter, consisting of large and small fibrous particles while the remaining 750 tonnes was dissolved in fresh water. Sivasubramanian *et al*. (2008) analysed the effluent from alginate extraction from the brown algae *Sargassum* and found it contained high levels of dissolved organic nitrogen, dissolved organic phosphorous, dissolved silicon and iron. It is reasonable to assume that similar high levels of these nutrients may have been found in the effluent from the Barcaldine plant.

7.2 Aims

The closure of the alginate factory has resulted in both a loss of dissolved organic carbon (DOC) and a reduction in the supply of DON, DIP, DSi and Fe to Loch

Creran. This chapter will attempt to quantify the size of this loss and try to determine the possible effects this reduction in material may have on the phytoplankton community in the loch.

7.3 Results

In order to determine if this loss of DOC could effect the growth of diatoms, in particular *Skeletonema* spp. it is necessary to establish a link between the growth of diatoms and the level of organic carbon in their environment.

Tett, (1977), carried out a preliminary experiment to establish if the effluent from the Barcaldine alginate factory would have any effect on the phytoplankton in loch Creran. It is worth noting here that, from the report, one of the main reasons for carrying out the experiment appears to have been to demonstrate the efficacy of using chemostats to study phytoplankton growth dynamics rather than an in depth investigation into the effluent. However it does provide an idea of the possible influence the alginate factory effluent may have had on the phytoplankton in Loch Creran.

Using controlled culture techniques on an assembly of natural phytoplankton from the loch Tett (1977) subjected them to three nutrient regimes. In the first no additional nutrients were added to the sample. In the second extra nitrate, silica and trace minerals were added but no extra phosphate until day nine. The last mirrored the second except that on day nine, rather than adding phosphate, effluent was added instead.

Figure 7.1 has been re-drawn from the data provided in the report (Tett 1977). It can be seen that in the first sample (the dot and dash line), in which no supplementary

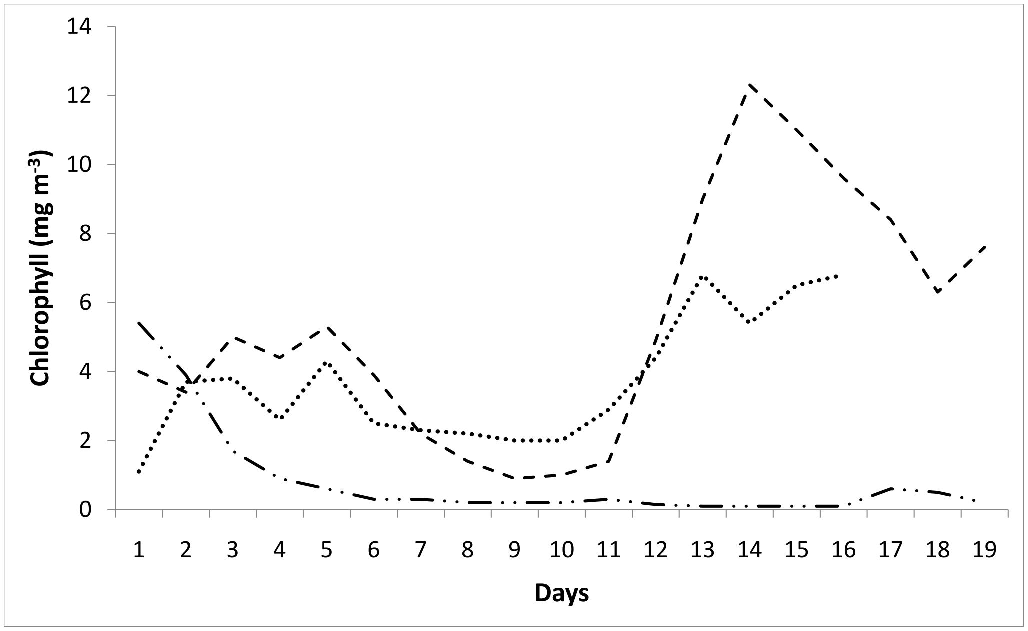


Figure 7.1: Results of subjecting a culture of phytoplankton from Loch Creran to different nutrient regimes. The dot and dash line represents the first, in which no additional nutrients were added. The dotted line represents the sample where, with the exception of phosphate, extra nitrate, silicate and trace minerals were added on day 9 and the third, represented by the dashed line is the result of adding effluent alone from the alginate factory on day 9. Diagram was re-drawn from Tett (1977).

nutrients were added, the population steadily declined, and had become limited by phosphate by day nine. In the second (the dotted line) with the exception of phosphate, the culture was supplied with additional silicate, nitrate and trace minerals. In this case, although the culture continued to grow until day five, by day six it had started to decline steadily. After the addition of phosphate on day nine the sample again achieved a steady growth.

In the final experiment (represented by the dashed line) the culture was also supplied with extra nutrients and trace minerals but again no phosphate and after an initial period of growth started to rapidly decline. On day nine after the addition of effluent from the alginate factory there was a rapid increase in both the growth rate and the concentration of phytoplankton in the culture.

Sample two had also been provided with additional nutrients including phosphate on day nine and yet did not match the rapid growth rate and the increase in the abundance of phytoplankton observed in the third sample. This suggests that the chemical composition of the effluent enhanced phytoplankton growth in some way. Tett (1977) estimated that a dilution of effluent of 1 in 1000 could result in a 30% increase in the expected summer levels of phytoplankton.

Nevertheless, although the effluent appears to enhance phytoplankton growth could the waste from the alginate factory have reached sufficient concentrations to have an appreciable affect on the phytoplankton community in the loch?

Cronin and Tyler (1980), in a study in which they disregarded the effects of sediment re-suspension or diffusion estimated the following annual inputs of organic material to Loch Creran:

Rivers	1100 tonnes	± 150 tonnes
Phytoplankton	800 tonnes	± 150 tonnes
Macro-Algae	300 tonnes	± 100 tonnes
Alginate Factory	800 tonnes	± 100 tonnes

From these figures it can be estimated that in addition to the natural load of organic material supplied to the loch by rivers, phytoplankton and macro-algae, during its operation, the alginate factory supplied between 30% and 42% extra organic material to the loch.

Of course this makes the large assumption that all of the macerated algal waste from the factory would be re-mineralised within the loch and in a relatively short time. At the time no studies were carried out on the decomposition rates of the algal waste in Loch Creran. Nevertheless some evidence for the relatively quick re-mineralisation of macro-algae does exist.

Paalme *et al*. (2002) studied the *in situ* decomposition rates of the macro algae species: *Cladophora glomerata* and *Pilayella littoralis* in the Baltic sea. They found that under aerobic conditions *C. glomerata* lost 46% of its mass after 35 days, a linear loss of 1.4% per day. Under anaerobic conditions this increased to 56% with 30% of the weight being lost in the first week. For *P. littoralis*, under aerobic conditions, the loss was 99% in 35 days a linear loss of 2.8% per day.

Although Paalme *et al*. (2002) studied *Cladophora glomerata*, a filamentous algae and different from the species of *Laminaria* used in the alginate factory, the process of removing the alginate, whereby the algae is macerated, should result in a finely shredded waste that could be expected to present a similar surface area for microbial action as that found in *C. glomerata*.

Loh et al. (2008) studied the degradation of terrestrially derived organic material in Loch Creran and found that the diagenesis of organic material was increased partly by a high degree of bioturbation and by the regular exchange of water with the Lynn of Lorn. This maintained a well oxygenated water column, thereby facilitating the decomposition of organic material in the Loch.

Pearson, (1982) studied the decomposition of pulp mill waste in Loch Eil, Scotland. He observed that the rate of respiration in the sediments mirrored the increase in organic material to the sediment and surmised that the two were approximately in balance. He concluded that all of the carbon input to the sediments was quickly remobilised and entered the loch.

If the assumption is made that this was also true for Loch Creran then the organic material input to the loch was 3,250 tonnes of carbon extended over a 50 week production year. As the effluent was discharged into the surface layer of the middle basin it can be assumed that very little of it would reach the upper basin. The mean volume of the middle basin, assuming chart datum plus 2.6 metres is 150.52 million cubic metres, (Tyler, 1983) so the annual effluent concentration in the loch would be:

$$\frac{3250x10^9}{150.52x10^9} = 21.59\ mg\ \mathrm{l}^{-1}$$

This concentration however assumes no tidal exchange with the Lynn of Lorne. The alginate factory had a production year consisting of 50 weeks giving an organic material input to the loch of 6.5 x 10 ^{7} g/week, (Cronin 1977), If we assume a tidal flushing time for the loch of approximately 7 days then the effluent concentration would be:

$$\frac{6.5x10^7}{150.52x10^6} = 0.43\ mg\ \mathrm{l}^{-1}$$

7.3.1 Modelling the effects of effluent on phytoplankton growth rate

The model described in chapter 10 allows various scenarios to be investigated, albeit, in this case, somewhat simplistically. Determining the possible effects effluent from the alginate factory may have had on the phytoplankton community is difficult without more information about its chemical composition. However the study by Sivasubramanian *et al*. (2009) suggests that it would be high in DIN, DOP, DSi and Fe. By modelling the effect an increase in the local inputs of phosphate, nitrate and silicon would have on the concentration of phytoplankton in the loch it may be possible to estimate the effect this would have on phytoplankton growth.

Studying the concentrations of trace metals in Giant Kelp, *Macrocystis*, North (1980), gives values for nitrogen and phosphorous concentrations of 840 μg - at/g and 93 μg - at/g respectively. Taking these figures and converting the annual concentration to a daily value and assuming that the effluent consisted almost entirely of macerated algae, the outflow from the alginate factory was constant throughout the year and that nutrient would disperse throughout the main basin within a day, would yield a concentration of 4.22 mmol m^{-3} of nitrogen and 4.93 mmol m^{-3} of phosphorus being added daily. However adding these daily inputs to the single box model failed to show any difference in the concentration of the phytoplankton in the loch. Indeed increasing these values by a factor of ten still did not reveal any changes in phytoplankton concentration. This is of course a very rough calculation making large assumptions but it does suggest that the volume of the discharge may have been too low to affect the much larger volume of the main basin. However it does neglect local concentrations, particularly around the outflow pipe, where they could be expected to be considerably higher.

Nevertheless looking at figure 7.1 it appears that not only is the final concentration of phytoplankton much higher in the experiment where effluent was added but the rate of growth of the population was also greater. Again using the model it is possible to investigate the effect of increasing the growth rate. Figure 7.2 is the result of forcing a change on the calculated growth rate in the model. Here the blue line represents the unaltered annual concentration of chlorophyll while the dashed red line represents an increase in the growth rate of 10% and the red line represents an increase of 25%. It is interesting to note that at the higher growth rate not only does the spring bloom attain a higher concentration than otherwise but the peak of the bloom occurs several days earlier.

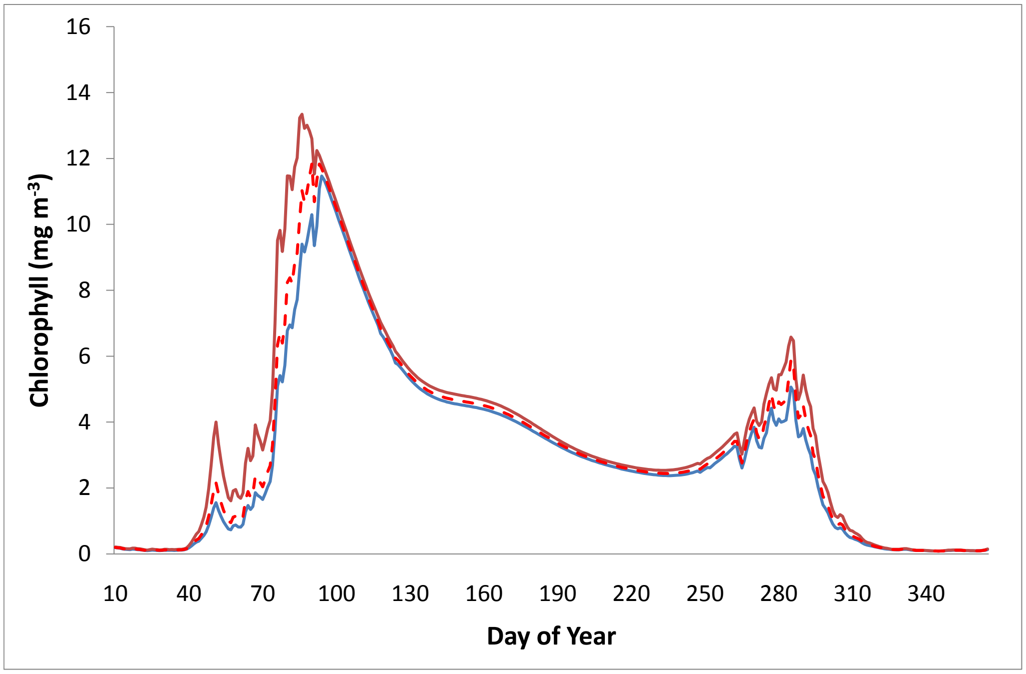


Figure 7.2: Results of changing the growth rate of a population of phytoplankton in a single box model of Loch Creran. The blue line represents the concentration of phytoplankton throughout the year with no changes to the rate of growth. The dashed red line represents the result of increasing the growth rate throughout the year by 10% and the red line is the result of increasing the growth rate by 25%.

7.4 Discussion

The closure of the alginate factory at Barcaldine in 1996 resulted in a substantial loss of organic carbon and nutrients into Loch Creran. In a study into the changes affecting the phytoplankton community in the loch it would be remiss not to consider the effects this loss could have. Unfortunately very little information was available concerning the alginate operation at Barcaldine. The factory had already began to scale down its operation before the Scottish Environmental Agency had come into being, so no discharge information was available. The experiment by Tett (1977) provides the best evidence that the effluent from the factory had the potential to alter the growth dynamics of the local phytoplankton community. Whether the local concentrations of effluent in the loch ever reached high enough levels to affect phytoplankton growth however is open to speculation.

In a similar experiment Prakash, *et al.*, (1973), added different concentrations of humic acid ranging from 2.6 μg/ml to 18.2 μg/ml derived from *Laminaria* to cultures containing *Skeletonema* spp. and *Thalassiosira nordenskioldii*. They found that cell numbers increased by between 19% and 88% when compared with control samples. Interestingly they did not observe any increase in the exponential growth rate of the phytoplankton and surmised that although the growth rate did not increase the period over which growth occurred appeared to last longer.

Ake-Costillo *et al.*, (2008) found a similar effect in a coastal lagoon in the Gulf of Mexico where they attempted to analyse the relationship between phytoplankton dynamics and inputs from plant derived organic material. Considering the response of humic acid in a range of phytoplankton they found that diatoms responded well to low to medium concentrations of humic acid but appeared to be inhibited if the concentrations became too high. Jackson and Hecky, (1980), found a similar result when studying phytoplankton in freshwater lakes in Canada while Rivera-Monroy, *et al.*, (1998) studying primary productivity in the Terminus Lagoon, Mexico found that phytoplankton growth was increased by over 50% on the addition of humic acid provided the concentration was between 0.3% and 1.7% of the total volume. They found that additions in excess of 3% led to growth inhibition.

While it appears that phytoplankton growth is indeed stimulated by the addition of humic acids the mechanism by which this takes place is still unclear. Bushaw-Newton and Moran, (1999), found that on irradiation with natural sunlight, humic substances broke down producing among other compounds, ammonium and primary amines. They concluded that humic substances provided an extra source of labile nitrogen to the marine environment.

In a separate experiment Tani, *et al.*, (2003) looked at the availability of iron, an essential nutrient for phytoplankton growth, and compared the vertical distribution of iron (III) in the open sea with humic acid fluorescence. They came to the conclusion that the distribution of soluble Iron (III) was dependent on the distribution of humic substances and that this solubility was controlled by complexation with the natural organic ligands in the humic material. They felt that this solubility was connected to the release of organic iron (III) chelators from the organic material.

This interaction was also considered by Hirose, (2007), who found that a key function of dissolved organic matter in seawater was its ability to form complexes with bio-active trace metals. He concluded that organic ligands in the humic material played an important role in controlling the free metal ion concentrations at a level suitable for the growth of marine micro organisms such as phytoplankton.

In conclusion it appears that there is solid evidence to suggest that humic substances can play a significant role in enhancing the growth of phytoplankton. While the exact mechanisms by which this enhancement takes place is still unclear the evidence that it can play a significant role in phytoplankton dynamics should be considered. Whether or not it played a part in enhancing the growth of phytoplankton in Loch Creran is still uncertain.

Chapter 8

Losses due to Grazing

8.1 Introduction

Anecdotal evidence from local *Nephrops* fishermen suggests that in recent years the water clarity in Loch Creran has increased and turbidity has decreased since the introduction of mussel farms into the loch.

There are many other possible reasons why the clarity of the water in Loch Creran may appear to have improved. Changes in the patterns of precipitation falling on the Loch Creran catchment area can alter the amount of run-off reaching the loch, leading to a change in the levels of turbidity in the loch.

Changes in run-off or in direct inputs of organic material to the loch can also alter the concentration of humic acid, ”gelbstoff” literally, the yellow stuff, present in the water column, (see chapter 9). If the improvement in water clarity is indeed linked to the introduction of mussel farms the question of how this change can come about must be addressed.

Mussels are suspension feeders that filter large quantities of water removing particulate organic matter, small flagellates and phytoplankton from the water column. For the mussels farmed in the loch to be having an appreciable effect on the apparent clarity of the water they would have to capable of filtering a large proportion of the volume of water in the loch. If they were responsible, even in part, for the observed decrease in the population numbers of *Skeletonema* spp., not only would they have to be consuming appreciable amounts of phytoplankton, they would also have to be selectively grazing on *Skeletonema* spp.

This raises two questions; Are the numbers of mussels farmed in Loch Creran high enough to affect the phytoplankton biomass? And are mussels able to selectively choose the species of phytoplankton upon which they graze? It may be that this second question is not quite as important regarding a reduction in *Skeletonema* spp. during the spring bloom. Microscopic analysis of the composition of the phytoplankton present in the loch during the early months of the year indicate that there are very few species of phytoplankton present and these are dominated by *Skeletonema* spp. So it may be that regardless of whether the mussels are grazing selectively or not they may have little choice in their selection of food.

8.2 Aims and Rationale

The aim of this chapter is to review the existing literature and attempt to determine if:

1: Mussels can differentially select and graze on different phytoplankton species.

2: The numbers of farmed mussels and oysters in Loch Creran can have an appreciable effect on phytoplankton biomass and to model the outcome of elevating grazing levels in the loch.

8.3 Results

Mussels and other bivalves are both economically and ecologically important marine organisms. They form a link between the pelagic and the benthic components of the ecosystem and in some instances they may be the dominant benthic organism. Their importance in marine aquaculture and nutrient recycling has long been recognised and many studies have been carried out investigating various aspects of their ecology.

In an attempt to answer the first question i.e. Are the mussels in Loch Creran present in large enough numbers to affect the concentration of phytoplankton in the water? It may be helpful to view the question as two distinct parts. The first concerns the actual numbers of mussels farmed in the loch and to answer this should simply require contacting the farms and determining their stock levels (see table 8.1). However to answer the second part it is necessary to try and determine if bivalves are actually physically capable of altering the concentration of phytoplankton in the water column.

In a related study carried out in the U.S.A., Cloern (1982) estimated that the bivalves present in San Francisco Bay, were capable of filtering a volume of water equivalent to the volume of the bay at least once a day. Cloern concluded that grazing by benthic suspension feeders was the main mechanism for the control of phytoplankton in the bay. Prins, *et al.*, (1996) made the observation that in estuaries where high numbers of bivalves were present, the potential existed for the entire volume of water to be filtered within a few days. They further noted that low concentrations of phytoplankton were often associated with high densities of bivalves.

Dolmer, (2000), carried out a field investigation on a population of *Mytilus edulis* during September 1998 in the North of Limfjorden, Denmark, and also found that the mussels quickly reduced the population of phytoplankton. However Dolmer found that the mussels only grazed until a threshold concentration of phytoplankton was reached. Below this value they stopped filtering the water. This observation was also made by Riisgard, *et al.*(2007), who found that when the concentration of algae drops below a certain threshold value the mussels close their valves and stop feeding. Riisgard surmised that this was possibly an adaptation to fluctuating levels of phytoplankton. Flume studies by Butman, *et al.*,(1994) showed that when a current of water containing phytoplankton flowed over a community of bivalves there was a significant reduction in the phytoplankton biomass. This result corroborates a previous finding by Asmus & Asmus,(1991) who during February 1984 and April 1985, also carried out in situ flume experiments near the island of Sylt in the Wadden Sea during which, they found that phytoplankton biomass was reduced by 37 $\pm 20\%$.

Further support comes from a review of nineteen years of data from the Skive Fjord in Denmark, Mohlenberg, *et al.*(2007) came to the conclusion that an increase in mussel biomass led to reduced levels of chlorophyll and increased transparency in the water column over the long term. Mohlenberg also found however that in the short term, turbulent mixing actually led to increases in the phytoplankton which, they attributed to nutrients being re-suspended after being accumulated by the mussels as faeces and pseudo faeces.

In order to reduce this effect of sedimentation and re suspension Prins, *et al.*,(1994) set up a semi natural mussel bed in a 40m x 5m x 1m deep concrete tank that was continuously fed with natural seawater. During the experiment the tank was kept sheltered from the wind to limit the amount of wind induced turbulence, under these conditions they found that while clearance rates of phytoplankton were relatively high, (standardized values for an individual animal of 1.0 - 2.0 l$g^{-1}h^{-1}$), resuspension of bio-deposits were negligible.

Riisgard, *et al.* (2007) came to the conclusion that the impact of grazing on the phytoplankton population depends on hydrodynamic processes such as wind mixing, turbulence, stratification and horizontal mixing. While benthic suspension feeders can filter large quantities of water their impact on the phytoplankton population depends on the efficiency of the water mixing throughout the water column.

Age and size of an individual animal can also play a role in its ability to filter water. During a study in 1982, Officer, *et al.* (1982) observed that filtration rates fall as an individual animal grows larger. They concluded that optimally, to exert top down control on a phytoplankton population, the mussels should be small sized and the water depth should be shallow between 2 and 10 m. They estimated that a population of mussels approximately a few hundred grams per m^2 could act as a control on a population of phytoplankton consisting of 2 to 3 μg/l. However while many of the studies carried out on the effect of grazing on phytoplankton by bivalves conclude that bivalves do appear to exert a top down control on phytoplankton populations, others find the relationship between bivalves and algae to be slightly more subtle.

Ogilvie, *et al.* (2003), carried out four in situ enclosure experiments at Wilson Bay, New Zealand between December 1998 and January 1999 and between May and July 1999. Mussels in the experiment were placed into nylon mesh bags and suspended in 3 metre deep polyethylene bags which were moored amongst mussel longlines. The numbers of mussels and the amount of nitrogen were manipulated in each enclosure. Ogilvie's team found that, in comparison with control enclosures lacking mussels, in enclosures where mussels were present, the concentration of chlorophyll increased significantly during the summer months. Conversely this result was reversed in winter months with a significant decrease in chlorophyll in enclosures where mussels were present. They concluded that during winter, phytoplankton were light limited rather than limited by nitrogen and remineralisation of nitrates by the mussels made no difference, whereas in summer their growth is limited by a scarcity of nitrogen and the extra nitrate provided by the presence of the mussels would lead to higher growth rates.

A similar result was found by Trottet *et al.* (2007) who carried out a study in the Grande-Entree Lagoon, Quebec, Canada. They looked at the influence of mussel farming in the lagoon on local phytoplankton communities and compared two stations inside and outside the mussel farm over a four month period during summer 2003. They found no significant differences in phytoplankton concentrations within the farm; however they did find that phytoplankton productivity was higher inside the farm possibly enhanced by the re-suspension of nutrients by the mussels. Prins *et al.* (1998), also found that the interactions between suspension feeding bivalves and phytoplankton consisted of a series of positive and negative feedbacks varying with time and hydrodynamic conditions.

8.3.1 Selective Feeding

To address the second question regarding the ability of bivalves to select food is perhaps more controversial. For a long time speculation has existed regarding the issue of selective feeding in bivalves. As methods of investigating this question improve, particularly in methods of observing the animals behaviour while still alive, new insights into the feeding behaviour of these organisms continue to be gained. Forming a link between pelagic and benthic ecosystems, suspension feeding marine bivalves such as *Mytilus edulis* play an important part in marine ecology. This has led to several studies on the various factors that affect feeding rates in these organisms.

In 2003, Rouillon and Navarro (Rouillon & Navarro 2003), carried out an investigation in which mussels *Mytilus edulis* were fed a mixture of a diatom, *Phaeodactylum tricornutum* and a flagellate, *Tetraselmis sueccica*. While they failed to find any significant difference in the retention time on the gills they did find a significant difference in the stomach contents with the mussels appearing to preferentially retain the diatom.

Milke and Ward, (2003), also looked at the influence of diet on the residence time of particles in the pallial cavity and on the labial palps of two species of bivalve: the oyster *Crassostrea virginica* and the mussel *Mytilus edulis*. Using a varied mixture of *Rhodomonas lens*, ground *Spartina sp.* and fluorescent 10 μm beads. They found that the quality of the diet fed to the bivalves had a significant effect on the residence times in the pallial cavity of *C. virginica* but no significant difference in *M. edulis*. Interestingly Ward, *et al* (2003) found that the quality of food particles does effect the speed at which they are transported along the ctenidia of *M. edulis* also from personal observations they made they found that M. edulis did not feed on *Spartina sp.* as readily as they fed on *Rhodomas lens*. Milke and Ward, (2003), did find however that the residence times of particles in the pallial cavity of *M. edulis* were significantly affected by temperature and particle concentration and concluded that as temperatures approach 5 degrees centigrade a physiological threshold may be reached below which the cilia of *M. edulis* fail to respond possibly due to the changes in water viscosity, and its associated effect on mucus fluidity, associated with lower temperatures.

In a separate study Bougrier, *et al.*, (1997) analysed selective grazing in *M. edulis* by flow cytometry. Feeding the mussel a mixture of the diatom *Skeletonema costatum*, the flagellate *Pavlova lutheri* and the flagellate *Tetraselmis suecica* they found that the mussel preferentially selected the flagellate *T. suecica* over the other two species. Bougrier and his colleagues while unsure of the selective mechanisms employed by *M. edulis* speculate that the shape of many diatoms, with their characteristic silicate projections, may cause them to be retained on the gills of bivalves, however the flexible membranes of flagellates may allow them to pass more readily through the gill filters.

Espinosa *et al.* (2007), also used flow cytometry to study particle selection in the oyster *Crassostrea virginica* and in the ribbed mussel *Geukensia demissa*. They fed the bivalves a mixture of *Isochrysis sp.*, *Nitzschia closterium*, *Tetraselmis suecica*, *Thalassiosira pseudonana* and *Thalassiosira weissflogii* but prepared different diets with one consisting of algae in the exponential growth phase and another with the algae in a stationary growth phase. They found that not only did the bivalves selectively choose particular species of algae but that this selection changed depending on the growth phase of the algae.

Interestingly Ward & Targett, (1989) fed *M. edulis* with polystyrene beads coated with microalgal ectocrines taken from algae at the end of their exponential growth phase and also found that, depending on the algae used, the mussel either significantly chose or rejected the treated particles. The idea that bivalves select their food, at least in part, by extracellular metabolites, has also been investigated by

Pales & Espinosa,(2008) who encapsulated living microalgal cells in alginate microcapsules. They found that the bivalves were able to selectively choose or reject different species of microalgae and concluded that extracellular metabolites have an important role to play in food selection in suspension feeding bivalves. Ward *et al.*,(1992) came to a similar conclusion after studying the sea scallop *Placopecten magellanicus*. They found that the scallop changed both its clearance and ingestion rates in response to metabolites from the diatom *Chaetoceros muelleri*.

Ward (1996) separated suspension feeding into three distinct processes; the movement of water over suspension feeding structures, removal of particles suspended in the water column and transport of captured particles to the mouth. In bivalves this is usually carried out by hydrodynamic processes and by the use of mucus of varying viscosities. In an attempt to determine the actual mechanisms used in *M. edulis*, Beninger & St-Jean, (1997) used video endoscopy to observe the movements of particles on the labial palps of living specimens. They observed that the palps were extremely mobile and agile, and concluded that these extremely complex organs are responsible for ingestion, volume control and particle selection in *M. edulis*.

Jorgensen, (1996) hypothesised that bivalves were merely filter pumps with only one mode of control in the form of the width of the gape. In conclusion however it would seem that rather than being organisms which simply automatically filter large volumes of water, bivalves employ a varied suite of complex processes to obtain the nutrients they need. Studies continue to show that they are able to mediate their rate of filtration, their rate of rejection and ingestion of particles, and also vary their selection of food particles. There is much that is still unclear regarding the complexity of suspension feeding mechanisms but it seems clear that they are far from being simply filtering automatons

8.3.2 Calculation of clearance rates in Loch Creran for farmed bivalves

Three of the four shellfish farmers responded to a request for information regarding their production levels. The fourth, owned by; Isle of Shuna, is up for sale and it is uncertain whether they will continue to produce mussels. However estimates of their production levels for 2008 have been supplied by the other farmers including the previous owner. These figures are summarised in table 8.1 below.

Table 8.1: The quantity of bivalves farmed in Loch Creran. Data was supplied by local farmers. As they requested that their production levels be kept confidential individual farms are listed by number rather than by name.

Farm	Species	Production (kg)
1	*Crassostrea gigas*	32×10^3
2	*Crassostrea gigas*	16×10^3
3	*Crassostrea gigas*	100×10^3
4	*Mytilus edulis*	80×10^3

This gives a total of 148 x10^3 kgs of oysters and 80 x10^3 kgs of mussels for the middle basins of Loch Creran. Smaal and Zurburg (1997) calculated clearance rates for oysters and mussels in the Marennes-oleron Bay of between 4 and 7 L/g Ash free dry weight(AFDW)/hr and between 0.9 and 2.7 l/g (AFDW)/hr respectively.

The weights supplied above refer to living bivalves, and this must first be converted to an ash free dry weight. Stirling and Okumus, (1995), estimated that the ash free dry weight of *M. edulis* was 5.8% of the live weight while Cheshuck *et al.* (2003) calculated this value to be 7%. Making the assumption that this relationship can also be applied to *Crassostrea gigas* gives an estimated ash free dry weight range of between 8.58 $x10^6$ g and 10.36 $x10^6$ g of oysters and between 4.64 $x10^6$ g and 5.60 $x10^6$ g of mussels.

Applying the clearance rates calculated by Smaal and Zurburg (1997) gives a range of:

3.43 x 10^7 and 7.25 x 10^7 litres/hr for *Crassostrea gigas* and

0.42 x 10^7 and 1.51 x 10^7 litres/hr for *Mytilus edulis*

Landless and Edwards (1976) calculated a flushing time for Loch Creran of 151 hours. Assuming that the bivalves filtered continuously for this period they would, potentially, be able to clear between 5.81 x 10^6 m^3 and 13.26 x 10^6 m^3 of water.

This calculation does not take into account the proportion of phytoplankters in the water to other organic matter consumed by the bivalves, nevertheless Bacon *et al.* (1998) found that the feeding activity in some species of bivalve decreased as seston concentrations in the water column increased. Nor does the calculation take account of recruitment to the phytoplankton population through growth and through immigration from the open sea. It does, however provide a conservative idea of the potential effect of farmed bivalves on the loch phytoplankton population.

Tyler (1983) calculated a mean volume for the main basin in Loch Creran i.e. chart datum plus 2.6 m, of 150.05 x 10^6 m^3. Applying the above range of clearance rates the bivalves would be capable of filtering between 3.87% and 8.84% of the main basin during a flushing period.

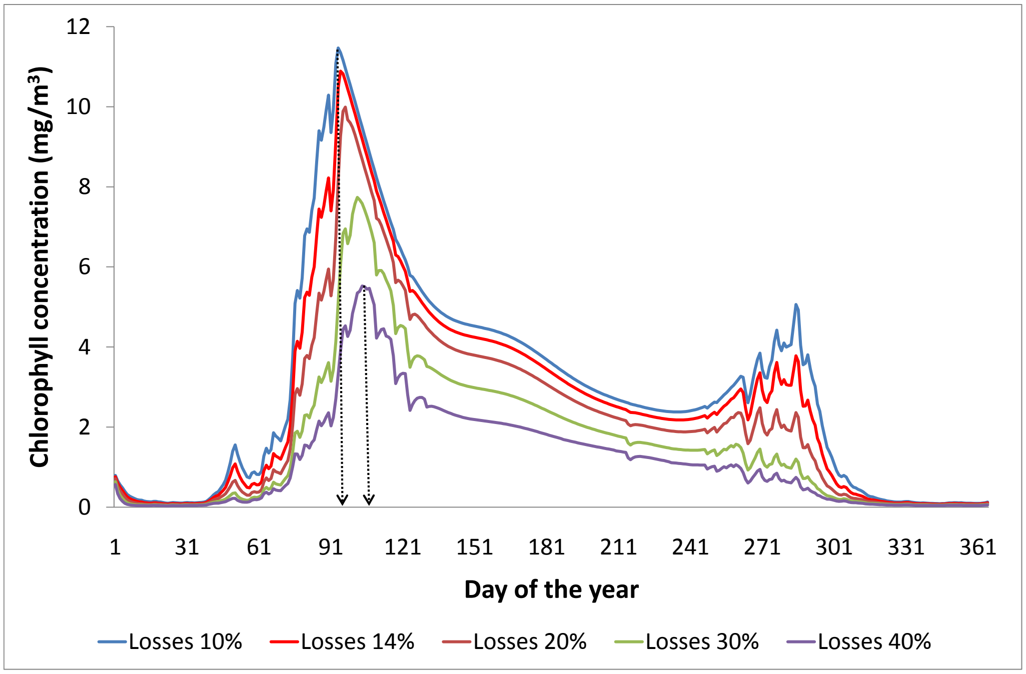


Figure 8.1: Plot showing the affect on chlorophyll concentration of applying different levels of grazing intensity in Loch Creran. The dotted arrows show a delay in the onset of the spring bloom as grazing intensity increases.

8.3.3 Modelling the effects of increasing grazing rates

It would be both expensive and time consuming to carry out an investigation of the bivalve clearance rates in Loch Creran *in situ*. However by using the mathematical model developed in chapter 10 it is possible to gain an approximate idea of the impacts an increase in grazing would have on the phytoplankton in the loch.

Figure 8.1 is a plot of the annual chlorophyll concentration in the loch when subjected to different loss rates i.e. 10%, 14%, 20%, 30% and 40%. The model normally includes losses of 10%. This value represents an amalgamation of different loss factors including cell lysis and sinking as well as losses due to grazing. The value of 40% may appear rather high, however this rate has been included, as this is the level of grazing by wild suspension feeders that has been estimated to occur in Loch Creran, and this will be discussed further below.

The red line on the plot shows the result on the chlorophyll concentration after assuming losses of 14%. This assumes the original 10% plus an additional 4% to represent the losses due to bivalve farming in the loch.

The dotted arrows on figure 8.1 indicate the peak of the spring bloom in the loch. These have been included to illustrate that as levels of grazing are increased the onset of the spring bloom is delayed.

Of course it would be expected that loss rates in the loch would change throughout the year as larger heterotrophic phytoplankton follow a Lotka-Voltera type pattern (Thingstad and Sakshaug 1990). Nevertheless the model does provide a useful approximation of the changes that could be expected in the loch.

8.4 Discussion

It would appear that bivalves can indeed exert a top down pressure on phytoplankton. However the extent of this impact will depend greatly on local hydrodynamic processes.

Wind induced turbulence, vertical mixing and tidal currents will increase the amount of contact between bivalves, whether they are part of the benthos or are suspended on aquaculture ropes, and the water column. As the mussels in Loch Creran are suspended on lines several metres above the bed of the loch it may be safe to assume that apart from ammonium which they will release directly into the water column, any faeces and pseudo faeces that they produce will fall to the loch bed. Once there re-mixing of nutrients re-mineralised from this source will only occur sporadically as a result of vertical mixing and tidal currents.

The calculation of clearance rates of farmed bivalves in the loch is only an approximation but it is a conservative one. Glynn (1973) calculated that 91% of the phytoplankton flowing over a carribean reef was consumed by wild filter feeders. Closer to home, Segueira et al. (2007) have estimated that wild populations of benthic filter feeders in Loch Creran would be capable of clearing 40% of the volume of the loch per day. Figure 8.1 illustrates the effect this rate could have on the concentration of phytoplankton in the loch.

While this does indicate a significant reduction in phytoplankton abundance it still does not account for the losses observed in the loch. Moreover while there appears to be little information on the abundance and health of wild suspension feeders recorded in the literature, recent reports by Black *et al.* (2000) and Moore (1996) suggest that while the benthos in the loch is healthy, there is no evidence that the numbers of wild suspension feeders in the loch have significantly increased over the past 40 years. It must be assumed therefore that the number of wild suspension feeders in the loch now has not changed in any obvious way from the number present during the 1970's and that any losses due to grazing by wild suspension feeders can be considered as a "background" rate that has not significantly changed since the 1970's.

In conclusion, while grazing by filter feeders can have a significant impact on the concentration of phytoplankton in a semi-enclosed water body, the levels in Loch Creran do not appear to be high enough to account for the changes observed.

Nonetheless it is interesting to see that as the intensity of grazing increases the onset of the spring bloom occurs later in the season. This resonates with actual observations of the timing of the spring bloom in Loch Creran. It may be that at least part of the changes observed in the loch are due to changes in the grazing pressure exerted on the phytoplankton community.

Chapter 9

Variations in Local Weather

9.1 Introduction

As has been previously mentioned, phytoplankton growth is largely dependent on the availability of both nutrients and light. It also depends very much on the degree of turbulence found within the water column which in turn influences the mixing depth. In a sea loch such as Loch Creran the turbulence in the water column is the result of several factors including tidal exchange with the Lynn of Lorn, mixing due to the wind and stratification of the surface layers. The latter occurs as a result of freshwater flowing into the loch from rivers, run-off from the surrounding catchment area and to a lesser degree by solar insolation.

It can be seen then that the degree of stratification and mixing, and by extension the growth potential of the phytoplankton community, in the loch is very much influenced by variations in the local climate. In Scotland a large part of the interannual variability in the weather is the result of changes in the North Atlantic Oscillation (NAO).

The NAO describes fluctuations in atmospheric pressures measured at sea level between a region of low pressure above Iceland and a region of high pressure above the Azores (Hurrell 1995).

Inter-annual fluctuations in these pressure systems exert control over the strength and direction of westerly winds and storms moving across the North Atlantic. Indeed Ottersen *et al.* (2001) has stated that the NAO exerts the greatest influence on atmospheric conditions in the North Atlantic. An influence that is particularly pronounced during the winter.

These variations in the NAO are described by an index (see figure 9.1) that, when positive, i.e. when the differences in pressure between the Azores and Iceland are both enhanced, leads to stronger winds, cooler summers, increased rainfall and milder winters in Europe. Conversely when the index is negative winds are suppressed, winters are colder and rainfall is reduced (Ottersen *et al.* 2001; Hurrell 1995).

Changes in the NAO have also been connected with changes in biological populations (Hurrell *et al*. 2001) including zooplankton and the large scale distribution of both shellfish and fish.

From the early 1940's until the early 1970's the NAO exhibited a downward trend that was accompanied by lower than normal winter temperatures (Hurrell 1995). However over the past 40 years there has been an upward trend in the NAO which has been more or less positive since the late 1970's. This has generally led to an increase in surface temperatures (Hurrell *et al.* 2001).

There is no reason to believe that sea lochs on the West coast of Scotland are immune to changes in the NAO. However the effects of changes in the NAO vary

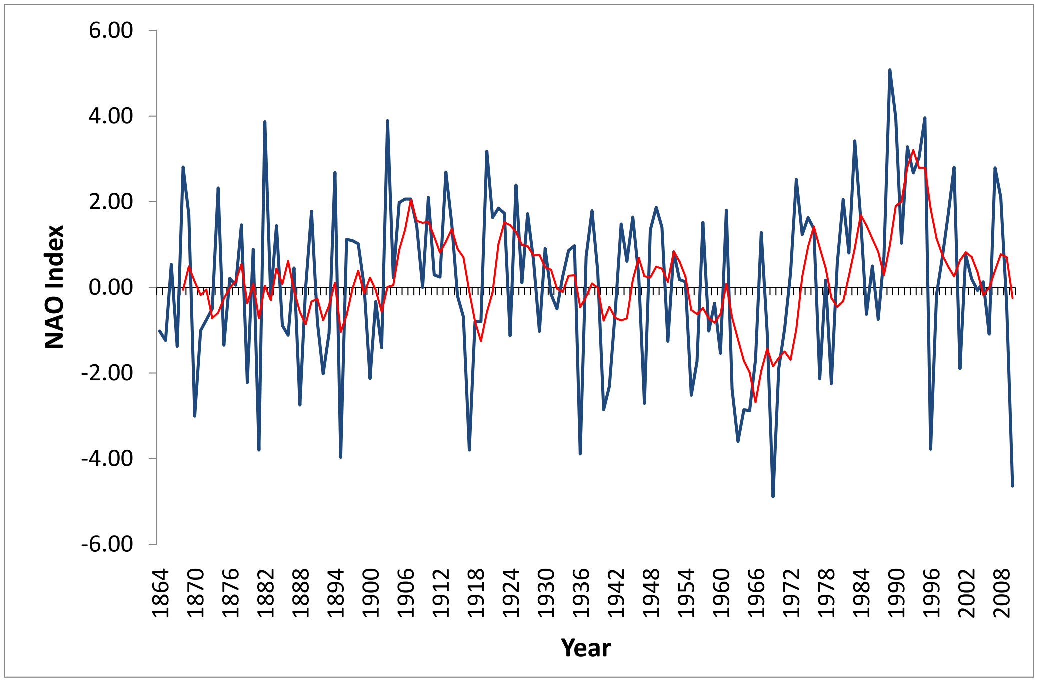


Figure 9.1: Plot of the NAO Winter station index calculated as the difference of normalized sea level pressures (SLP) between Lisbon, Portugal and Stykkisholmur/Reykjavik, Iceland since 1864. The index represents the mean of the values between December and January. E.g. they refer to an average of December 1863 and January, February and March of 1864, and so on. The red line represents a five year running mean. The graph was drawn from data provided by the University Corporation for Atmospheric Research (UCAR), Boulder, Colorado, USA (UCAR 2011).

both regionally and locally. To estimate the strength of any local changes in surface temperatures, wind strength and rainfall and to evaluate the possible impacts on the phytoplankton community in Loch Creran it is necessary to take local measurements of these climatic variables.

9.2 Aims

The aim of this chapter is to compare measurements of the wind speed, surface and sea temperature and precipitation levels in the vicinity of the loch made during the 1970's with those made during the 2000's. The assumption being that there has been no significant change in any of these variables over the past 40 years.

9.3 Methods

9.3.1 Temperature

Temperatures for both the 1970's and for 2008-2009 were averaged over the top ten metres of the water column.

During the 1970's temperatures in Loch Creran were measured with an N.I.O temperature/salinity bridge (S.M.B.A. number 3) that was calibrated against an almost simultaneous reversing thermometer (Jones 1979).

Between 2008 and 2009 temperatures were measured with an Ecotemp digital thermometer, catalogue number: 810-950, supplied by ETI Ltd, Worthing, West Sussex, for shore based sampling and an SBE 19plus SEACAT profiler supplied by Sea-Bird Electronics Inc. Washington 98005, USA and owned by Edinburgh Napier University, during shipboard transects. This was calibrated alongside a similar SBE 19plus profiler owned by the Scottish Association for Marine Science, Dunstaffnage, Argyll.

Shipboard measurements of water temperature were averaged over the top ten metres then combined to give a mean value for the loch. Shore based measurements were taken in the top two metres of the water column. As it was felt that shore measurements, particularly on sunny days, could bias the results, making the temperatures appear higher than they actually were, these results were omitted in favour of the measurements made via the CTD depth profiler. The data sets were analysed with a students T test.

Surface temperatures were obtained from the British Atmospheric Data centre (BADC) (BADC 2010) for the weather station located at Dunstaffnage, Argyll (BADC Station identifier src id 918). For analysis monthly mean temperatures were calculated, then as the data was normally distributed, compared with a students T test.

9.3.2 Windspeed

Wind speeds were obtained from the BADC, MIDAS land surface stations dataset (BADC 2010). As the weather station located at Dunstaffnage, Argyll had been rebuilt during the late 1990's and subsequently moved, there was the possibility that this would introduce uncertainties into the data. It was decided therefore to use wind data from the station located on the island of Tiree Argyll (BADC station identifier src id 18974) which had an almost unbroken record extending back to 1926.

This data was first binned into daily averages for the years 1972 to 1978 and 2004 to 2008. Means were then calculated for each day of the year between 1972 and 1978 and between 2004 and 2008 to create a "climatology" for each period. Although these climatologies could then be compared using a students T test for matched pairs it was felt that as the data formed a continuous time series, with each days value influenced by those of the days preceding it, a more robust approach was to plot the cumulative frequency and analyse these with a Kolmogorov-Smirnov (KS) test.

9.3.3 Rainfall

Daily precipitation levels were obtained from the BADC (BADC 2010) for the weather stations located at Dunstaffnage and Strath of Appin, Dungrianach, (BADC station identifier src id 13972). Data for the periods 1972 - 1980 and 2005 - 2009 was binned to obtain a climatology for each period. Although the station located at the Strath of Appin was ideally placed within the Loch Creran catchment area its data set was not as extensive as that for Dunstaffnage. Therefore the data from Dunstaffnage was used as a comparison with that available from the Strath of Appin.

Similarly to the wind data, the values for precipitation formed a continuous time series, it was decided therefore to plot cumulative frequencies then use a Kolmogorov-Smirnov test to analyse this data.

9.4 Results

9.4.1 Water temperature

Figure 9.2 illustrates the changes in water temperature that have occurred in Loch Creran. The blue line represents the climatology that was created from the daily mean water temperatures measured in the top ten metres of the water column between 1971 and 1981. The dashed lines represent the 5th and 95th percentiles of this data and encompass much of the variability in temperature observed during this period. The red line is the mean water temperature recorded in the loch between 2008 and 2009 again in the top ten metres. The error bars represent one standard deviation.

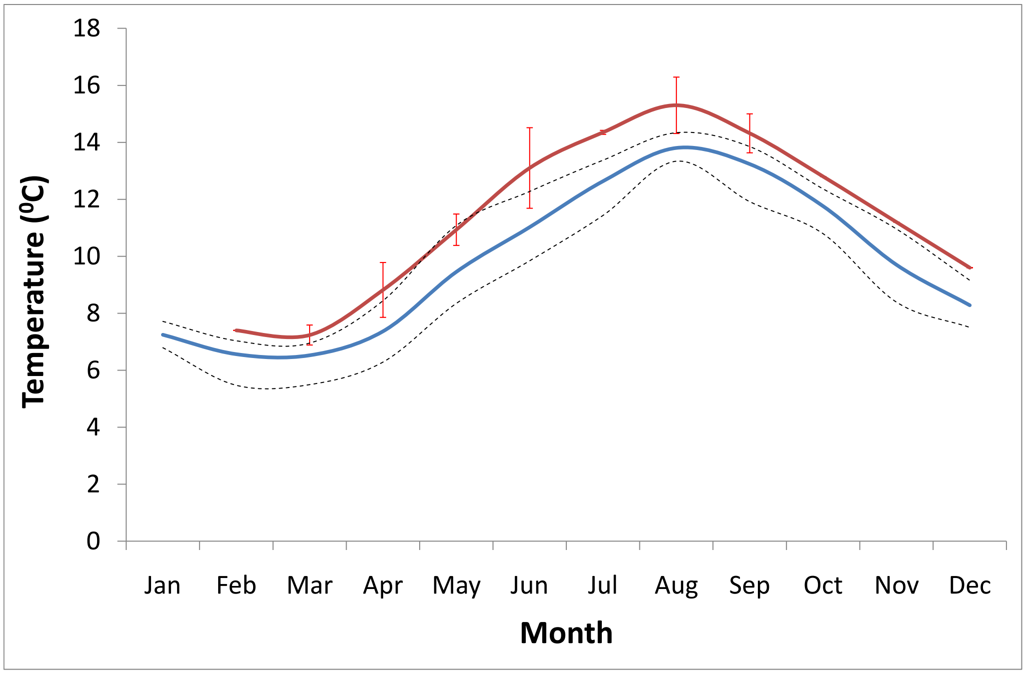


Figure 9.2: Plot of mean water temperatures in Loch Creran measured over the top ten metres of the water column. The blue line represents the climatology created from the temperatures averaged between 1971 and 1981. The red line represents temperatures averaged between 2008 and 2009. The dotted black lines represent the 5th and 95th percentiles for the water temperatures averaged between 1971 and 1981. The error bars represent one standard deviation.

A paired T test analysis of these two datasets; $T = -11.7$, $p < 0.0001$, indicates that over the past three decades, there appears to have been a significant increase in temperature in the loch. Nevertheless, while the climatology for the 1970's is based on a decade of measurements the data for 2008 - 2009 encompasses only two years and as such represents a relatively limited amount of data. It is therefore quite possible that the increase in temperature seen in the loch is only a temporary anomaly or even the result of error in the measurements.

It would be helpful then if this finding could be corroborated in some way. Lolis et al. (2002) and Bartzokas et al. (2003) have found that there is a correlation between sea temperature and land surface temperature. They have shown that sea

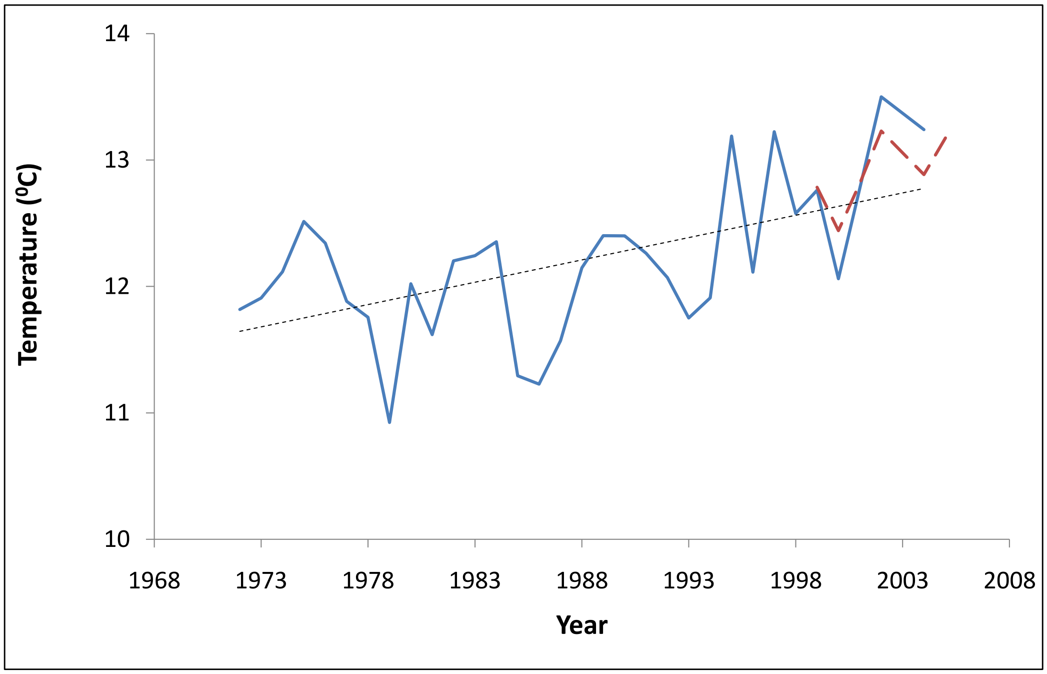


Figure 9.3: Plot of the annual mean surface temperatures recorded at Dunstaffnage between 1972 and 2005. The dashed red line represents the mean surface air temperatures measured at Oban airport for a comparison. The dashed line represents a linear trendline fitted to the Dunstaffnage data. All data was obtained courtesy of the BADC (BADC 2010).

temperatures generally rise and fall in line with the surface air temperature. It may be possible then to examine air temperatures for the area around Loch Creran to see if there has been any such change in the temperature.

Figure 9.3 is a plot of the mean annual surface temperature recorded at Dunstaffnage between 1972 and 2005. The red portion represents the temperatures measured at Oban airport, a mile or so to the north of Dunstaffnage and is included as a comparison. The dashed line superimposed on the data is a linear trend-line which shows that there has been an upward drift in temperatures since the early 1970's.

This visibly upward trend suggests that the rise in water temperatures observed in the loch is an actual one and can therefore, be accepted as a reasonable indication of the present state of the loch.

9.4.2 Windspeeds

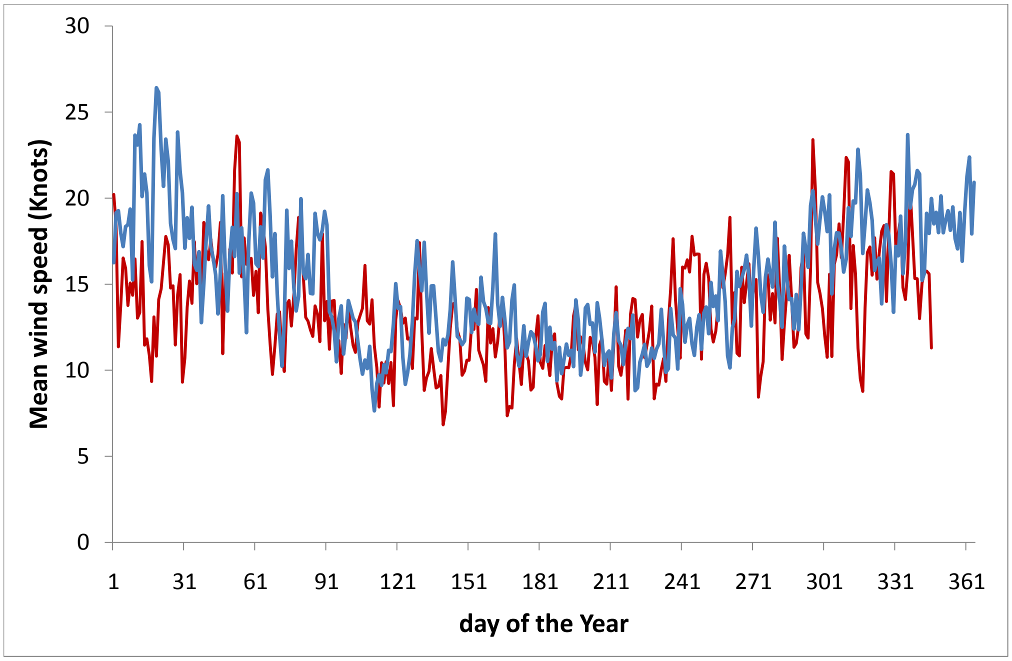


Figure 9.4: Plot of wind speeds (knots) recorded on the isle of Tiree, Argyl. The blue line represents a climatology created from daily mean wind speeds between 1972 and 1978. The red line represents a climatology created from measurements of daily mean wind speeds made between 2004 and 2008. The data was obtained courtesy of the BADC (BADC 2010).

Figure 9.4 shows a comparison of measured wind speeds on the isle of Tiree, Argyll. The lines represent climatologies created by taking means of the average daily wind speed over the period between 1972 and 1978 and between 2004 and 2008.

From the figure it is apparent that while some differences can be seen, particularly during January, there is a lot of overlap. It appears that there were higher wind speeds during the early part of the year in the 1970's but this is not clear.

Although the data could be analysed using a students T test for matched pairs as it forms a continuous time series it is perhaps more suitable to use a Kolmogorov-Smirnof statistical analysis to determine whether the two data sets differ in any

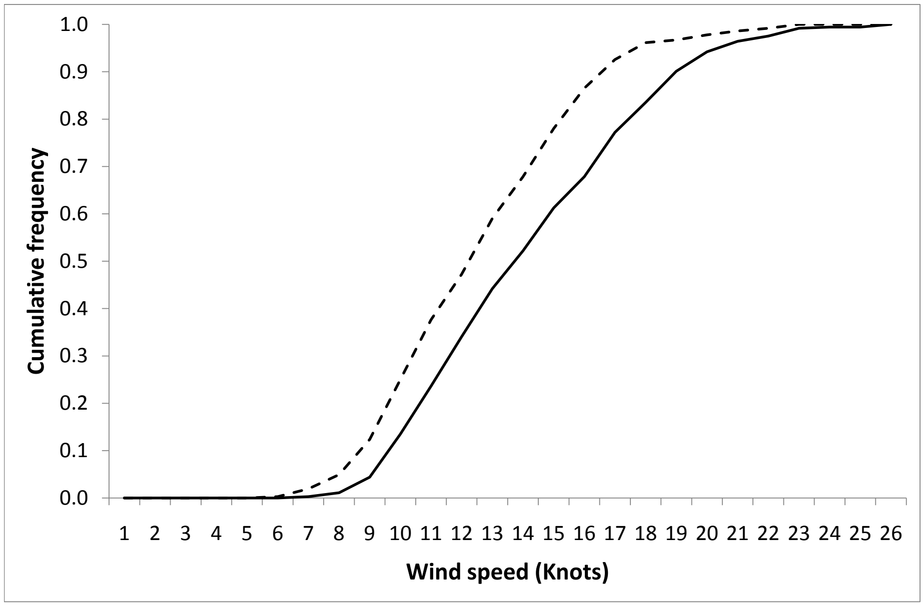
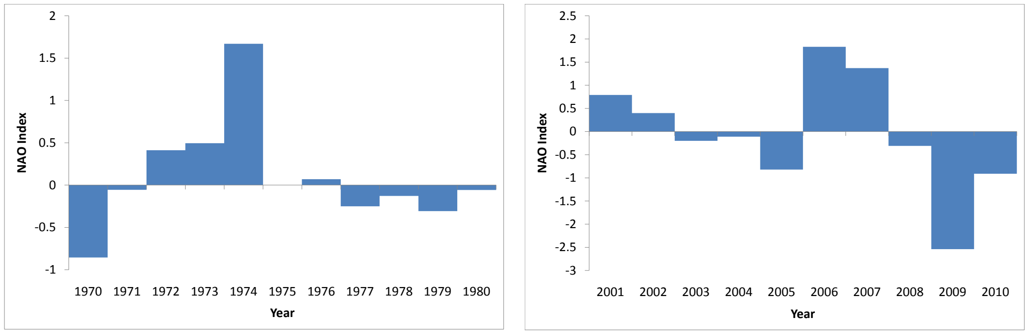


Figure 9.5: A cumulative frequency plot for wind speeds measured between 1972 and 1978 (solid line) and between 2004 and 2008 (dashed line) on the isle of Tiree, Argyll.

significant way. Figure 9.5 shows the result of plotting the cumulative frequencies for the two time periods. It can be seen from the figure that wind speeds measured during the 1970's were generally higher than those measured during the 2000's and indeed the Kolmogorov-Smirnof test showed a significant difference in the two datasets; $P < 0.01$.

This result may reflect changes in the NAO Index. Figure 9.6 shows a plot of the index between 1970 and 1980 (a) and between 2001 and 2010 (b). It is clear from figure 9.6 (a) that for a large part of the 1970's the index was either positive or only slightly negative. A positive NAO is associated with stronger Westerly winds. Figure 9.6 (b) shows a more mixed picture with the NAO fluctuating between positive and negative years. From 2007 and during the period of the study the index has been strongly negative. This may account for the weaker winds measured during this study.



(a) NAO Index 1970-80 (b) NAO Index 2001-10

Figure 9.6: NAO Index for the periods between 1970 and 1980 and between 2001 and 2010. Data was provided by the University Corporation for Atmospheric Research (UCAR), Boulder, Colorado, USA (UCAR 2011).

Support for the influence of the NAO can be found in Kratzer *et al.* (2003) who note that during the 1960s, 1970s and 1980s geostrophic wind strengths over the British Isles increased, before falling during the 1990s. This change has subsequently been attributed to changes in the NAO (Folland *et al.* 2007).

9.4.3 Irradiance

Figure 9.7 is a plot of the irradiance (W hr m^{-2}) recorded at Dunstaffnage during 1978 (black line) and 2009 (red line). The lines represent 30 day running means. It appears from the figure that there are differences between 2009 and 1978 i.e. less light during spring 2009 and more during summer. However a Kolmogorov-Smirnov test (figure 9.8 (a)) revealed no significant differences between the two years.

Nevertheless, after looking carefully at figure 9.7 it does appear as if there is a difference in irradiance during late winter and spring. Most of the changes that have occurred in the phytoplankton community in Loch Creran have also taken place during spring so it makes sense to determine if there are any significant changes in

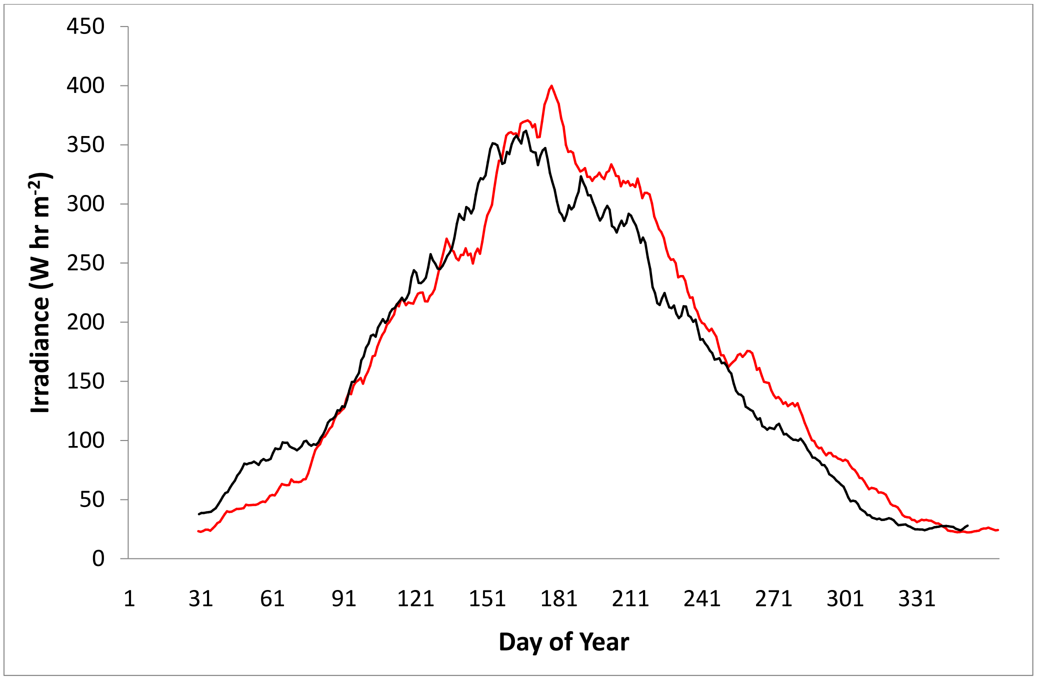
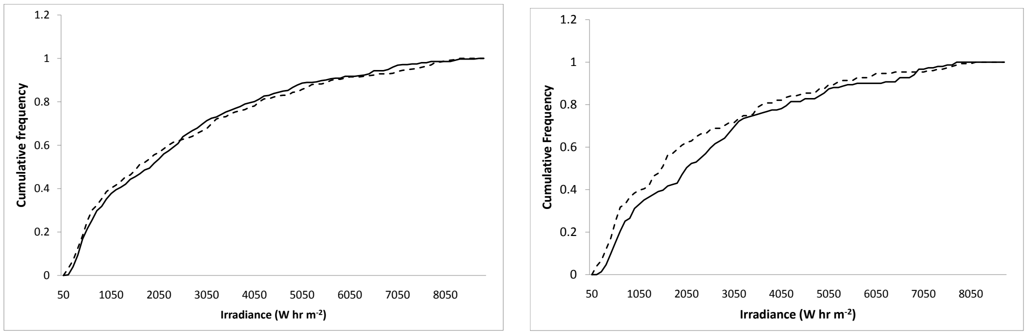


Figure 9.7: Plot of irradiance measured at Dunstaffnage, Argyll during 1978 and 2009. The black line represents the 30 day running mean recorded during 1978 and the red line represents the 30 day running mean recorded during 2009. Data was provided by the BADC (BADC 2010).

the early part of the year. Comparing irradiance levels between January and May in 1978 and 2009 does reveal a significant difference, $P < 0.05$ (Borkowski 2010), with irradiance levels appearing to have decreased significantly in 2009. This decrease in measured irradiance is most likely due to an increase in cloud cover during the early part of the year.

9.4.4 Rainfall

In chapter 4, measurements of the nutrient concentrations in the loch showed that while the levels of nitrate had increased those of phosphate had significantly decreased. It was speculated that one possible reason for this change in concentrations could be due to an increase in the amount of freshwater flowing into the loch.



(a) January to December (b) January to May

Figure 9.8: Cumulative frequency plots for Irradiance recorded at Dunstaffnage in 1978 and 2009.

The most obvious source of this freshwater is of course from rainfall. Edwards and Sharples (1986) calculated that freshwater run off from the Loch Creran catchment can be found by:

$$\text{Run-off} = \frac{(\text{Annual rainfall(mm) - 250(mm)} \cdot \text{Watershed (km}^2))}{1000} \tag{9.1}$$

Where the 250mm is an adjustment to allow for losses due to evaporation. With a catchment area of 164 Km^2, Edwards and Sharples (1986) estimated the annual run-off into Loch Creran to equal 286.3 million cubic metres.

Figure 9.9 is a plot of the mean daily rainfall between 1970 and 1980 compared with the mean daily rainfall between 2002 and 2009 recorded at the Dunstaffnage weather station. The data was supplied by the BADC (BADC 2010).

In a similar fashion to the climatologies created earlier the data was first binned into mean daily values and then those values for each day of the year were averaged over the eight years from 2002 until 2009 and from 1970 until 1980. The daily values have been omitted for clarity and the lines on the plot represent 7 day running means.

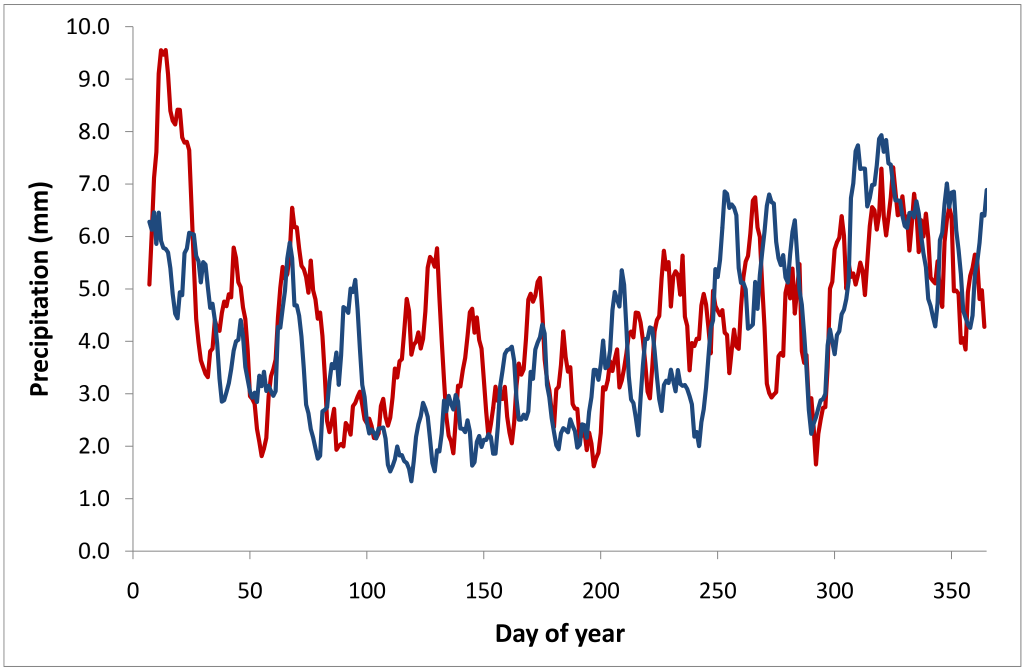


Figure 9.9: Plot of mean daily rainfall recorded between 1970 and 1980 and between 2002 and 2009 at the Dunstaffnage weather station. The red line represents the 7 day running mean for 2002-09 while the blue line represents the 7 day running mean for 1970-80. Data was supplied courtesy of the BADC (BADC 2010).

Although he weather station at Dunstaffnage provides a source of continuous data which extends from the present back to the 1970's it is located approximately 10 kilometres to the South of Loch Creran and lies outside the Creran catchment area. Another station located at the Strath of Appin, Dungrianach and near to the head of the main basin, is better situated but has only recorded rainfall since 1977.

Before using the data from Dungrianach it seemed prudent to compare the pattern of recorded rainfall there with that from Dunstaffnage to see if there was any correlation between the two and to determine whether or not the shorter time series could be expected to reflect the patterns of rainfall observed in the longer time series .

Figure 9.10 is a plot of the comparison between the two weather stations. Dungri-

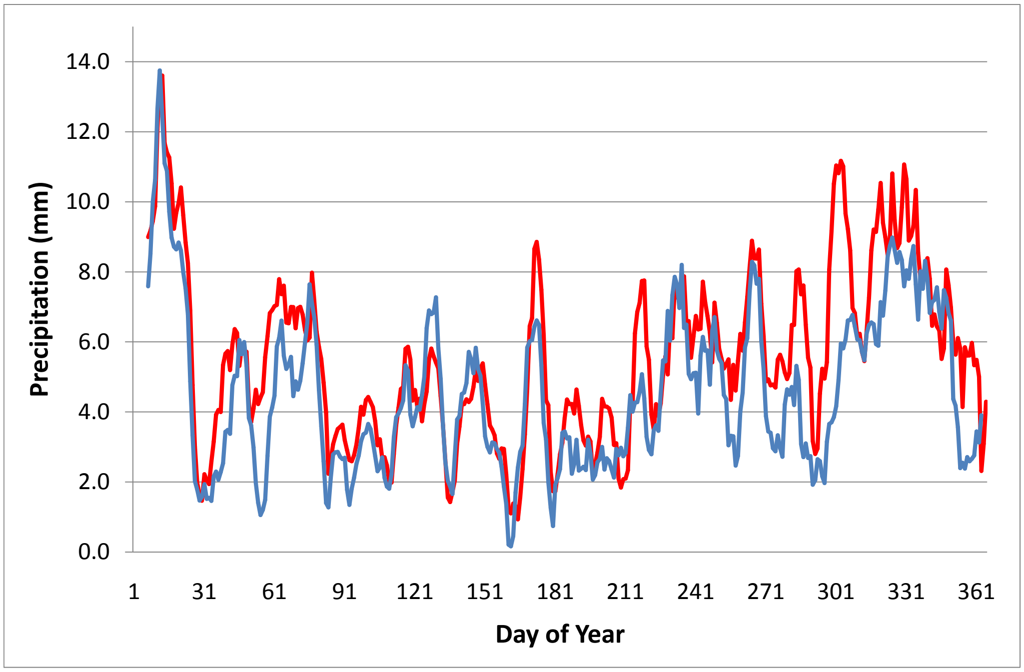


Figure 9.10: Plot comparing recorded mean daily rainfall between 2005 and 2009 at Dunstaffnage with that recorded at Dungrianach between 2005 and 2009. The red line represents the 7 day running mean for precipitation at Dungrianach and the blue line represents the 7 day running mean for Dunstaffnage. Precipitation data provided courtesy of the BADC (BADC 2010).

anach is represented by the red line which was drawn from the mean daily rainfall between 2005 and 2009 while Dunstaffnage is represented by the blue line, plotted from mean daily rainfall between 2005 and 2009.

It is immediately clear that although the levels of precipitation are higher at Dungrianach there is a good match between the patterns of rainfall at the two weather stations. The levels of precipitation at Dungrianach are slightly higher than those at Dunstaffnage however Dungrianach is backed immediately to the North East by Beinn Donn at 473 metres and Beinn Churalain at 549 metres. Given the proximity of these two hills to Dungrianach it would be expected that as the prevailing westerly winds rise up their flanks and condense, the levels of rainfall here would tend be higher.

It would seem reasonable then to accept the data from Dungrianach as best estimating the levels of precipitation falling on the Loch Creran catchment area. Figure 9.11 is a plot comparing the daily mean rainfall at Dungrianach between 1977 and 1980 and between 2005 and 2009.

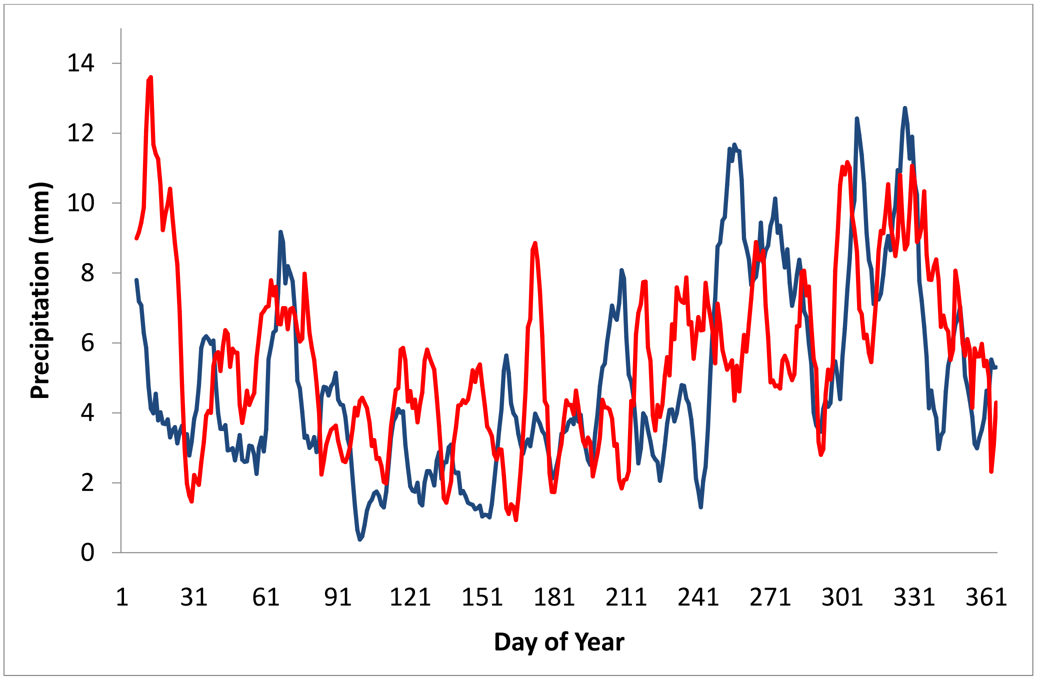
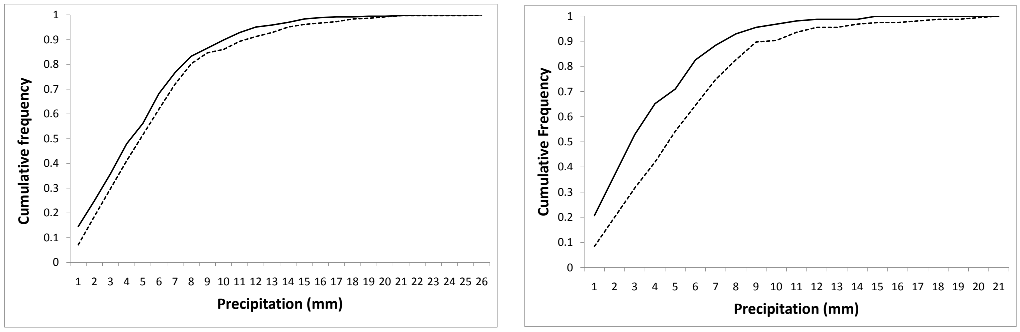


Figure 9.11: Plot of mean rainfall at Dungrianach, Argyll. Daily values have been removed for clarity. The red line represents the 7 day running mean for mean daily rainfall between 2005 and 2009. The blue line represents the 7 day running mean for mean daily rainfall between 1977 and 1981. Data obtained from the BADC (BADC 2010).

Again, as these datasets represent continuous time series, it was decided to analyse them using the Kolmogorov-Smirnov test statistic. Figure 9.12 is a plot of the cumulative frequencies. It is clear from figure 9.12 (a) that there is very little difference between the two datasets and indeed the Kolmogorov-Smirnov test indicated there was no significant difference between them, $P > 0.2$.

Nevertheless looking back at figure 9.11 it is apparent that at some times of the year, and it must be remembered that these represent climatologies not individual years,



(a) January - December

(b) January - May

Figure 9.12: Cumulative frequency plots for precipitation levels recorded between 1977-81 (solid line) and during 2005-09 (dashed line) figure (a) and between January and May for the same periods (b), recorded at Dungrianach, Strath of Appin, Argyll.

there is a change both in the amount and also in the timing of the rainfall, and this is most apparent during the early part of the year.

Figure 9.13 compares the amount of rainfall recorded at Dungrianach, Strath of Appin, falling between January and May for the periods between 1977 and 1981 (shaded blue) and between 2005 and 2009 (shaded red). It is clear that the pattern of precipitation has changed between these two periods with peaks in rainfall during the 2000's seeming to occur slightly later than previously recorded during the 1970's. The intensity of the rainfall also appears to have changed, increasing noticeably during January. A Kolmogorov-Smirnov test (see figure 9.12 (b)) shows this difference to be significant; $P < 0.01$.

Applying equation 9.1 to the mean rainfall recorded between 1977 and 1981 at Dungrianach gives an estimated annual run-off of 253.1 x 10^6 m^3. Between 2005 and 2009 the annual run-off was estimated at 302.1 x 10^6 m^3. An increase of 19%. However the same calculation carried out for the beginning of the year i.e. between January and May gave 47.5 x 10^6 m^3 for mean rainfall between 1977 and 1981 and 89 x 10^6 m^3 for mean rainfall between 2005 and 2009, an increase of 87.4%.

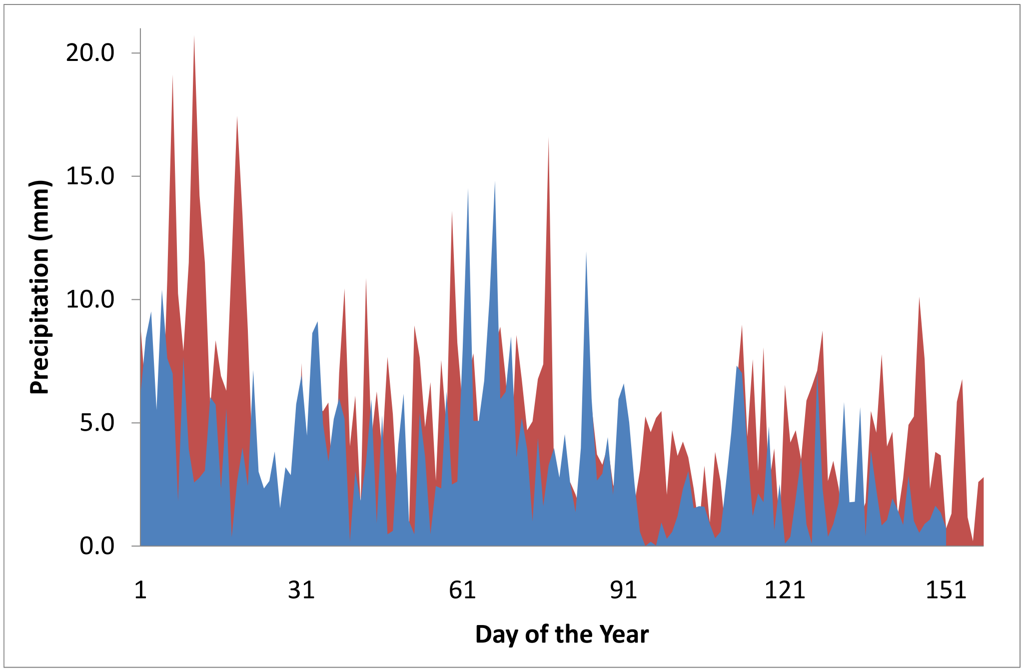


Figure 9.13: A comparison of the mean rainfall falling on Dungrianach, Strath of Appin, between January and May for the periods between 1977 and 1981 (in blue) and between 2005 and 2009 (in red). Data provided courtesy of the BADC (BADC 2010).

Changes in the amount of rainfall can affect the state of the loch in different ways. An increase in freshwater flowing into the loch can alter the amount of water displaced through tidal exchange, potentially raising the washout rate, of the phytoplankton i.e. the rate at which phytoplankton is moved out of the loch as the surface layer flows towards the larger Lynn of Lorn (Ross *et al*. 1994; Su *et al*. 2004; Lionard *et al*. 2008). Tett *et al.* 1986 suggests that an increase of the magnitude seen would be unlikely to significantly alter this rate . Nevertheless these figures are based on mean values. Tett observes that high levels of rainfall (three times the mean value) over short periods of time can conceivably result in an increase in the loss rate of phytoplankton.

Figure 9.14 is the result of subtracting the 1977 - 1981 mean rainfall from the 2005

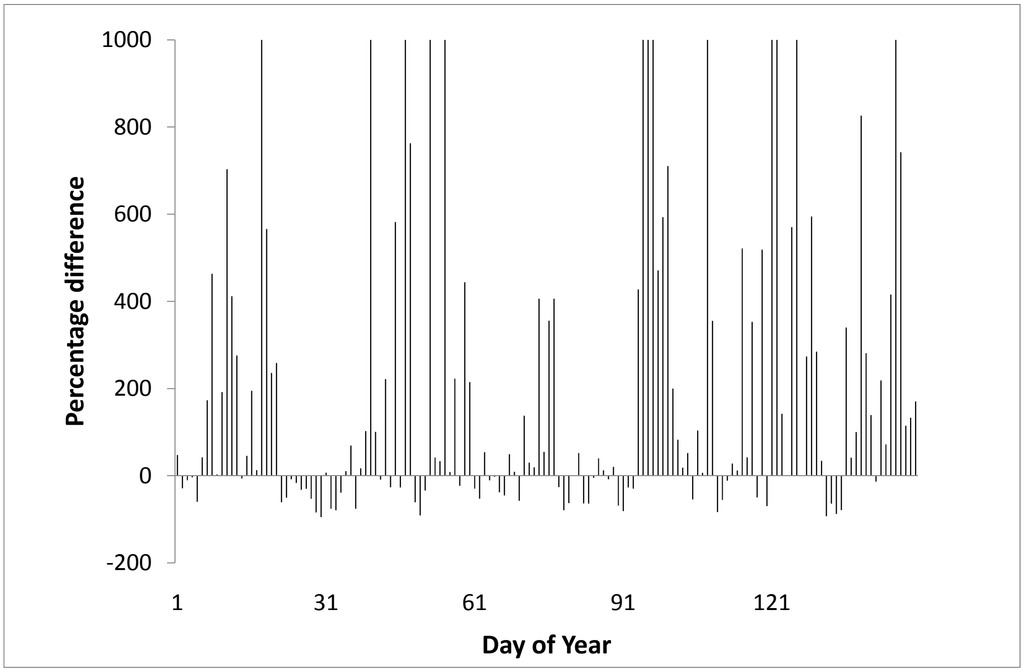


Figure 9.14: Plot of the percentage differences between the mean rainfall recorded between 2005 and 2009 and between 1977 and 1981 from January to the end of May at Dungrianach, Argyll.

- 2009 mean rainfall at Dungrianach, Argyll. The differences are expressed as percentages. For clarity the positive difference was restricted to 1000% although several days far exceeded this value. It can be seen that although there were days when less rain fell than in the past these are outnumbered by the number of days when rainfall was much greater than the 1977-81 levels. It is also clear that there are a considerable number of days that exceed mean 1977-1981 values by a factor of three. It seems reasonable to assume then that the rate of washout in the loch has increased during the spring months.

Run-off from the surrounding catchment area can introduce nutrients into the surface layers of the water column, potentially improving productivity, as well as strengthening stratification. However run-off can also increase the amount of turbidity in the loch by importing *"gelbstoff"*, chromophoric or coloured dissolved organic matter (CDOM). By altering the attenuation properties of the water this could possibly inhibit the growth of phytoplankton.

9.4.5 Coloured Dissolved Organic Material (CDOM)

Devlin *et al*. (2009) found that light attenuation in estuaries and coastal waters was highly correlated with the concentration of suspended particulates present in the water column. They went on to note however that in waters with a high level of freshwater inflow such as the Baltic sea and fjordic systems, suspended particulates play a lesser role than CDOM in controlling attenuation.

As it appears that the amount of precipitation falling on the lochs catchment area has increased significantly during the early part of the year it would be expected that the levels of CDOM entering the loch have also increased.

During 2008 and 2009 levels of CDOM in the loch were not measured directly. Therefore in order to estimate the affects of CDOM a simple salinity proxy was used instead under the assumption that salt and mass in the system are conserved, Bowers and Brett (2008), Foden *et al*. (2008). Work by McKee *et al.* (2002) in Loch Etive, a sea loch approximately 50 kilometres to the South of Loch Creran, and in neighbouring coastal areas has shown that there is a good correlation between salinity and CDOM, a finding supported by work in the Clyde sea by Binding and Bowers (2003), so this assumption seems acceptable. The proxy for CDOM was calculated simply as:

$$CDOM = S_o - S$$

Where S_o = the salinity in the open sea and S = the salinity measured on station.

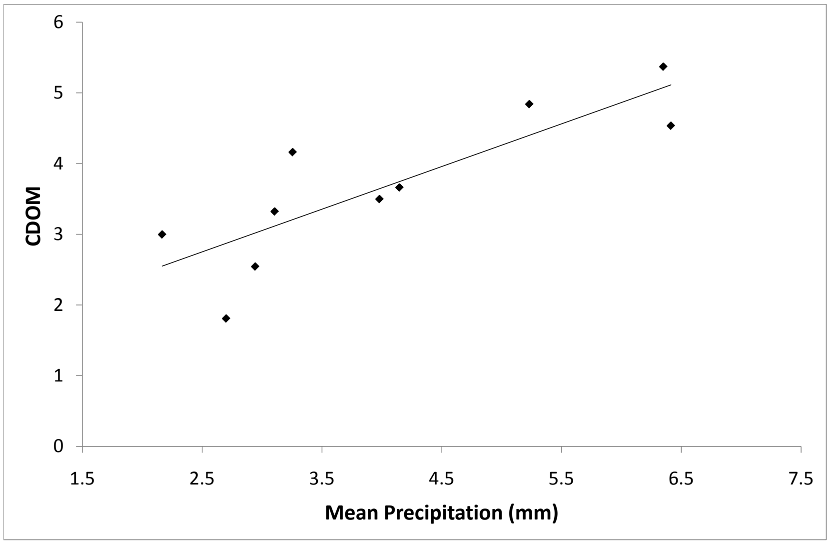


Figure 9.15: Regression of mean rainfall recorded at station C5 in Loch Creran against CDOM (salinity proxy). The rainfall data precedes the CDOM measurements by 7 days (see text for further explanation).

Figure 9.15 illustrates the mean rainfall recorded at station C5 in Loch Creran regressed against the CDOM (estimated from the salinity proxy) averaged over the top 12 metres of the water column. Observing the precipitation data it was noticed that there was a delay between periods of heavy rainfall and changes in the measured salinity in the surface waters of the loch. This delay was found to approximate 7 days and is assumed to be the time taken for water falling on the catchment area to find its way into the main basin of the loch.

The figure shows a strong positive correlation: $r^2 = 0.702$ between precipitation levels and CDOM concentrations in the loch and this correlation is significant at $p < 0.002$. It would seem reasonable to conclude that as levels of precipitation have risen, in the early months of the year, levels of CDOM in the surface waters of the loch will also have increased during this time.

Nevertheless even if concentrations of CDOM in the loch have increased this may not necessarily have any impact on the growth of phytoplankton in the loch. Before accepting the premise that the level of CDOM in the water column is affecting phytoplankton productivity it is necessary to determine if there is any link between chlorophyll concentrations in the loch and the amount of light penetrating the surface layers.

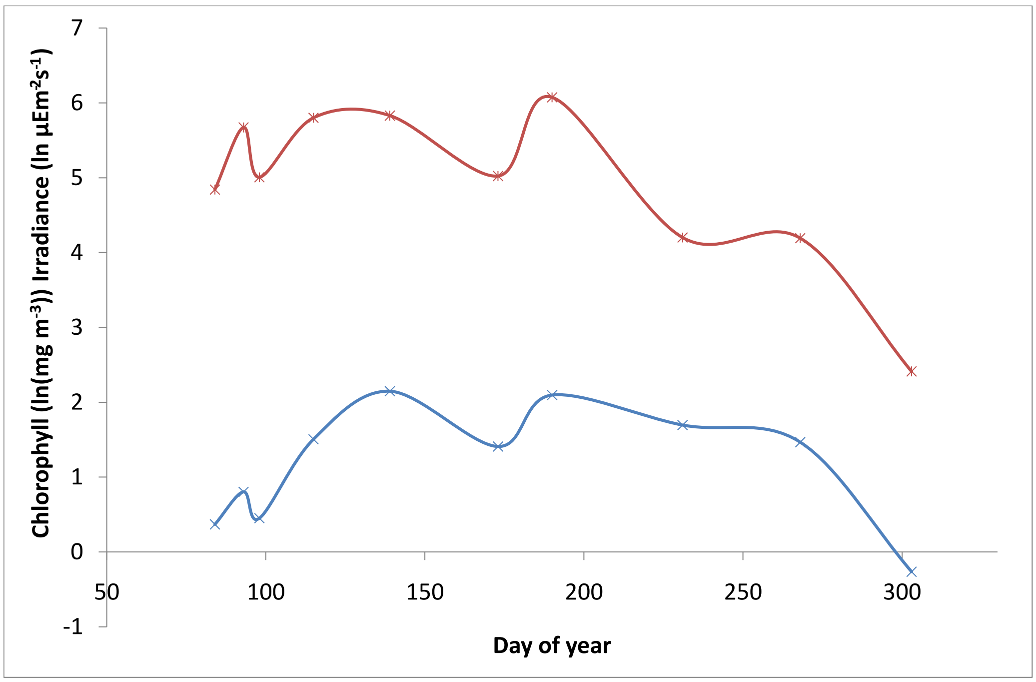


Figure 9.16: Sub surface Irradiance (I_o) (ln μE m^{-2} s^{-1}) (red line) measured in Loch Creran during 2008-09 plotted alongside the mean maximum chlorophyll concentrations (ln mg m^{-3}) (blue line) measured between the top 3 and 12 metres of water. The data points are indicated by crosses while the lines are included to illustrate the trends in the data.

Figure 9.16 illustrates the relationship between the intensity of light measured immediately below the water surface (I_o) (as defined in Tett 1990), and the concentration of chlorophyll recorded in the top 3-12 metres of the water column. It is apparent that there is a certain resonance between the two plots (see figure 9.17, r = 0.636) with the concentrations of chlorophyll generally rising and falling with the

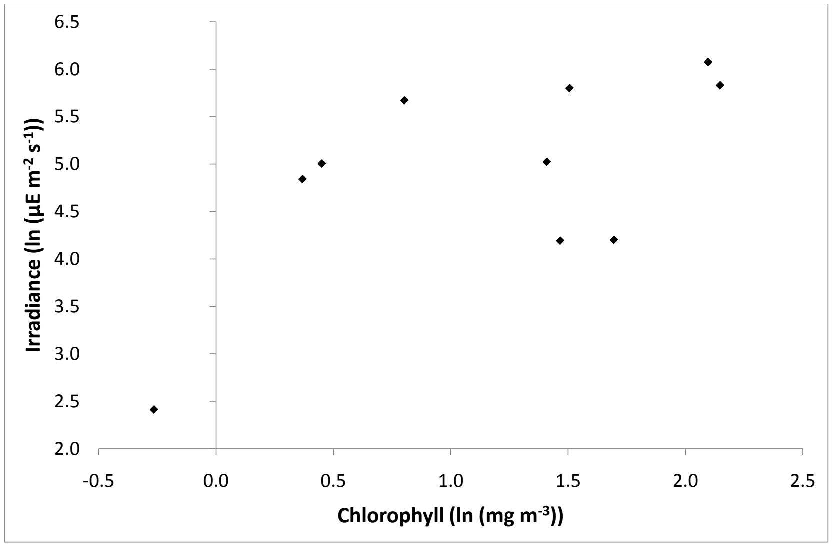


Figure 9.17: Sub surface irradiance (I_o)(ln μE m^{-2} s^{-1}) plotted against mean maximum chlorophyll concentrations (ln mg m^{-3}), r = 0.636.

changing intensity of light in the water column, particularly during the early months of the year and indeed this correlation is significant at $p < 0.047$. Nonetheless it must be remembered that the plots are drawn from mean values of measurements taken during ten transects of the loch during 2008-09. While the lines on figure 9.16 indicate trends in the data, more measurements would be needed before any firm conclusions could be drawn on the relationship between the intensity of light and the concentration of phytoplankton in the loch. Furthermore the intensity of light found in the water column will be affected by the presence of phytoplankton and other particulate matter that may attenuate the light. This can be particularly acute during the spring bloom when the large number of phytoplankton cells entrained in the top of the water column will effectively shade the cells below them. Although phytoplankton cells are constantly in motion throughout the photic zone, shading will impact on the amount of time they will be able to photosynthesise at optimal levels.

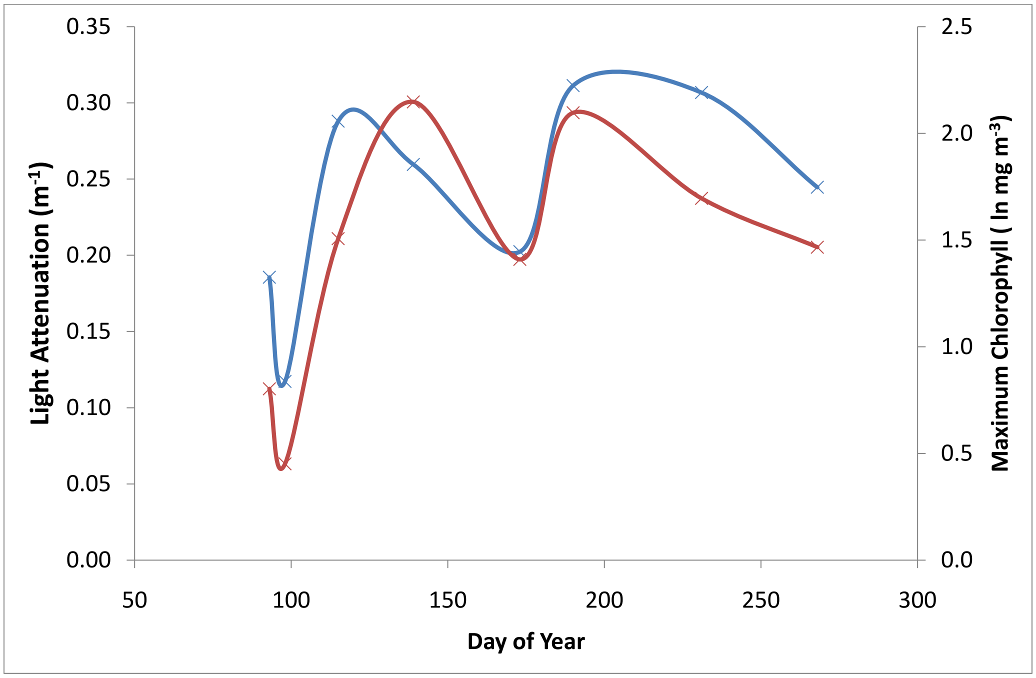


Figure 9.18: Plot of mean maximum chlorophyll recorded in the top 3-12 metres in Loch Creran during 2008-09 (red crosses) compared with the attenuation measured in the top 3-12 metres of the water column (blue crosses). The attenuation was calculated by subtracting mean photosynthetically active radiation (PAR) values from the value of PAR (I_o) available immediately below the surface and dividing by the depth. The red and blue lines have been included to indicate trends in the data.

Figure 9.18 is a plot of the maximum chlorophyll (red line) recorded in the main basin of Loch Creran averaged over the top 3-12 metres and plotted alongside it is the attenuation, again averaged between 3 and 12 metres, (blue line). The attenuation was calculated by subtracting the mean values for PAR, recorded in the top 3-12 metres of the loch and divided by the depth range, from the value of PAR available immediately below the surface (I_o). This was calculated (Tett 1990) from surface irradiance using the equation:

$$I_o = 1.91 \cdot m_1 \cdot E_o$$

where I_o = the PAR photon flux density immediately below the surface, 1.91 is a conversion factor that adjusts for the proportion of light falling on the Earth's surface that is photosynthetically active, and incorporates within it an energy to photon conversion factor, m_1 = 0.39, a correction factor adjusting for light reflected from the water surface (Tett 1990), and E_o = surface PAR (BADC 2010) recorded at Dunstaffnage during 2009. The first of the two peaks in chlorophyll corresponds with the spring bloom.

Again the lines on the plot are there to highlight the trends in the data however it does appear from figure 9.18 that there is a degree of correlation between the level of attenuation and the concentration of phytoplankton in the water column. It may be that much of the change seen in the attenuation will be due to changes in the density of phytoplankton. This should be particularly noticeable around the spring bloom when high concentrations of phytoplankton cells entrained in the water column will absorb or scatter a large part of the light penetrating the surface. This could be the cause of the drop in attenuation that can be seen in figure 9.18 after day 130. As phytoplankton exhaust the available nutrients, and possibly due to a degree of self shading, their numbers will drop allowing more light to penetrate the water column.

It is interesting however that at the point where the two plots intersect (day 139) on figure 9.18 it seems that although the concentration of chlorophyll is increasing the amount of attenuation measured is actually dropping. This would suggest that other factors besides chlorophyll may be influencing the amount of attenuation observed.

Figure 9.19 is a plot of the attenuation measured in the water column regressed against the maximum chlorophyll measured in the main basin of the loch between

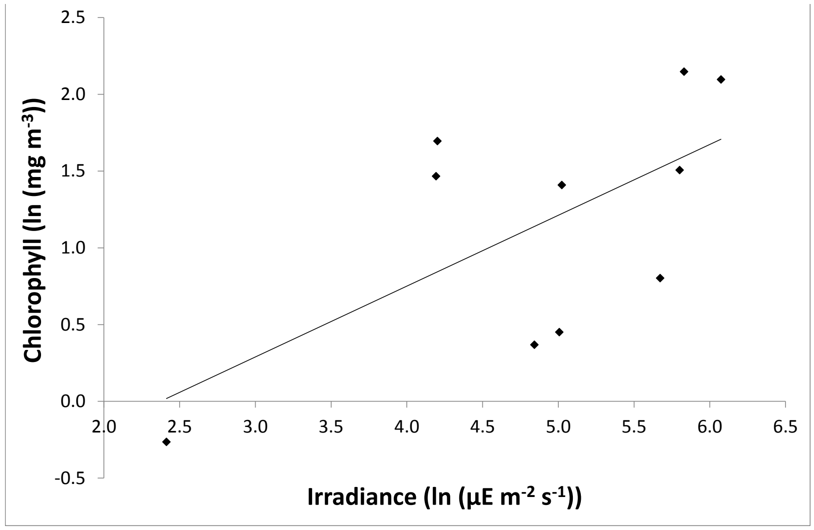


Figure 9.19: Maximum chlorophyll (ln mg m^{-3}) measured in the loch between April and October 2008-09 averaged between 3 and 12 metres plotted against the attenuation ((ln(μE m^{-2} s^{-1}) m^{-1}) averaged between 3 and 12 metres. $r^2 = 0.751$, $p < 0.005$.

April and October 2008-09. As has already been seen in figure 9.18 there is a good regression coefficient, $r^2 = 0.751$, between the two and this is significant $p < 0.005$. Although a correlation exists between attenuation and chlorophyll concentration it does not necessarily explain whether or not one is responsible for the other. However it seems reasonable to assume that as the density of phytoplankton increases it will absorb or scatter more of the light penetrating the surface.

Figure 9.20 shows the maximum chlorophyll concentration measured in the main basin of the loch plotted against the mean attenuation (K_D) values. In this case, K_D has been calculated by first determining the slope of the ln PAR values measured from a vertical profile at each sampling station and then taking the mean of the values from the different stations to achieve a mean K_D value for the main basin of the loch. The maximum chlorophyll concentration was calculated by taking the mean chlorophyll concentrations recorded between 3 and 12 metres at each sam-

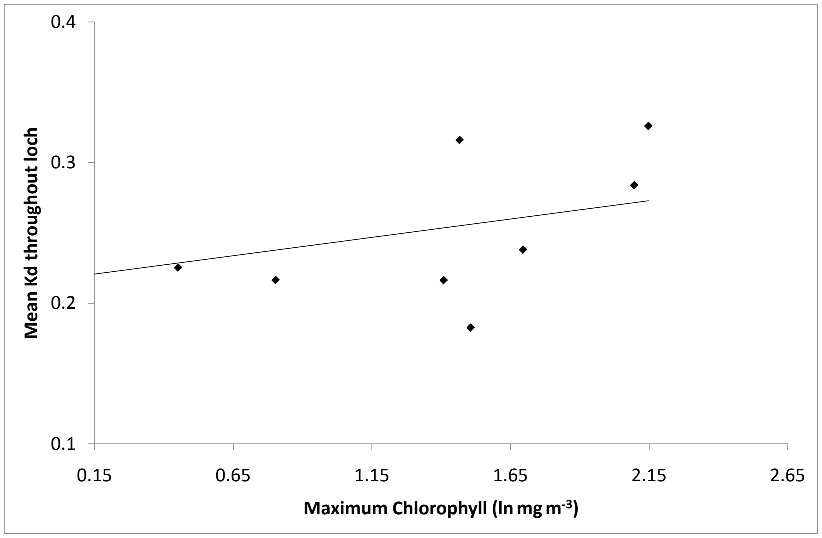


Figure 9.20: Maximum chlorophyll (ln mg m^{-3}) measured in the loch between April and October 2008-09 averaged between 3 and 12 metres plotted against K_D. Where K_D calculated by determining the slope of the ln PAR values over the depth of the entire water column, $r^2 = 0.179$, $p < 0.189$.

pling station and taking the one with the highest value. It is immediately obvious from the figure that the correlation is very slight. This may in part be because the light attenuation was calculated over the entire depth of the water column whereas much of the chlorophyll as well as the highest concentrations of CDOM would be expected to be contained within the stratified upper layer.

While the value for K_D will contain within it part of the attenuation due to CDOM and chlorophyll, for the most part it seems to be a measure of the attenuation by the water itself. Indeed Branco and Kremer (2005) found that in 40 out of 53 samples, collected at three locations over four years, there was no significant correlation between chlorophyll concentration and K_D values. This may have been, however, due partly to their choice of study sites. Cloern (1987) has reported that light attenuation in estuarine systems is strongly influenced by suspended particles in the water column. The systems studied by Branco and Kremer however, all exhibited low concentrations of suspended particles.

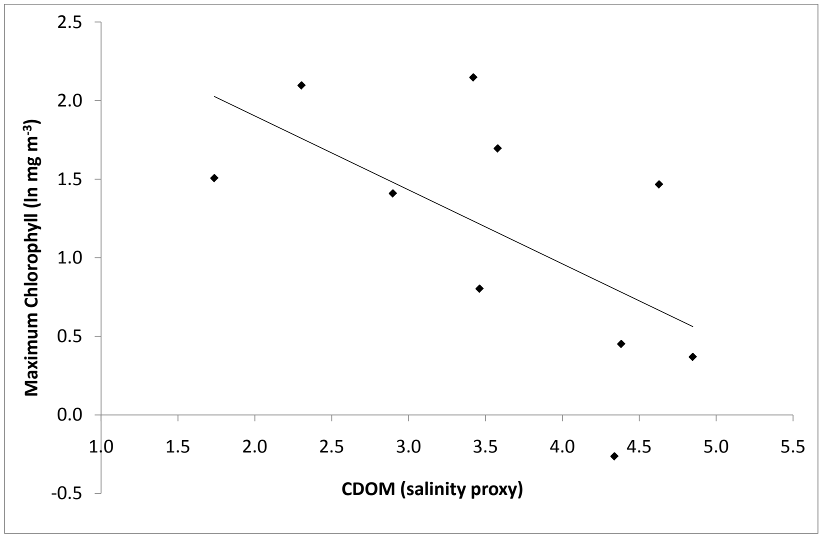


Figure 9.21: Maximum chlorophyll ($\log_{10}$ mg m^{-3}) measured in the loch between April and October 2008-09 averaged between 3 and 12 metres plotted against CDOM (salinity proxy) averaged between 3 and 12 metres. $r^2 = 0.367$, $p < 0.063$.

Nevertheless, Foden *et al.* (2008) studying various water bodies around the British Isles found a significant correlation between CDOM, suspended particulates (SPM) and K_D, calculating, in multiple regression models, that CDOM and SPM explained 94% of the variance in K_D. Devlin *et al.* (2009) also found that when attempting to predict K_D as a function of CDOM, SPM and chlorophyll, CDOM improved the fit slightly. They did however conclude, that the most accurate predictor of K_D in transitional waters was SPM.

The original premise was that CDOM in the loch was detrimentally affecting the growth of phytoplankton. Figure 9.21 shows the result of plotting the maximum chlorophyll observed in the loch averaged over the top 3-12 metres against the observed CDOM again averaged between 3 and 12 metres. A regression analysis shows that, although small, there is a negative relationship between the amount of CDOM measured and the concentration of chlorophyll observed, $r^2 = 0.367$. How-

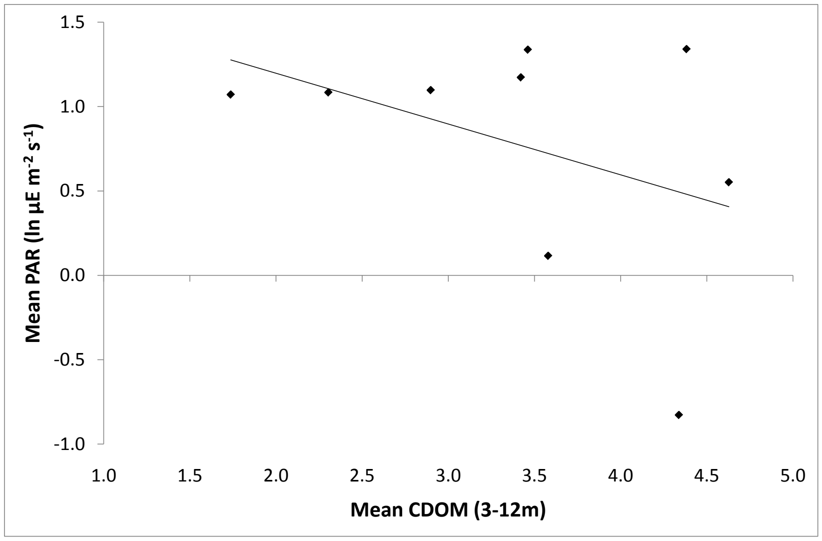


Figure 9.22: CDOM (salinity proxy) plotted against the mean ln PAR (μE m^{-2} s^{-1}) measured in the top 3 to 12 metres of the main basin of Loch Creran between April and October 2008-09, $r^2 = 0.167$, $p < 0.390$.

ever this is not significant $p < 0.063$. Again it cannot be inferred from this that CDOM concentrations cause the decrease in chlorophyll. CDOM has been calculated as a salinity proxy in other words an increase in CDOM means an increase in freshwater flowing into the loch, from both run-off and rainfall. It is possible that the associated drop in chlorophyll could be the result of increased flushing rates causing more of the phytoplankton in the loch to be washed out.

Figure 9.22 is the result of plotting CDOM against mean ln PAR in the top 3 to 12 metres of the main basin of Loch Creran between April and October 2008-09. Regression analysis indicates a very weak negative correlation, $r^2 = 0.167$ but this is not significant at $p < 0.39$. Does this indicate that, unlike other coastal areas and sea lochs (Branco and Kremer (2005), McKee *et al*. (2002), Vahatalo *et al*. (2005)) , CDOM has a limited role in Loch Creran?

CDOM is often known by its other name "*gelbstoff*" or yellow stuff. As such it forms a yellow filter in the water column that could be expected to predominantly filter blue light (McKee *et al.* 2002) particularly between 500 and 600 nm (Vahatalo *et al*. 2005) a part of the light spectrum that is particularly important for photosynthesis (Branco and Kremer 2005). The measurements made during 2008-09 did not differentiate between different wavelengths of light but included all visible light. Perhaps this partly accounts for the low correlation between light and CDOM observed in Loch Creran.

9.5 Discussion

This chapter has looked at the different climatic variables that can have an influence on the biological processes in Loch Creran. It has also, with regards to an increase in rainfall, considered some of the possible affects of changing CDOM levels in the loch.

Chapters 2 and 3 concluded that there have been significant changes in both the numbers of phytoplankton and the composition of the phytoplankton community in Loch Creran. These changes have been largely confined to the early part of the year and are particularly noticeable around the time of the spring bloom. Most of the changes found amongst the climatic variables, apart from water temperatures, also appear to occur during the early part of the year.

Water temperatures appear to have risen significantly throughout the year. This apparent rise could possibly be accounted for by a short term anomaly, by measuring errors or by improper calibration of the profiler employed. Nevertheless, various researchers have found a close correlation between sea temperatures and air temperatures ((Lolis *et al*. 2002; Bartzokas *et al*. 2003). Data from the BADC for mean surface temperatures recorded at Dunstaffnage indicate that there has been an upward trend in surface temperatures over the last 40 years. It seems likely then that the rise in water temperatures recorded in the loch are real.

Rising water temperatures could potentially have an effect on the herbivores resident in the loch, especially increases in water temperatures during winter and early spring. Although elevated temperatures often lead to terrestrial ecosystems experiencing an early onset of spring events (Schwartz *et al.* 2006)), this is often not the case in marine environments. Wiltshire *et al.* (2008) have observed that at Helgoland Roads and the German Bight raised temperatures have led to a delay in the onset of the spring bloom. They suggest this may be due to the survival of zooplankton grazers into the autumn and early winter which will lower the numbers of phytoplankton left to seed the spring bloom.

There is also the possibility that raised water temperatures will accelerate heterotrophic processes. In a system such as Loch Creran where the onset of the diatom spring bloom is light limited in the early months of the year this can potentially lead to a mismatch between the numbers of grazers and phytoplankton. In a series of mesocosm experiments Sommer *et al.* (2007) found a significant increase in the numbers of ciliates and other protozoans when water temperatures were raised coupled with an earlier onset of growth. Sommer *et al.* (2007) surmised that some of the increase in ciliate numbers was due to a reduction in the numbers of larger copepods that usually prey upon them, as a result of the higher temperatures.

In terms of wind speed, by comparing the climatology created for the 1970's with that for the 2000's it is apparent that the average wind speed has decreased. A careful examination of figure 9.4 indicates that the biggest change has occurred during winter and early spring. This lends support to the premise that wind speeds over Western Europe are affected by fluctuations in the North Atlantic Oscillation (Otterson *et al*. 2001; Hurrell 1995).

Wind speed is known to affect the degree of mixing in a water column (Gillibrand *et al*. 2005; Reynolds 2006) and the mixing depth strongly influences the potential for phytoplankton growth particularly when it exceeds the depth of the photic zone (Estrada *et al*. 1987) thereby reducing the time available for the phytoplankton to photosynthesise.

In addition, by inducing turbulence, the speed of the wind can also have an effect on the re-suspension of sediments, especially those in shallower water. This can potentially alter both the supply of nutrients and the number of resting diatom cells diffusing into the water column (McQuoid and Godhe 2004; Chen *et al*. 2009). Unfortunately the role resting cells play in providing an inoculum of phytoplankton in early spring has not been investigated in Loch Creran. The loch does however have a flushing time of between 3 and 12 days (Edwards and Sharples 1986). It appears from figure 9.4 that the biggest difference occurs during December and January and it is unlikely that resting cells re-suspended in the loch at this time would remain long enough to seed a spring bloom.

As wind speeds were found to be lower during 2004-08 than in the 1970's it would follow that wind induced turbulence during the 1970's would have been greater. Diatoms such as *Skeletonema* spp. the dominant species during the spring bloom are more opportunistic and better adapted to turbulent conditions in the water column than dinoflagellates (Margalef 1978; Reynolds 2006), quickly taking advantage of new inputs of nutrients. In chapter 4 it appeared that concentrations of DIP were lower than expected in Loch Creran however DIN and DIP in the loch are supplied by rivers and run-off into the loch and it seems improbable that a reduction in the number of re-suspension events can account for the deficit in the surface water.

Irradiance levels have also decreased significantly in the early part of the year and this most likely reflects the higher levels of rainfall experienced during 2004-09 which will have resulted in an increase in the amount of cloud cover.

In the past it was often assumed that phytoplankton are light limited during the winter and nutrient limited during the summer (Bernhard and Peele 1997; Roelke et al. 1999; Kocum *et al*. 2002), however the affect light limitation can have on the productivity of phytoplankton throughout the year is becoming recognised (McKee *et al*. 2002; Kocum *et al*. 2002). It is interesting to see that, between April and October, chlorophyll concentrations observed in Loch Creran appear to rise and fall in a similar way to the light levels (I_o) recorded immediately below the surface.

Perhaps most significant is the change that was found in both rainfall pattern and intensity. In a fjordic system such as Loch Creran the inflow of freshwater both from the rivers and from run-off is responsible for a large part of the stratification throughout the year. Given enough light, phytoplankton cells entrained into this buoyant surface layer will grow until limited by the lack of nutrients. But where do these cells come from? Some may survive, overwintering in the loch but given the flushing time of approximately 3 to 12 days (Edwards and Sharples 1986) this seems unlikely. Cells may also survive as resting spores in the loch sediments waiting to be re-suspended during turbulent conditions in early spring. However the abundance and viability of resting cells in the loch was not explored during this study. Finally they may be brought into the loch from the outside. The abundance of cells found in the Lynn of Lorn has not changed significantly (see chapter 2) since the 1970's and this seems a reasonable source of new cells coming into the loch.

This raises the question, if the number of phytoplankton cells in the Lynn of Lorn has not changed why are the numbers in the loch so low? As already mentioned above it may be that, as a result of higher water temperatures, the prevalence of herbivorous protozoans in the loch is greater than before. However, in terms of rainfall, the increases in the early part of the year, combined with the changes in the pattern of precipitation may be playing a large part in the changes that have been observed in the loch. Heavier rainfall will tend to mean more stratification, perhaps isolating the surface layer before enough inoculum has been entrained. Of more significance however is the likelihood that the sporadic but heavy rainfall, greater than three times the expected mean levels, in the early part of the year is having a strong effect on the flushing rates in the loch. This would result in an increased level of phytoplankton being washed out of the loch (Ross *et al.* 1994; Su *et al.* 2004; Lionard *et al.* 2008). Occurring at the same time as the expected spring bloom, this could result in a decrease in the intensity of the bloom.

In addition to an increase in flushing rate, more rainfall can also introduce more coloured or chromophoric dissolved organic material (CDOM). The presence of CDOM in the surface layers of coastal waters and sea lochs is sometimes overlooked and this is often the case when building models of the aquatic ecosystem. Many times attenuation is dealt with by linking it to the concentration of chlorophyll in the system and including a fixed value to represent background attenuation. Indeed this is the way that attenuation is modelled in the simple box model described in chapter 10.

Brought into the loch from run-off and river flow this CDOM will have a tendency to remain in the buoyant surface layer. There it will act as a yellow filter effectively absorbing light between 500 nm and 600nm. This an especially important part of the light spectrum for phytoplankton photosynthesis (Branco and Kremer 2005). Any increase in the concentration of CDOM, particularly during the early months of the year, could have a deleterious affect on the growth of the phytoplankton in the loch.

In conclusion Loch Creran appears to have experienced significant changes in the temperature, wind speed, irradiance and precipitation levels, particularly during late winter and early spring. These changes have led to alterations in the light climate in the loch and may be affecting the levels of turbulence. The timing of these changes corresponds to the timing of the changes to the phytoplankton community. It would seem reasonable to assume that at least some of the changes observed in the loch are the result of these changes in local weather patterns. It also appears that these changes may be associated with changes to the North Atlantic Oscillation. If this is indeed the case future studies of the phytoplankton community in Loch Creran may find that in times when the NAO index is positive the abundance of phytoplankton in the loch will increase. Whether this will return the loch to the conditions observed during the 1970's however, is not clear.

Chapter 10

Developing a model to investigate Loch Creran

10.1 Introduction

The possibility that phytoplankton growth in Loch Creran is being adversely affected by the input of antifouling paints, particularly zinc pyrithione and copper, has already been discussed (See chapter 10.8). While environmental toxicity tests can provide information on the likely effects that these compounds may have on marine organisms, the minute concentration levels at which they become damaging, can make them very difficult and expensive to isolate and analyse.

One potentially useful way around this problem is to create a mathematical model which can simulate, in a simplified fashion, the biological and hydro-dynamic features at work in the loch. By changing the various parameters used in such a model it can then be used to explore different scenarios, thereby giving an idea of the range of possible outcomes that may be expected. As such, it provides a useful tool, even if it is only used as an indicator pointing the way to more fruitful lines of research.

Indeed several models already exist to calculate the fate of chemicals transported into the marine environment and one of these; the comprehensive MAM-PEC model, developed by Delft Hydraulics and the Institute of Environmental Studies at Vrije Universiteit, Amsterdam, (Van Hattum *et al.* 2002), commissioned by the European Paint Makers Association (CEPE), was chosen. This well validated model (OECD 2005; EPA 2011) calculates the predicted environmental concentration of anti-fouling products in any one of five generalised environments. These include a shipping lane, a commercial harbour, a marina, the open sea and an estuarine harbour.

Although none of these pre-set environments exactly match the situation in Loch Creran where leisure boats sit at open moorings, the MAM-PEC model settings can be altered extensively to suit particular environmental conditions as well as a wide range of anti-fouling compounds . And as such it provides a useful tool to estimate the environmental concentration of anti-fouling products being emitted from the current number of leisure boats presently in use in the loch.

However for the purposes of this investigation it is necessary to know, not just the point concentration of these chemicals but the way in which they will be dispersed throughout the water column and how they will interact with the biological component of the lochs ecosystem. In order to determine this, a model is needed that can represent both the physical water exchanges and the biological processes taking place within and adjacent to the loch.

10.2 CSTT Model

The model used in this study is based on one developed by the Comprehensive Studies Task Team (CSTT) and further developed by Tett (2003) and Laurent (2006). The CSTT was set up to consider methods to aid in identifying water bodies that were vulnerable to ecological changes such as eutrophication under the Urban Waste Water Treatment Directive. Intended as a tool for ecological managers the model aimed for simplicity by incorporating, where possible, steady state conditions and by making the assumption that all of the dissolved available nutrient in the system is converted to phytoplankton chlorophyll.

Devised around a microbiological model the original included three pelagic compartments and six independent state variables (Lee *et al.* 2003). Essentially taking the microplankton compartment, including planktonic protozoa and bacteria (microheterotrophs) and photo-autotrophic phytoplankton and putting them into a single box. The mesozooplankton, rather than being treated as a dynamic compartment was symbolised as a grazing pressure (Tett 1987).

10.3 LESV Model

The LESV model (Portilla *et al.* 2009) is an enhanced version of the dCSTT model (Laurent 2006). It uses a physical system including surface, intermediate and deep water layers where processes are driven by tidal exchange, freshwater inflow and mixing by the wind.

It also includes two microplankton components; one autotrophic and one heterotrophic, each using a microbial loop and each including chlorophyll. The model also simulates the concentration of the nutrients nitrogen, phosphorus, silicon, dissolved oxygen and water transparency (Portilla *et al.* 2009) and links these to the production of chlorophyll by the use of yields (Gowen *et al.* 1992). The model has been validated for Loch Creran and has been found to be successful at predicting both the seasonal cycle of phytoplankton and the growth limiting nutrients.

10.4 The Microplankton Compartment

The microplankton compartment is comprised of all those pelagic micro-organisms less than 200μm. This includes photo-autotrophic cyanobacteria, diatoms, dinoflagellates, flagellates, etc as well as heterotrophic bacteria and protozoa such as cilliates, zooflagellates and heterotrophic dinoflagellates (Tett 1987). Lee *et al.* (2003) points out that this is a different description of microplankton than that proposed by Sieburth (1979) who drew a line between microplankton, picoplankton and nanoplankton. Tett's insight (Tett and Wilson 2000) was to see the microplankton as a soup of chloroplasts and microchondria which, through photosynthesis, convert light to energy and use it to drive metabolism. Nutrients either enter this soup from external sources or are recycled through the metabolic activities of the heterotrophs (See figure 10.1 below for a summary).

In this view any organic material derived from photosynthesis has to meet the requirements of phytoplankton, protozoa and bacteria and photo-autotrophically assimilated nutrients have to be distributed (by consumption) between heterotrophs. In practical terms this means that the yield of chlorophyll in situ will be less than that determined experimentally in mono-cultures of algae (Tett 2010, unpublished). In other words the microplankton model describes autotrophic and heterotrophic

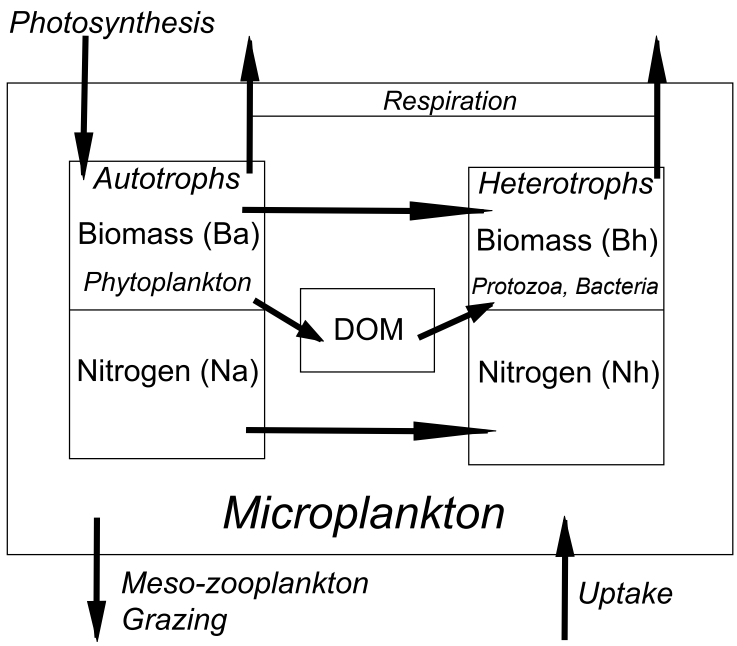


Figure 10.1: A diagram of the microplankton box and the processes taking place within. B and N represent biomass and nitrogen respectively. Nutrients pass into the compartment through uptake at rate $u_a(S) \cdot B_a$. Losses from the box are represented through grazing (G) at rate: G·B or G·N. Photosynthesis by the autotrophs is at rate: $\alpha \cdot I \cdot X$ where X = chlorophyll and I = irradiance. The diagram was redrawn from Lee *et al.* (2003).

processes rather than autotrophic and heterotrophic organisms (Lee *et al.* 2003). In this model these processes are dealt with by the inclusion of the parameter η which is defined as the ratio of the microheterotrophic to autotrophic biomass (B):

$$\eta = \frac{B_h}{B_a + B_h} \tag{10.1}$$

where the subscripts a and h represent autotrophs such as phytoplankton and heterotrophs respectively. It should be noted that in the version of the model described the value of η used remains constant throughout the simulation. This is obviously a gross simplification of the real system in which η would be expected to vary throughout the course of the year, peaking during the summer months. It is also assumed that organic matter, which, due to metabolic processes, may be eliminated by phytoplankton or which may escape as a result of sloppy feeding by heterotrophs is quickly re-assimilated by bacteria and remains within the microplankton. A similar assumption is made regarding heterotrophic excretions of inorganic nutrients which are assumed to be rapidly assimilated by autotrophs. The model estimates phytoplankton growth on a daily basis so assuming that the turnover times for these processes is less than a day allows them to be ignored (Lee *et al.* 2003).

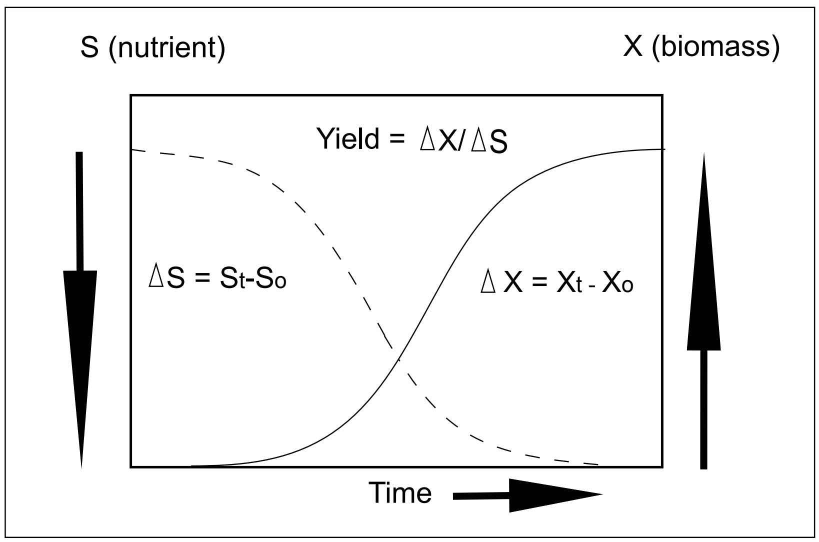


Figure 10.2: Diagram illustrating the idealised behaviour of a nutrient (S) and a population of phytoplankton (X) growing in a batch culture. Figure redrawn from Tett (2010).

10.5 Yield

As mentioned in chapter 1, Justus von Liebieg, in 1885, popularised a principle first developed by the German botanist Carl Sprengel, (Jungk 2009) that later became known as the *Law of the Minimum*. This proposed that the yield from a crop was dependent on the availability of the required nutrient in shortest supply (see figure 10.2). When grown in culture containing a fixed concentration of nutrients, algae follow a logistic growth curve initially growing exponentially when nutrients are freely available but approaching zero as these become depleted. Assuming that all of the available nutrient in the system is turned into phytoplankton chlorophyll Gowen *et al*. (1992) suggested the following equation for calculating the biomass of phytoplankton resulting from an input of nitrogen:

$$X_{max} = X_o + q \times S_0 + \frac{s_i}{(E \times V)} \tag{10.2}$$

where q represents the yield and was calculated by the regression of chlorophyll concentrations against nitrate concentrations obtained from a survey of nitrate concentrations in Scottish sea lochs (Gowen *et al*. 1992). X_{max} gives an estimate of the maximum concentration of chlorophyll obtainable under optimal conditions and as such is unlikely to be exceeded. S_o represents the background concentration of a given nutrient, s_i represents local inputs of the nutrient and E and V represent the daily exchange rate of the water body with the open sea and the volume of that water body respectively (Tett 2010).

10.6 Physical model

Providing an introduction to the Equilibrium Concentration Enhancement Model (ECE), Tett *et al*. (2008), consider the case of a substance (S) dissolved in a water body. Regardless of whether it is a nutrient or an anti fouling compound its concentration will change according to the equation:

$$\frac{\delta S}{\delta t} = -\nabla\varphi_S + \beta_S + \Gamma_S \tag{10.3}$$

Where symbols are explained in Table 10.1

Table 10.1: Symbols used to describe physical processes acting in the loch.

Symbol	Representing	Units
S	State variable - concentration of substance (S)	mmol m^{-3}
S_{eq}	Concentration of substance S at equilibrium	mmol m^{-3}
φ_S	Physical transport flux vector (advection and diffusion)	$m^{-3}d^{-1}$
β_S	Sum of biological and chemical sources and sinks	mg m^{-3}
Γ_S	Local inputs of substance S	mmol m^{-3}

So, for example, If S represents the concentration of a nutrient, such as nitrate, present in a body of water with a volume of V m^3 and this water body exchanges some of its water at a fixed daily rate (E) with an adjacent body of water containing nitrate at concentration S_o then the divergence term ∇_S which in this case only has one cross boundary flux can be solved by:

$$\nabla_{\varphi S} = E(S - S_o) \tag{10.4}$$

Where, E represents the daily rate of exchange, (see below for an explanation). So, if the assumption is made that there is no biological input then $\beta_S = 0$, and the input of an antifouling compound from a series of moorings is S_{AF} mmol m^3d^{-1} spread uniformly through the water body then $\Gamma_S = \frac{S_{AF}}{V}$ and equation 10.3 becomes:

$$\frac{dS}{dt} = -E(S - S_o) + \frac{S_{AF}}{V} \tag{10.5}$$

Assuming a steady state then;

$$S_{eq} = S_o + \frac{S_{AF}}{EV} \tag{10.6}$$

Tett *et al*. (2008) refer to the right hand term $\frac{S_{AF}}{EV}$ as the equilibrium concentration enhancement (ECE) and in this case it provides an indication of the ecological load placed on the loch by an anti fouling compound. However this equation only represents a steady state whereas the input of nutrients and anti fouling products into Loch Creran will tend to vary over time. If these variations in inputs are to be accounted for then the dynamic equation 10.6, referred to by Tett *et al*. (2008) as a seasonal ECE model provides a better option to represent the conditions in Loch Creran.

The situation is further complicated by the input of freshwater from several rivers into the Loch, the foremost of these being the river Creran and by the presence of a significant biological component in the form of phytoplankton. One simple way to model this situation (see figure 10.3.) is to consider the loch as a box with fixed volume (V), and parameterise the two physical processes; the freshwater inflow (F), simply the summation of all freshwater inputs to the loch and the exchange rate (E), which, represents the instantaneous probability averaged over a full tidal cycle, that an arbitrary parcel of water from a water body containing a nutrient at concentration S will be exchanged for a similar parcel of water from an adjacent water body with the same substance at concentration S_o, (Portilla and Tett 2006). In other words, the amount of substance S that leaves the loch each day is equal to E.V.S and this amount is replaced by (E - $\frac{F}{V}$)$.V.S_o$ from the sea plus F.S_f from the river. As Laurent *et al.* (2006) point out however, these are actually only representative of the instantaneous rates. Nevertheless Tett (1986), recorded salinity and river flow for several Scottish lochs and this empirical data can be used to calculate E from the well established steady state equation:

$$E = \frac{F}{V} \times \frac{C}{(C_o - C)} \tag{10.7}$$

Where C represents the salinity in the loch and C_o represents the salinity in the open sea.

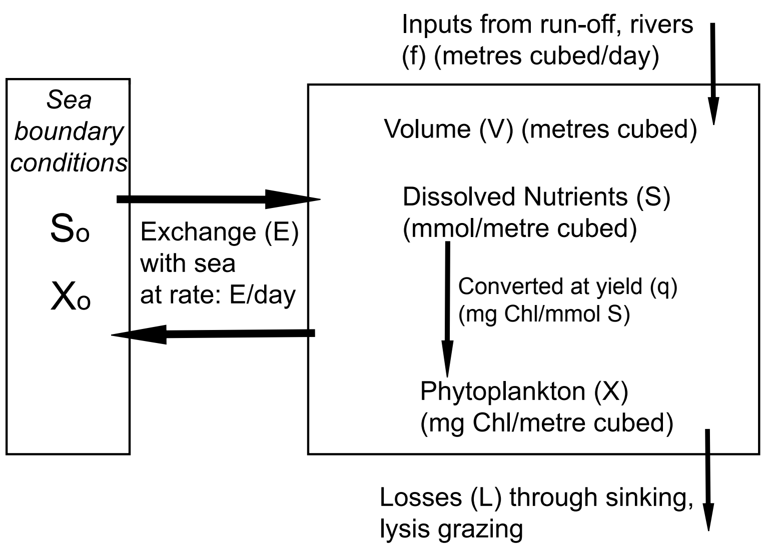


Figure 10.3: Diagram illustrating the processes modelled in the Single Exchange Box Model, Re-Drawn from Tett, (2006)

This raises an interesting point worth noting. While many of the parameterisations used in the box model to describe physical and biological processes may appear simplistic they are however based on a great deal of empirical data as well as results from more complex models. The argument for simplicity lies in the knowledge that while several such intricate models exist, it can be difficult to redefine the necessary parameters and state variables required if they are to be used to describe alternative locations. The level of computation they employ can also make them rather obscure and difficult to implement for any but experts.

Returning to the box model and expanding equation 10.7 above to include the input from rivers gives;

$$\frac{dS}{dt} = (E - \frac{F}{V}) \times \mathrm{S}_o + \frac{F}{V} \times \mathrm{S}_f - E \times \mathrm{S} \qquad (10.8)$$

Where symbols are explained in table 10.2.

Table 10.2: A List of the parameters used in the physical exchange model.

Symbol	Representing	Units
E	Exchange rate	d⁻1
F	River flow into box	m^3d^{-1}
V	Box Volume	m^3
S	Concentration of substance in the box	mmol m^{-3}
S_o	Concentration of substance in the sea at boundary	mmol m^{-3}
S_f	Concentration of substance in river	mmol m^{-3}

Equation 10.8 then gives a useful representation of the physical exchange processes at work in Loch Creran and will allow the concentration of nutrients in the loch arising from river input and exchange with the sea to be calculated. However it is possible that internal processes within the loch may also alter the nutrient load, such as inputs from a fish farm, or the presence of organisms in the loch, for example phytoplankton which may act as either a source or a sink of a particular nutrient. And so it is necessary to include two further terms into the physical exchange model Γ_S to take account of any additional inputs to the nutrient load in the loch, and β_S

to represent the biological processes of interest. These additions give equation 10.9 below;

$$\frac{dS}{dt} = (E - \frac{F}{V}) \times \mathrm{S}_o + \frac{F}{V} \times \mathrm{S}_f - E \times \mathrm{S} + \beta_{\mathrm{S}} + (\frac{\Gamma_{\mathrm{S}}}{V}) \qquad (10.9)$$

Where symbols are explained in table 10.3

Table 10.3: Terms introduced in equation 10.9.

Symbol	Representing	Units
β_{S}	Biologically derived source or sink of substance Concentration	concentration d^{-1}
Γ_{S}	Local input of substance	amount d^{-1}

The biological term β_{S} is a non conservative variable, which is introduced because particular nutrients present in the water column will be consumed or deposited by marine organisms. In the case of nutrients such as nitrate, phosphate and silicate they will be assimilated by the phytoplankton during their growth. The efficiency by which the phytoplankters use these nutrients to produce biomass (a state variable measured as the concentration of chlorophyll (X)(mg m^{-3})) can be assessed and used to estimate the amount of phytoplankton growth that can be expected for a given amount of nutrient, in other words the yield (q), Gowen *et al.* (1992). The non conservative term β_{X} representing the flux in chlorophyll concentration can be determined by:

$$\beta_{\mathrm{X}} = \mu.(I, S) \times \mathrm{X} - L \times \mathrm{X} \qquad (10.10)$$

Where μ.(I, S) is the growth rate day^{-1} as a function of irradiance levels (I) and nutrient concentration (S) and L represents the losses due to grazing by pelagic zooplankton and the benthos or through sinking. (Laurent *et al.* 2006). Phytoplankton growth is dependent on there being sufficient concentrations of the necessary nutrients and sufficient light (PAR). The growth rate then becomes a threshold function of PAR and the dissolved nutrients;

$$\mu(\mathrm{I,S}) = min\{\alpha.(I - I_C), \mu_{max}(\frac{N_{OS}}{N_{O_{kS}} + N_{O_S}}),\\ \mu_{max}(\frac{P_{O_S}}{P_{O_{kS}} + P_{O_S}}), \mu_{max}(\frac{Si_{O_S}}{Si_{O_{kS}} + Si_{O_S}})\} \tag{10.11}$$

Where symbols are described in table 10.4

Table 10.4: List of parameters used in the biological component of the model.

Symbol	Representing	Units
μ_{max}	Maximum Growth rate	d^{-1}
N_{OS}	Nitrates	mmol m^{-3}
P_{OS}	Phosphates	mmol m^{-3}
Si_{OS}	Silicates	mmol m^{-3}
N_{OkS}	Half saturation constant for Nitrates	mmol m^{-3}
P_{OkS}	Half saturation constant for Phosphates	mmol m^{-3}
Si_{OkS}	Half saturation constant for Silicates	mmol m^{-3}

In other words the growth rate of phytoplankton can not exceed the rate determined by the nutrient, or light, in least supply. However, as the phytoplankters assimilate nutrients the concentration of chlorophyll will vary and this will have an effect on the level of nutrients in the loch. The non conservative equation to describe the concentration flux of these nutrients is;

$$\beta_\mathrm{S} = \frac{-\mu(I,S).X}{q_\mathrm{S}} + \frac{L.X}{q_\mathrm{S}} \tag{10.12}$$

Where q represents the yield of chlorophyll from a nutrient in mg chl (mmol S)$^{-1}$ (Gowen, *et al.*, 1992), and S represents nitrate, phosphate or silicate. The use of q in this equation necessitates making two assumptions; firstly that all forms of an assimilated nutrient will have the same effects on the growth of phytoplankters (Tett and Droop, 1988) and secondly that the nutrient will be proportionately and constantly partitioned between phytoplankters, grazers and detritus and will not change significantly during for example an algal bloom, (Gowen, *et al.*, 1992).

10.7 Irradiance

The original CSTT model incorporated the following linear equation to calculate light limited growth:

$$\mu(I) = \alpha(I - I_{\mathrm{C}}) \tag{10.13}$$

This equation was devised to calculate $\mu(I)$ for phytoplankton growing in water bodies exhibiting high levels of turbidity or where the water column was relatively well mixed. It treats photosynthetic efficiency (α) as a constant and I is taken as the 24 hour mean photosynthetically active radiation (PAR). It also makes the assumption that the semi saturation constant I_k is larger than I and that "all photons are equal" (Tett 2010) regardless of the conditions. For a list of the parameters used in this section please see table 10.5.

This may not always be the case in well lit surface waters where phytoplankton photo-systems can be saturated for a large part of the day and so it was felt that the way that light was modelled should be modified to take this into account.

Tett (1990) derives an equation for light saturated growth beginning with one of the simplest equations for calculating photosynthesis in high light levels:

$$p^x(I) = p^x_{max} \cdot \frac{I}{I + I_k} \tag{10.14}$$

where I is the daily irradiance, α represents photosynthetic efficiency, the superscript x represents chlorophyll and I_k represents the half saturation value for irradiance.

Microplankton growth μ(I) under light limited conditions is photosynthesis minus respiration (r):

$$\mu(I) = p(I) - r \tag{10.15}$$

and microplankton photosynthesis is:

$$p(I) = p^x(I) \cdot^x q^B \tag{10.16}$$

where ${}^x q^B$ represents the chlorophyll:carbon ratio for microplankton and is given by:

$${}^x q^B =^x q^B_a \cdot (1 - \eta) \tag{10.17}$$

${}^x q^B_a$ represents the chlorophyll:carbon ratio for autotrophs and η represents the heterotrophic fraction of the microplankton biomass. To calculate a value for respiration the primitive autotrophic and heterotrophic microplankton parameters r_o

and b representing the basal and growth components respectively are included giving:

$$r = r_o + b \cdot \mu(I) \tag{10.18}$$

Tett (1990) then combines equations 10.15 and 10.18 to obtain:

$$\mu(I) = \frac{p(I) - r_o}{1 + b} \tag{10.19}$$

and combines this with equations 10.14 and 10.16 to obtain:

$$\mu(I) = \frac{p^x_{max} \cdot \frac{1}{I + I_k} \cdot^x q^B - r_o}{1 + b} \tag{10.20}$$

For well illuminated surface waters the assumption is that irradiance (I) >> than the half saturation irradiance (I_k) giving:

$$\mu(I) \rightarrow \mu(I)_{max} = \frac{p^x_{max} \cdot^x q^B - r_o}{1 + b} \tag{10.21}$$

and this allows Tett and Lee (2003) to approximate equation 10.20 by the bi-linear equation:

$$\mu(I) = min\,\{\alpha \cdot (I - I_c), \mu(I)_{max}\} \tag{10.22}$$

However as the concentration of phytoplankton increases so does the possibility that cells will begin to shade one another and thus reduce the overall photosynthetic efficiency of the population. To take account of this the model uses a modified formulation of α given by:

$$\alpha = \frac{\alpha^{-}}{(1 + b)} \tag{10.23}$$

where:

$$\alpha^{-} = k \cdot \phi \cdot (m \cdot a^{*}_{PH}) \cdot^{x} q^{N}_{a} \cdot Qmax_{a} \cdot (1 - \eta) \tag{10.24}$$

(Tett 1990), and the slope of microplankton respiration on microplankton growth rate b is found by:

$$b = b_a \cdot (1 + b_h \cdot \eta) + (b_h \cdot \eta) \tag{10.25}$$

The compensation depth I_c (see table 10.5 for a list of the parameters) i.e. that depth where phytoplankton photosynthesis is equal to its respiration, is given by:

$$I_c = I^{-}_{c} \cdot (1 + b) \tag{10.26}$$

where:

$$I^{-}_{c} = \frac{r_o}{\alpha^{-}} \tag{10.27}$$

and the microplankton basal respiration rate r_o is given by:

$$r_o = r_{oa} \cdot (1 + \eta) + r_{oh} \cdot \eta \cdot (1 + b_a) \tag{10.28}$$

The terms r_{oa} and r_{oh} represent the basal respiration rates for autotrophs and heterotrophs respectively and were determined from experiments carried out on algal cultures (Lee *et al*. 2003).

As light penetrates the sea it is quickly lost due to absorption and scattering by the water molecules and by particles, including phytoplankton, in the water column. This decrease with depth is more or less exponential and can be described by the Beer-Lambert Law. Where I_h represents the irradiance at a depth h, giving:

$$I_{\mathrm{h}} = I_o \cdot \mathrm{e}^{(-k_D.h)} \tag{10.29}$$

To calculate the mean irradiance (I_{mean}) in a water column of layer depth h the model expands this expression giving:

$$I_{mean} = \mathrm{m} \cdot I_o \cdot \frac{(1 - exp^{(-k_D \cdot \mathrm{h})})}{(k_D \cdot \mathrm{h})} \tag{10.30}$$

where the attenuation K_D is calculated during a model run by modifying K_D^{θ} which represents the background attenuation.The value for K_D^{θ} was derived from *in situ* photosynthesis experiments carried out in loch Striven in 1927 by Marshall and Orr, (Tett 1990).

$$K_D = K_D^{\theta} + (m \cdot a_{PH}^{*} \cdot X) \tag{10.31}$$

The term m is a factor to compensate for losses in polychromatic light near to the sea surface. This factor is dependent on the method used to calculate the minimum value of K_D and was found to vary from 0.34 to 0.39 in turbid coastal and fjordic

Table 10.5: List of parameters used in the light component of the model.

Symbol	Representing	Units
I_o	PAR flux density below surface	$\mu E m^{-2} s^{-1} d^{-1}$
h	Depth of the water layer	m
K_D	Attenuation coefficient	m^{-1}
K_D^{θ}	Background Attenuation coefficient	m^{-1}
m	Correction for loss of polychromatic light	ratio
I_{mean}	Mean Surface irradiance	$\mu E m^{-2} s^{-1} d^{-1}$
I_c	Compensation Irradiance	$\mu E m^{-2} s^{-1} d^{-1}$
α	Photosynthetic efficiency	$d^{-1}(\mu E m^{-2} s^{-1} d^{-1})^{-1}$
r_o	MP basal respiration rate	d^{-1}
r_{oa}	autotroph basal respiration rate	d^{-1}
r_{oh}	Heterotroph basal respiration rate	d^{-1}
b	slope of MP respiration rate	ratio
b_a	slope: autotroph respiration/growth rate	ratio
b_h	slope: heterotroph respiration/growth rate	ratio
q^a_{max}	Maximum autotroph nitrogen content	mmol N (mmol C)$^{-1}$
a^*_{PH}	Absorption cross section	m^{-2}(mg Chl)$^{-1}$
${}^x q^N_a$	Chlorophyll:Nitrogen ratio (autotroph)	mg Chl (mmol N)$^{-1}$
η	Heterotroph fraction	ratio
X	Chlorophyll:Carbon ratio	mg Chl (mmol C)$^{-1}$
ϵ	Attenuation cross section	m^{-2}/(mg Chl)
L	Loss rate	d^{-1}
m_2	loss of polychromatic light correction	ratio
m	1/Mean cosine downwelling photons	m^{-1}
k	Units conversion factor	d^{-1}mmol (nmol)$^{-1}$
ϕ	Quantum Yield	nmol $O_2 \mu E^{-1}$

waters, (Tett 1990).

10.8 Anti fouling Compounds

As mentioned above the MAM-PEC model, (Van Hattum *et al.* 2002) outputs the predicted environmental concentration of a given anti fouling compound. However this concentration refers to a localised area such as a harbour or a marina. To determine the effect these compounds will have on the phytoplankton in Loch Creran it is necessary to establish their concentration in the loch as a whole. This can be achieved by treating the antifouling compound in the same way as a dissolved nutrient, and inputting the values gained from the MAM-PEC model into the exchange model.

Once the environmental concentration (PEC), of the anti fouling compound has been predicted for the loch the model compares the ratio of this value to the environmental concentration of the compound found to have no effect on marine organisms (PNEC), a value that has been established through toxicological testing, to determine the risk quotient (RQ);

$$RQ = \frac{PEC}{PNEC} \tag{10.32}$$

Devilla *et al.* (2005) and Macedo *et al.* (2008), studying the effects of anti fouling compounds on phytoplankton found that they acted by impairing their photosynthetic efficiency thus impairing their ability to grow. The model therefore determines the RQ for a particular anti fouling compound. If the ratio is found to be less than 1 the environmental risk is assumed, by the model, to be negligible and no action is taken. If however the RQ is found to be greater than 1 then the model will reduce the value of the photosynthetic efficiency α in equation (10.23). As each species of phytoplankton varies in its sensitivity to different anti fouling compounds it is necessary to alter the amount by which photosynthetic efficiency is reduced and the model carries this out via a series of switches that can be set manually. Although the effect of an anti-fouling compound in the water column would most likely follow a typical dose response curve (Cullen and Lesser 1991) for simplicity and to err on the side of caution, the model assumes a simple cut off point based on the RQ value.

It proved difficult to find relevant toxicity studies in the literature for the various anti-fouling compounds available. It was decided therefore to introduce a range of uncertainty factors into the calculation of the RQ value. These were made available to the user through a set of drop down menus and effectively decreased the PNEC value. This had the benefit of making the model more conservative given the range of toxic concentrations found in the literature and had the added benefit of introducing the concept of scientific uncertainty to the stakeholders.

10.9 Model Implementation

The model, based on the CSTT assimilative capacity model for eutrophication (Tett et al. 2003) has been implemented in the EXTENDSIM 7 simulation software package supplied by Imagine That Inc., California, U.S.A. The author enhanced the existing model by adding a compartment to estimate yield and growth rates from silicon, a compartment to calculate the effects of anti-fouling compounds on phytoplankton growth rates an integrated economics model and an interactive user interface. Due to the presence of switches in the model the equations were calculated using Euler's method with a time step of 0.125 days, a time period that proved to give the best compromise between model accuracy and computational demand. Boundary conditions have been obtained from various sources; Hydrological data for river flow was taken from Tyler, (1983). Nutrient concentrations from field data collected from the Greag Isles were obtained from Laurent *et al.* (2006) and for 1975 from Jones, (1979). Data for the mean Irradiance over Loch Creran for 1975 was taken from Jones, (1979), while data for 2008 was supplied by the British Atmospheric Data Centre (BADC). Values for the expected reduction in photosynthetic efficiency were taken from Devilla *et al.* (2005). The model contains several state variables; chlorophyll concentration, concentration of phosphates, nitrates and silicates and the concentration of anti fouling compounds. For a list of the state variables and parameters used in the model see table 10.6.

10.10 Sensitivity Analysis

During the conceptual modeling phase information on the imagined functioning of a system is collected and eventually used to formulate the equations that will be used to construct a mathematical model. Unfortunately regardless of the time and effort spent gathering this information there will always be an inevitable level of uncertainty associated with the output from any model. This uncertainty can arise from several causes. These can include; sampling errors, errors in measurements, lack of information and a poor or partial understanding of the various drivers and forcing mechanisms acting either on the system as a whole or on its various subsystems. All of these can lead to a lack of trust in the output of a model. In an attempt to increase confidence in a model an analysis of the sensitivity of various parameters to changes in their value is carried out. In this way the parameters that have the biggest effect on system dynamics can be identified and a better understanding of the importance and relevance of the various inputs can be gained. In addition to gaining trust in the model this process can also increase our knowledge and understanding of the system, often revealing interesting insights into the actual way it seems to function.

Sensitivity analysis was carried out using a one factor at a time approach (OAT) (Campolongo *et al.* 2007), varying each parameter by ± 50% of the initial parameter value. The results at each time step were then subtracted from the original results and standardized (Kohberger *et al.* 1978). The effects of changing a specific factor are assessed by using an indicator μ to determine the overall influence of that factor on the models final output (Campolongo *et al.* 2007; Portilla *et al.* 2009). A high value of μ indicates that the input factor has a high degree of influence on the model results. Each parameter Xi where i = 1,...,K, was varied by ± 50% of the initial parameter value. So that for any given value of X, the effect of the ith impact factor is defined as:

$$di = \frac{(f(X + \Delta Xi) - f(X))/f(X)}{\Delta Xi/Xi} \tag{10.33}$$

However the distribution of values of di may include both positive and negative values which would have a tendency to cancel each other out and produce a low value of μ. To overcome this Compolongo *et al.* (2007) suggested using the value μ* which is the value of the mean of the distribution of the absolute values (Brito 2010).

The sensitivity analysis of the phytoplankton growth model was carried out with regards to the chlorophyll production. As can be seen from figures 10.4 and 10.5, where the parameters with the biggest impact are distinguished by the darkest colours, variations in most of the parameters had very little impact on the model. However the model did respond to changes in both the loss rate and the exchange rate. This suggests that the model is largely driven by changes to the boundary conditions. To examine this possibility a second sensitivity analysis was carried out on those parameters that were found at the system boundary. As can be seen in figure 10.5, the model was found to be most sensitive to the levels of chlorophyll present in the open sea.

A further analysis was carried out regarding uncertainty in the range of parameters found in the literature in particular widely varying estimates of the exchange rate between the loch and the open sea and in the level of losses which ranged between 10% and 25%, as can be seen in figure 10.6. The model is sensitive to changes in both these variables.

As mentioned earlier the model is built around a representation of the loch as a single box and as such it disregards the diffusion of nutrients, mineralized in the deeper layers, into the upper layer of the loch. However given that the model is only concerned with capturing the response of phytoplankton in the upper layer to the presence of anti-fouling compounds this simplification seems justified. The model also makes the assumption that all of the nutrient available in this upper layer is converted to chlorophyll and again, erring on the side of caution, this simplification seems reasonable.

Although sensitivity analysis was not carried out on the nutrients present in the system they are important state variables in the phytoplankton growth model. While

Variable/parameter	
Exchange rate E	
Yield from Nitrogen (q_n)	
Yield from Phosphate (q_p)	
Yield from silicate (q_{si})	
layer depth (h)	
Loss rate (L)	
Autotroph basal respiration rate (r_o)	
Heterotroph basal respiration rate (r_{Oh})	
slope autotroph on heterotroph respiration (b_a)	
slope heterotrophic respiration on algal respiration (b_h)	
Photosynthetic efficiency (α)	
Attenuation coefficient (K_D)	
Quantum yield (ϕ)	
Absorption cross section (a^*_{PH})	
Attenuation cross section (Є)	
Background Attenuation coefficient ($K^{Ø}_{D}$)	
Chl:Nitrogen (algae) ratio ($^{X}q^{N}_{a}$)	

μ*	
	0.01-0.05
	0.05-0.1
	0.1-0.15
	0.15-0.2
	0.2-0.25
	0.25-0.3
	0.3-0.35
	0.35-0.4
	0.4-0.45
	0.45-1.00

Figure 10.4: A sensitivity analysis was carried out on the the parameters and variables listed above to determine how changes to these values would impact on the growth of phytoplankton measured as the concentration of chlorophyll (mg/m^3). While most of these terms are parameters and remain constant for a single run of the model, a few are calculated during a single model run and should therefore be regarded as variables. A high value of μ^* indicates that the input factor has a high degree of influence on the model results.

historic data of nutrient concentrations in the loch was available to carry out a hind cast of the model it was not so easy to find data on the boundary conditions, particularly for the hind cast. In the case of dissolved inorganic nitrogen (DIN) the data used to drive the model was derived from a ”climatology” of nutrient levels extrapolated from observations taken over several years and as such there is the possibility that short term changes in nutrient levels will have been smoothed out. A similar solution was used to fill any gaps in the silicate data.

Variable/parameter	
River flow (F_r)	
Diss Inorganic Nitrogen in sea (DIN_s)	
Diss inorganic phosphate in sea (DIP_s)	
Diss inorganic silicate in sea (Si_s)	
Chlorophyll conc in sea (Chl_s)	
Diss Inorganic Nitrogen in river (DIN_r)	
Diss inorganic phosphate in river (DIP_r)	
Diss inorganic silicate in river (Si_r)	

μ*	
	0.01-0.05
	0.05-0.1
	0.1-0.15
	0.15-0.2
	0.2-0.25
	0.25-0.3
	0.3-0.35
	0.35-0.4
	0.4-0.45
	0.45-1.00

Variable/parameter	
Exchange rate (E)	
Loss rate (L)	

μ*	
	0.35-0.4
	0.4-0.45
	0.45-1.00

Figure 10.5: Results of a sensitivity analysis carried out on those parameters found at the boundaries of the system. A high value of μ^* indicates that the input factor has a high degree of influence on the model results.

Variable/parameter	
Exchange rate (E)	
Loss rate (L)	

μ*	
	0.35-0.4
	0.4-0.45
	0.45-1.00

Figure 10.6: When attempting to parameterise these variables the literature yielded a wide range of values. This uncertainty was analysed in the same way as those in figures 10.4 and 10.5 where each variable was altered by ± 50% of the initial parameter value. Both variables were found to have high values of μ^*.

10.11 Model Calibration

The model was based on the existing dCSTT model (Laurent *et al* 2006.) Although several changes, including the incorporation of a new light component, silicates and the introduction of anti-fouling compounds had been made, the boundary conditions and the various parameters used to run the original dCSTT model were available in the literature. This allowed a reasonable comparison to be made between the different models. Further, historic data from the 1970's was available including observations of chlorophyll, nitrogen and phosphorus concentrations in Loch Creran. This made it possible to construct an envelope encompassing the 5th and 95th percentile of the available data. Given the large amount of inter-annual variability of chlorophyll and nutrient concentrations observed in Loch Creran it is difficult to calibrate the model against any single year and achieve meaningful results. Instead it seemed more appropriate to compare the model simulations against the envelopes created from all of the chlorophyll and nutrient observations made during the 1970's. In this way model results that lay within the envelope could be accepted as providing a reasonable simulation of phytoplankton growth and nutrient concentrations in the loch. The data used to create the envelopes came from Cottrell *et al* (1973) and from Jones (1979) PhD thesis. The data was extracted by a MATLAB script (HPLP4Nb) written by Paul Tett which, first sorted the data by the day of the year into blocks of 10 or 20 values, before creating the 5th and 95th percentile envelopes.

Figure 10.7 shows the chlorophyll concentration (mg/m^3) in the loch predicted by the single box model and plotted against the envelope. The initial conditions were set according to data available for the 1970's. Where data was unavailable it was replaced by suitable values generated statistically. While, apart from a prediction of higher growth in the late autumn, the output from the model lies largely within the envelope, growth during the spring bloom appears to be delayed. The decrease in chlorophyll after the bloom also appears less severe than actual observations made during 1975. Represented by black crosses, these were made by Tyler (1979) and are an average of measurements made between 0 and 11 metres between January and December in Loch Creran. The frequency of sampling varied throughout the year with the highest frequency (weekly samples), occurring during March.

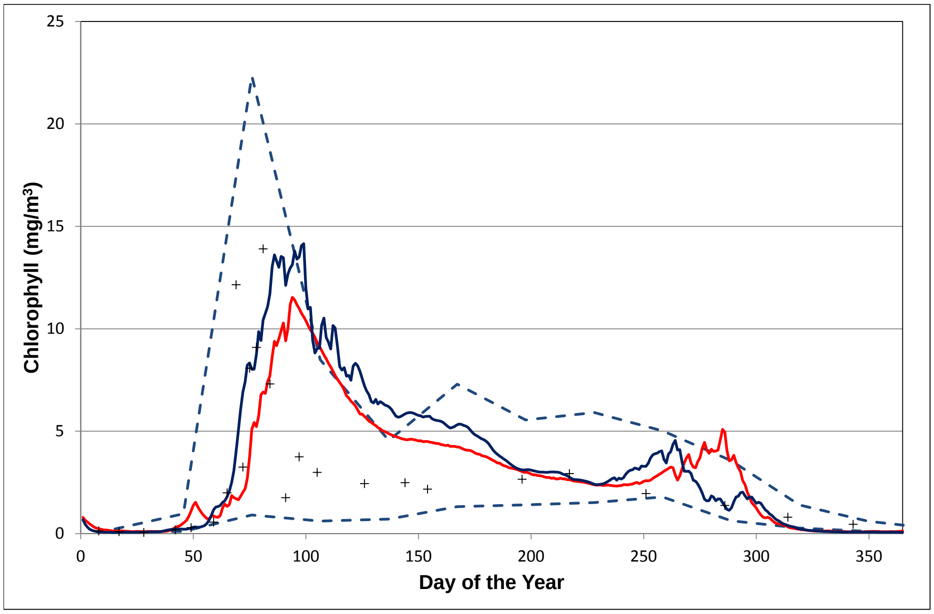


Figure 10.7: Predicted Chlorophyll output from the single box model (red line) plotted alongside the chlorophyll concentration predicted using boundary conditions determined by the LESV model (blue line). Both outputs have been plotted against the 5th and 95th percentile envelope (dashed lines) created from measurements of chlorophyll concentration made in Loch Creran during the 1970's. The data to create the envelope came from Cottrell *et al.* (1973) and Jones (1979) PhD Thesis and represents all the measurements made between 0-10 metres for all the stations sampled in Loch Creran. This data was first sorted by the day of the year into blocks of 10 or 20 values and the result used to create the envelope. The data was extracted using a MATLAB script written by Paul Tett.

While the model was programmed to explore the growth of phytoplankton under various loads of anti-fouling compounds it is also useful to look at its predictions of the concentration of nutrients, such as nitrogen and phosphorus, in the loch. The levels of these nutrients are intrinsically linked to the amount of phytoplankton present. By plotting the predicted concentrations against the 5th and 95th percentile envelopes obtained from measurements made during the 1970's a further indication of the accuracy of the model can be obtained. Figure 10.8 shows the result of plotting predicted nitrogen levels against the envelope. Again we find a reasonable fit within the envelope although levels during the spring and again during the autumn are rather high.

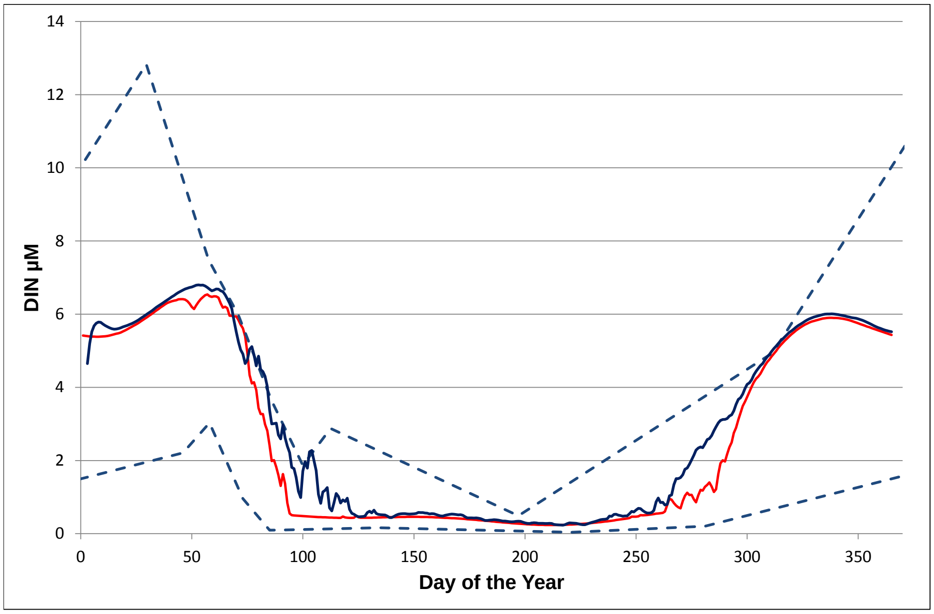


Figure 10.8: Predicted Nitrogen output from the single box model (red line) plotted alongside the nitrogen concentration predicted using boundary conditions determined by the LESV model (blue line). Both outputs are plotted against the 5th and 95th percentile envelope (dashed lines) created from measurements of DIN concentration made in Loch Creran during the 1970's. The data to create the envelope came from Cottrell *et al*. (1973) and Jones (1979) PhD Thesis and represents all the measurements made between 0-10 metres for each of the stations sampled in Loch Creran. This data was first sorted by the day of the year into blocks of 10 or 20 values and the result used to create the envelope. The data was extracted using a MATLAB script written by Paul Tett.

Figure 10.9 illustrates the predicted levels of phosphorus again plotted against the 5th and 95th percentile envelope for 1970's measurements. Again the model predictions lie within the envelope apart from a period towards the end of the year when levels appear to be rather high.

While not perfect, the model does appear to be capable of simulating the seasonal cycles of phytoplankton in the loch to a degree suitable for examining the possible effects of anti-fouling loading. As mentioned in the introduction this is a one box model, exchanging water and nutrients with the larger Lynn of Lorn and containing only one microplankton component. A more realistic approach would be to represent the loch as a series of layers, where water at a density commensurate with

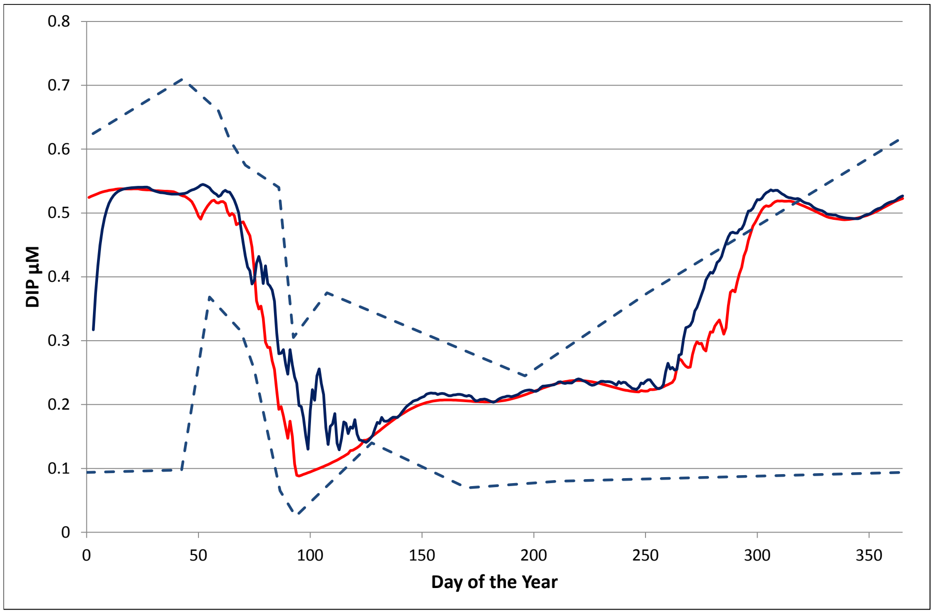


Figure 10.9: Predicted Phosphorus output from the single box model plotted alongside the concentrations predicted using boundary conditions determined by the LESV model (blue line). Both are plotted against the 5th and 95th percentile envelope (dashed lines) created from measurements of DIP concentration made in Loch Creran during the 1970's. The data to create the envelope came from Cottrell *et al.* (1973) and Jones (1979) PhD Thesis and represents all the measurements made between 0-10 metres for each of the stations sampled in Loch Creran. This data was first sorted by the day of the year into blocks of 10 or 20 values and the result used to create the envelope. The data was extracted using a MATLAB script written by Paul Tett.

that at the depth of the sill would flow landwards into the loch at an intermediate depth. Through mixing this water would gradually become entrained into the surface layers. A layer containing water at a higher density may also be present in the deeper parts of the loch, exchanging water less frequently but possibly containing a relatively abundant concentration of re-mineralised nutrients.

To re-programme the model to include this greater level of complexity would involve more time than that justified by the question posed regarding anti-fouling loading. However, a compromise allowing the effects of this simplification to be examined, was possible. By using another model i.e. the three layer LESV model described below, it was possible to set it up with the same initial conditions then extract the values calculated for exchange between the intermediate and surface layers of the loch. These values could then be input into the one box model as boundary conditions.

Figure 10.7 illustrates the simulated chlorophyll concentration in loch Creran (blue line) plotted against the 5th and 95th percentile envelope (dashed lines) created from the 1970's data. The model was run using values for boundary conditions that were derived from the LESV model and an altered exchange rate to reflect exchange with an intermediate water layer rather than the Lynn of Lorn. While the simulated chlorophyll concentration lies within the envelope for most of the year it proves to be a bad fit during the spring.

Figure 10.8 again shows the output from the one box model (red line), in this case simulated DIN concentrations, using the boundary conditions and exchange rate extracted from the LESV model. Comparing this with the output using the LESV derived data (blue line), shows a large degree of similarity in the two outputs with perhaps slightly better responsiveness exhibited when using the LESV derived boundary conditions.

The same is true for figure 10.9 which, illustrates the simulated concentration of dissolved inorganic phosphorus using boundary conditions extracted from the LESV model (blue line). Again there appears to be a strong similarity to the simulated DIP from the one box model shown in red.

Although the simulated concentrations of chlorophyll, DIN and DIP produced by using values derived from the LESV model indicate slightly better responsiveness, overall they do not appear to produce a noticeable improvement over the results obtained from the one box model. Therefore, for the sake of simplicity, it would be preferable to use one model rather than two to achieve the stated objective.

10.12 Conclusions

Sensitivity analysis shows that the model is very sensitive to changes in the exchange rate and losses in the loch and to the concentration of chlorophyll outside in the Lynn of Lorn. While the chlorophyll concentration in the Lynn of Lorn does not appear to have changed significantly since the 1970's (see chapter 2), both the rate of losses and the exchange rate will change throughout the year. Indeed altering these rates can significantly change the output of the model (see chapter 8). However very little data was available to enable these variations to be incorporated into the model and so it was decided to use a steady rate for both these processes.

While the model fails to capture all of the variability in chlorophyll concentration observed during 1975 (see figure 10.7), it does simulate the general annual trend in chlorophyll concentration. The same is true for DIN (figure 10.8) and DIP (figure 10.9). However, intended for use as an exploratory, rather than a predictive, model it has proven itself to be sufficiently robust to investigate possible changes to the phytoplankton community in the loch and has been used to good affect in this capacity throughout this study. Of course, it must be remembered, the model was created to investigate the potential detrimental impact, anti-fouling compounds were having on phytoplankton numbers in Loch Creran, and the model has proved to be more than adequate to carry this out (see chapter 6).

Table 10.6: Complete list of model parameters, variables and State Variables.

Symbol	Description	Units
α	Photosynthetic efficiency	day $(\mu E \mathrm{m}^{-2}\mathrm{s}^{-1}\mathrm{d}^{-1})^{-1}$
β_S	Biologically derived source/sink of substance	mmol $\mathrm{m}^3\mathrm{d}^{-1}$
E	Exchange Rate	d^{-1}
F	River Flow	$\mathrm{m}^3\mathrm{d}^{-1}$
Γ_S	Local Input of Substance S	mmol $\mathrm{m}^3\mathrm{d}^{-1}$
I_{mean}	Mean Irradiance	$\mu E \mathrm{m}^{-2}\mathrm{s}^{-1}\mathrm{d}^{-1}$
$\mathrm{I_C}$	Compensation Irradiance	$\mu E \mathrm{m}^{-2}\mathrm{s}^{-1}\mathrm{d}^{-1}$
$\mathrm{I_O}$	24 hour Mean Sub-Surface Irradiance	$\mu E \mathrm{m}^{-2}\mathrm{s}^{-1}\mathrm{d}^{-1}$
$\mathrm{K_D}$	Attenuation coefficient	m^{-1}
$\mu_{\max}$	Maximum Growth Rate	d^{-1}
$\mathrm{N_{OS}}$	Nitrate Concentration	mmol m^{-3}
$\mathrm{N_{OkS}}$	Half saturation constant for Nitrates	mmol m^{-3}
S	Concentration of substance in Box	mmol m^{-3}
S_f	Concentration of Substance in River	mmol m^{-3}
$\mathrm{Si_{OS}}$	Silicate Concentration	mmol m^{-3}
$\mathrm{Si_{OkS}}$	Half saturation constant for Silicates	mmol m^{-3}
S_O	Concentration of substance in Sea	mmol m^{-3}
$\mathrm{P_{OS}}$	Phosphate Concentration	mmol m^{-3}
$\mathrm{P_{OkS}}$	Half saturation constant for Phosphates	mmol m^{-3}
V	Box/Layer Volume	m^3
r_o	MP basal respiration rate	d^{-1}
r_{oa}	autotroph basal respiration rate	d^{-1}
r_{oh}	Heterotroph basal respiration rate	d^{-1}
b	slope of MP respiration rate	ratio
b_a	slopJ: algal respiration/growth rate	ratio
b_h	slopJ:heterotroph respiration/growth rate	ratio
q^a_{max}	Maximum algae nitrogen content	mmol N (mmol C)$^{-1}$
a^*_{PH}	Absorption cross section	m^{-2}(mg Chl)$^{-1}$
${}^x q^N_a$	Chlorophyll:Nitrogen ratio (algae)	mg Chl (mmol N)$^{-1}$
η	Heterotroph fraction	ratio
X	Chlorophyll:Carbon ratio	mg Chl (mmol C)$^{-1}$
ϵ	Attenuation cross section	m^{-2}/(mg Chl)
h	Layer depth	metres
L	Loss rate	d^{-1}
m_2	loss of polychromatic light correction	ratio
m	1/Mean cosine downwelling photons	m^{-1}
k	Units conversion factor	d^{-1}mmol (nmol)$^{-1}$
ϕ	Quantum Yield	nmol $\mathrm{O}_2\mu E^{-1}$

Chapter 11

SPICOSA and Wicked Problems

11.1 Introduction

As mentioned earlier this studentship was funded by SPICOSA, an acronym for Science and Policy Integration for Coastal Systems Assessment. This project which began in February 2007 was part of the European Unions Sixth Framework Programme. The project involved 54 partners in 22 different countries collaborating in an attempt to develop and test a framework that could be used to assess the different policy options available to coastal managers and policy makers.

Coastal zones are increasingly under pressure from human activities. Over exploitation of resources, pollution, development and uncontrolled tourism all threaten coastal ecosystems. Managing human activities in the coastal zone is exacerbated by the dynamic nature of these ecosystems which often traverse both national and institutional borders. This further fragments attempts at coastal management.

SPICOSA's aim was to apply a systems approach to the often socially complex issues involved in coastal zone management and to this end scientists from fields as varied as ecology, economics, social geography, mathematical modelling and sociology were brought together to create an integrated approach to coastal zone science in the hope that the link between science and policy could be strengthened.

Methods and tools developed during the project were tested at 18 study sites spread across the member countries each with its own unique ”issue”. The site chosen to represent the United Kingdom was the Clyde Sea on the West coast of Scotland. The study site was managed by Dr Tavis Potts a lecturer in marine policy at the Scottish Association for Marine Science and focused on an issue raised by the Scottish Government in which, they called for an increase of between 50% and 100% in leisure boating and step ashore sites in the Firth of Clyde.

This was to be accompanied by a similar increase in aquaculture. This issue resonated with local stakeholders who expressed concern that higher numbers of leisure boats and their crews could lead to an increase in pollution levels in the loch with detrimental effects on the local aquaculture.

This link between leisure boats and pollution levels in the Clyde Sea mirrored preliminary suggestions that the cause of the decrease in phytoplankton, observed in Loch Creran, may have been due to an increase in anti-fouling compounds, introduced to the loch on the hulls of yachts. It was felt therefore, that following the SAF process, while trialling the systems approach method, would also provide a useful framework around which the investigation of the phytoplankton community in Loch Creran could be built. Indeed, as the project progressed, while the Clyde Sea and in particular Loch Fyne remained as the theoretical area of study in terms of the SPICOSA project (see section 11.3.2), all practical work was focussed on Loch Creran and the reasoning behind this will be discussed in more detail in the results section.

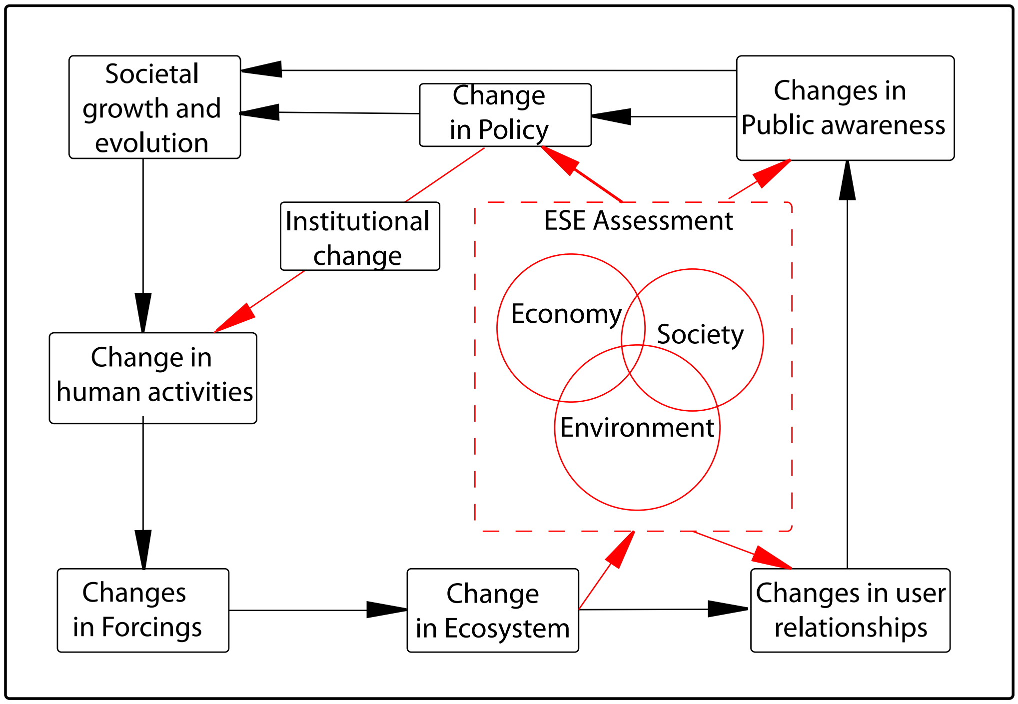


Figure 11.1: Coastal zone information feedback loop. The series of black arrows illustrates the traditional feedback loop. In this loop policy changes occur slowly as the public gradually become aware of the loss of benefits from the coastal zone. The red arrows show the SPICOSA loop where policy makers are provided scientifically robust information, based on optimal economic, social and ecological analyses, and are encouraged to make changes in realistic and beneficial time scales. The ESE box represents the core activities of SPICOSA. Diagram was re-drawn from SPICOSA website (SPICOSA 2011).

Figure 11.1 illustrates a simplified coastal zone information feed back loop. The black arrows depict the more traditional loop whereby policy change is driven by public pressure. This pressure arises as the public gradually become aware that changes to their coastal ecosystem are depriving them of the expected benefits from those ecosystems. Unfortunately these changes are often irreversible on realistic time scales and any changes in policy occur too late to avoid large remediation costs if indeed remediation is possible.

The SPICOSA loop, represented by the red arrows, attempts to supply scientifically robust information to policy makers allowing them to implement changes in realistic time scales. This information can be based on cost benefit analyses designed to optimise the social, economic and ecological benefits to society (SPICOSA 2011).

While SPICOSA developed a wide range of tools to assist coastal managers some of the most prevalent amongst the various study sites were integrated ecological, economic and social (ESE) models of the system under study. These models attempted to combine robust, validated ecological models with an economic model of an ecosystem. These integrated models also attempted to include a social model. However in many cases this proved too difficult to achieve in the time scales provided.

Nevertheless, understanding the ecosystem, defining the ecological dysfunction and the creation of these models included a significant input from local stakeholders. This involvement continued throughout the lifetime of the project and ensured that regardless of whether or not local societal interactions were mathematically modelled they were still inherent in the finished models.

11.2 Methods

11.2.1 System Design

The Systems Approach Framework (SAF) process has four main steps: System Design, System Formulation, System Appraisal and System Output and these are illustrated in figure 11.2. The process begins with system design and this is further broken down into various tasks. The first of these requires that the coastal zone

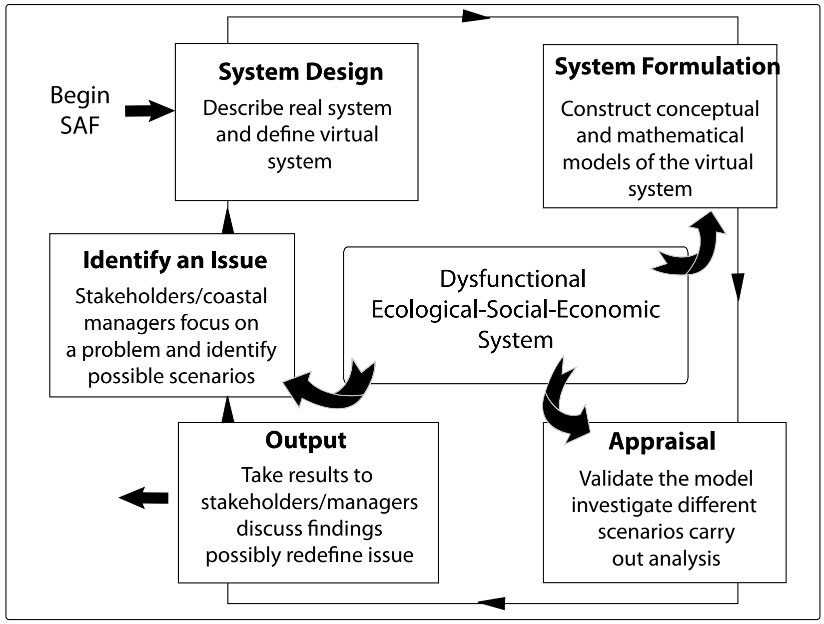


Figure 11.2: Diagram representing the SAF process. To complete the SAF may require several iterations of the process. Re-drawn from The SAF handbook (SPICOSA-SAF 2011).

system, exhibiting some dysfunction, be properly described. This description of the "real world" must then be refined into a virtual system, particularly in those aspects that are relevant to the issue that has previously been identified. It is this definition of a virtual system that is vital if different scenarios are to be successfully modelled. In other words, it is this virtual system, rather than the real world, that is the subject of the design step (SPICOSA-SAF 2011).

Defining the coastal system, first requires an understanding of the possible cause and effect chains acting within that system, and these involve not only ecological affects, but also include a socio-economic component (SPICOSA-SAF 2011). It is not enough for coastal managers to simply try and impose new methods of working. If change is to be truly effective the people or *stakeholders* affected by those changes must be fully engaged in the process. One of the first tasks then in defining the system is to determine which stakeholders are involved. Vanderlingen *et* *al.* (2011) outlines methods that can be used to *map* stakeholders, organising them into functional groups. However, in the first stages of this process it can prove beneficial to limit the number of stakeholders who are asked to participate. Selecting a small reference group of involved members can often help to highlight the key issues concerning them.

Further, for changes in the coastal system to be effective, it may be necessary for the relevant institutions involved in coastal management to make changes to their normal way of work. McFadden *et al.* (2010) note that institutional mapping can be an important method of implementing institutional reform. However institutional and stakeholder mapping should not be seen as separate activities. Rather they are two sides of the same coin. As Mcfadden *et al.* (2010) point out institutional mapping helps to highlight the potential roles stakeholders and institutions may play and identifies potential coalitions that can offer support, assess possible risks and help to create meaningful scenarios and strategies.

During this process of defining a system it is also very important to determine those boundaries that will be applied to the virtual system. Without clear limits, be they administrative, spatial or physical it will be very difficult to obtain meaningful results. Studying the effects of anti-fouling compounds on boat hulls in Loch Fyne would be quite a different undertaking if it was extended to the entire Firth of Clyde. By determining boundaries the system will have both an ”inside” and an ”outside” component and this was represented, in the Firth of Clyde site, as a set of boundary conditions with movement between the two compartments represented as a series of fluxes (SPICOSA-SAF 2011).

This process can appear somewhat linear in nature, however in reality each step of the SAF process may require several iterations, as ideas are altered and refined through ongoing discussion. Each stakeholder will have their own particular view of the real system and this may differ from the ideas of other stakeholders. While these views can be expressed by different virtual systems, ultimately these systems must agree with the information available and the observations made in the real system. At this stage it may also be beneficial to construct a conceptual model of the virtual system. In meetings with stakeholders this provided a focus for meaningful discussion and laid a foundation for the construction of a mathematical model.

11.2.2 System Formulation

System formulation is the process that takes the results of the earlier discussions on what constitutes the virtual system, and the final conceptual model, and begins to quantify them with the aim of constructing simulation models of the systems behaviour.

During system design the boundaries of the system are identified and a preliminary list of the various inputs and outputs to the system, including those to be included as part of the planned scenarios, are compiled. The different state variables or indicators that are to be used for testing the model are chosen at this stage. It is also necessary to acquire as much of the needed data as possible and in the event that it is not available decide on an alternative source or proxy. In some situations this can prove to be a major obstacle particularly when no regular monitoring has taken place. Indeed this was the case in Loch Fyne where insufficient data was available to allow the model to be fully appraised. This made it necessary to return to the stakeholders to further clarify the requirements of the model and point out possible limitations and alternatives.

Once the relevant data has been obtained, the equations to be used in the various parts of the ESE model can be formulated. In the Firth of Clyde study site the phytoplankton growth model was based on an existing box model; the dCSTT (Laurent *et al.* 2006) and adapted to include the effects of anti- fouling compounds entering the system. A mussel growth model was needed and the one chosen was based on the dynamic mussel growth model developed by Grant and Bacher (1998) These were then re-programmed into the project software: EXTENDSIM 7 (Imagine That Inc. 2011). Economic models were based on data available for existing operational marinas and mussel farms in Loch Fyne with additional information from Scottish government economic tables.

11.2.3 System Appraisal

Simply stated, system appraisal involves testing the model, the virtual system, against observations made in the real system and determining how well they are correlated. In Loch Fyne, due to a lack of data, there was no practical way to validate the mussel growth model in the time given. Nor was there any way to validate the accuracy of the economic models which were based on idealised businesses operating on the assumption that they must be making a profit or they would not exist.

There was however sufficient historic data from Loch Creran, a sea loch to the North of Loch Fyne, to allow the phytoplankton growth model to be appraised. If the model was to be applied to Loch Fyne, several parameters in the model would have to be changed and this appraisal would have to be re-run to suit conditions in Loch Fyne.

A full explanation of the model appraisal including a sensitivity analysis and an uncertainty analysis can be found in chapter 10.

11.2.4 System Output

One of the main purposes of developing a model of the dysfunctional ecological-socio-economic system was to facilitate an ongoing and fruitful discussion between scientists, policy makers and stakeholders in the study area. To this end a meeting of the stakeholders was arranged at the Scottish Association for Marine Science, Dunstaffnage to present the outcome of the model building task.

11.3 Results

11.3.1 Stakeholder Mapping and Governance

The first part of the SAF process; System design, included a strong element of *Issue resolution* which in SPICOSA terminology refers to the task of focussing attention onto some ecological dysfunction or issue of governance.

Part of the SPICOSA ethos required taking, in part, a bottom up approach to coastal management. To this end the participation of stakeholders was central to the development of a model that could be considered to be fit for purpose. Stakeholders were primarily defined as people or institutions (*Actors*) with a legal and/or moral interest in the chosen issue. Other actors involved in the process would include those with a degree of technical expertise and knowledge (e.g. scientists) and those who had been elected by the wider society to make decisions on their behalf (e.g. coastal managers, planning officers) (Tett *et al.* (2011 in press.).

Hosting a devolved parliament within the United Kingdom (U.K.) which itself is a member state within the larger European Union (E.U.). Scotland has several levels of governance pertinent to coastal zone management. While the U.K. parliament retains responsibility for offshore, E.U. and international environmental issues, the devolved parliament in Scotland holds responsibility for marine policy and management within 12 nautical miles of its national borders including fisheries, renewable energy and conservation.

The management of Scotland's seas is undertaken by various institutions. Chief amongst these is Marine Scotland, a government department that oversees marine policy, planning and grants various licences. Environmental regulation is the purview of the Scottish Environment Protection Agency (SEPA), a public body overseen by the Scottish parliament and responsible for the local implementation of wider U.K. and E.U. legislation. The agency given overall responsibility for nature conservation in Scotland is Scottish Natural Heritage (SNH). SNH provides statutory advice and implements E.U. legislation pertaining to the Habitats and Birds directive (Tett et al. (2011 in press.).

The third tier of governance in Scotland is represented by elected local authorities. In the Firth of Clyde study site this is the Argyll and Bute council who manage local services, planning, and licensing. With the recent introduction of the Marine (Scotland) Act, requiring the Scottish parliament to implement national and regional marine plans, in 2010 local councils are now also responsible for marine planning in areas under their control.

Argyll and Bute was formerly part of the larger Strathclyde region, one of the nine local government regions in Scotland, which in 1996 was sub-divided into 12 unitary council areas. Encompassing such a large area prompted the formation of the Firth of Clyde Forum. A voluntary partnership of local communities, businesses, organisations and local authorities, that was formed to promote the sustainable use of local resources (Tett *et al.* (2011 in press.).

Although a comprehensive list of potential stakeholders who may have been interested in local environmental issues was drawn up it proved difficult to engage those classified as belonging to *civil society*. Instead the majority of those interested in taking part came from the Argyll and Bute council, The Firth of Clyde Forum and from SEPA. For the most part these were professionals with some previous experience of environmental management, but who did not really consider themselves to be stakeholders in the strict sense of the word.

11.3.2 The Issue

After discussions with various stakeholder groups and the Firth of Clyde Forum it was decided to focus on the possible affects of an increase in the leisure and tourist use of the Firth of Clyde. In particular, as previously mentioned, a desire by the Scottish government to increase the revenue from tourism by 50% by 2015 (Scottish Executive 2006). At the same time Scottish ministers were also encouraging an increase in local aquaculture. It quickly became clear in the discussions that the priority for the local coastal managers was spatial planning. Unfortunately at the time the chosen software for the SPICOSA project (ExtendSim 7, Imagine That Inc.) was not suitable for spatial modelling nor did spatial planning justify an application of the SAF.

The Firth of Clyde was also deemed too large an area to fit within the scale and the resources of the project and so the focus was moved to Loch Fyne. Previous work developing box models of physical and biological processes in sea lochs (Tett *et al.* 2003; Laurent *et al.* 2006) combined with interest from the Argyll and Bute council suggested that the study should focus on the interactions between leisure boating and aquaculture in the loch. In the early stages of the SPICOSA project it was intended that there be two iterations of the SAF process. The first meant as a learning process. To this end some of the wider impacts of leisure boating, for example, an increase in the amount of sewage entering the loch, were disregarded and the issue was narrowed to look at anti-fouling compounds applied to the hulls of leisure boats, their effect on phytoplankton growing in the loch and the implications for shellfish productivity in Loch Fyne. In terms of the SAF this included both an ecological and a socio-economic element and was at an appropriate scale for the study (Tett *et al.* 2011 in press).

11.3.3 Potential Conflicts

Aquaculture has been an important source of employment and income to the local Loch Fyne community since 1977. In 2005, 20 people were employed by Loch Fyne Seafarms producing approximately 100 tonnes of queen scallops per year. Loch Fyne Oysters Ltd. produce a further 750,000 oysters and between 90 and 100 tonnes of mussels per year. Employing 109 staff and 20 seasonal staff with combined annual salaries amounting to £1.94 million, they recorded an annual turnover of £10 million in 2005. The company also spends approximately £2.37 million with local West of Scotland suppliers (Argyll and Bute Council 2009).

Recreation and tourism in and around Loch Fyne was estimated to generate £35.8 million in 2005 and employed around 630 people. Of the water based activities, sailing was the biggest contributor. There is no breakdown of figures for Loch Fyne, however, within the Clyde Estuary it is calculated that there are 2,700 permanent marina berth holders and an additional 2000 moorings. Each of these permanent berths is estimated to generate £7,000 per year. With the addition of a new marina at Portvadie, Loch Fyne has seen an increase in berths from 100, in the years preceding 2007, to 300 in 2010. Using the figures available for the Clyde estuary this would mean an annual income from sailing in Loch Fyne of around £2.1 million (Argyll and Bute Council 2009).

Perhaps the most obvious conflict arising between these two sectors is competition for space. Shellfish farms as well as having an aesthetic impact can potentially create a hazard to navigation. However shellfish farms also require good quality water. SEPA has designated much of the shoreline in both Loch Fyne and Loch Creran as *Shellfish Growing waters* (SEPA 2010) and as such it is subject to regular monitoring. Any deterioration of the water quality can result in locally farmed shellfish requiring costly depuration treatment.

Unfortunately marinas and collections of moorings can act as sources of pollution. Sewage discharged from the boats can contaminate the water with bacterial faecal coliforms that can easily be accumulated in the tissues of shellfish (Widdows *et al.* 1997). Boat hulls are also regularly treated with anti-fouling compounds. These compounds usually contain a base of copper or zinc enhanced with added biocides such as zinc pyrithione (Turner *et al.* 2008).

Applied to boat hulls in the form of paint these products slowly leach into the water column or are sloughed off as the vessel makes its way along the loch. Furthermore these compounds need to be regularly re-applied usually on an annual basis. This requires any old paint still remaining on the hull to be cleaned, generally by sand or hydro blasting. This can result in small particles of paint (circa 10 μm) being dispersed through the water column. These particles can be easily ingested by shellfish such as mussels (Turner *et al.* 2008) where they can have a negative impact on mussel growth (Stirling and Okumus 1995).

Nevertheless at the concentrations present in Loch Creran (see chapter 10.8) it is unlikely that the presence of these compounds will seriously affect shellfish. Anti-fouling compounds can however alter the growth rates of phytoplankton. Devilla *et al.* (2005) have found that some of the compounds in anti-fouling paint, such as zinc pyrithione can detrimentally affect the ability of phytoplankton to photosynthesise.

It is evident that there is plenty of scope for conflict between these two sectors. However there is also the potential for each to benefit the other. An increase in tourists and leisure boaters can increase the demand for local produce such as shellfish and at the same time an increase in revenue will inevitably find its way into the local economy benefiting local communities.

11.3.4 Conceptual Model

The construction of a conceptual model emerged as one of the more useful components in the SAF process. Beginning life as a series of *mind maps*, drawn up in several brainstorming sessions, the first conceptual models evidenced an overly complicated spider web of interconnections. These diagrams were gradually refined and simplified through meetings with stakeholders and scientists from the different disciplines involved. Developing these models helped to identify gaps in the data and provided a focus for discussion and debate. Not only did they allow the clarification of system boundaries but perhaps more importantly they highlighted the different assumptions and beliefs held by the various participants.

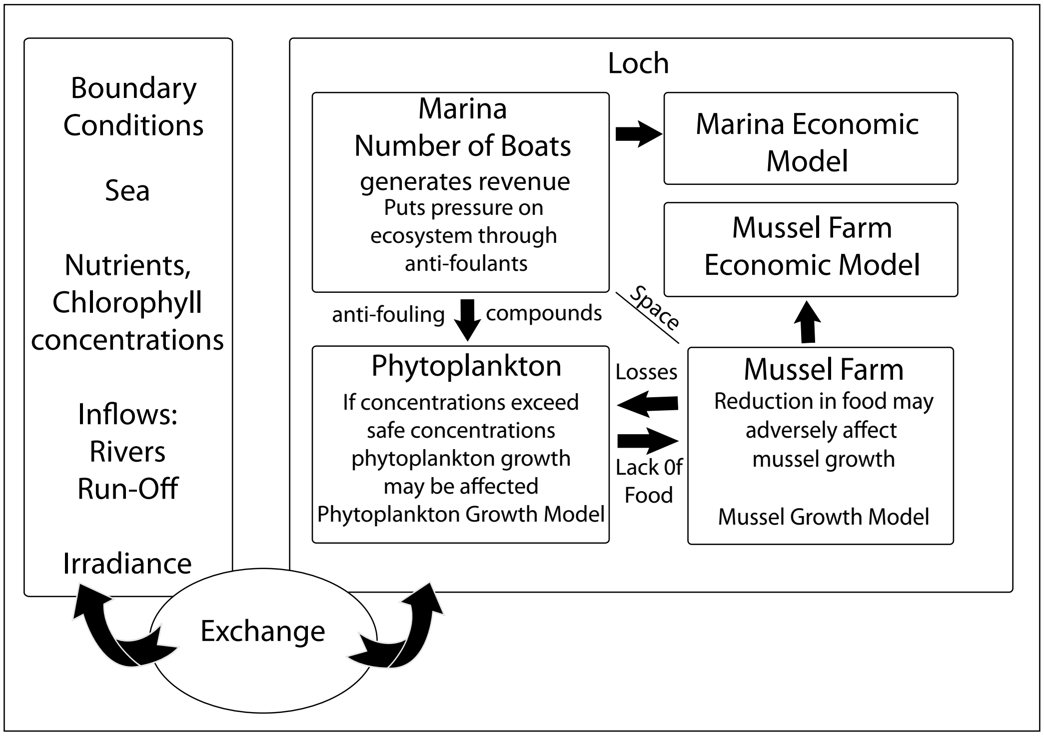


Figure 11.3: Conceptual Model of the virtual ESE system represented by a single box model of a sea Loch (in this case Loch Creran) exchanging nutrients and chlorophyll with the larger Lynn Of Lorn.

Figure 11.3 represents one of the final conceptual models used to describe the virtual system encompassing Loch Creran. It shows the main pathway whereby a rise in the number of occupied berths in a local marina, increases the load of anti-fouling compounds entering the water column, leading to the possibility that this will have an adverse affect on phytoplankton numbers in the loch and reduce the food available for local mussel farms with consequences for their profitability. As mussel numbers wax and wane, a feedback loop alters the severity of the losses to grazing in the phytoplankton growth model.

This simple conceptual model proved to be a very useful tool in discussions with team members and stakeholders and was eventually incorporated into the model/user interface. It was also the basis for the mathematical model helping to identify system boundaries and state variables and to give an idea of the mathematical relationships between the different components of the system (Tett *et al.* 2011 in press).

11.3.5 Simulation Model

Phytoplankton Model

It was decided to focus the model on Loch Creran rather than Loch Fyne at this point and the reasons behind this decision will be discussed in greater detail in section 11.3.2. The simulation model was comprised of four main components largely based on existing mathematical models; a single box model of phytoplankton growth and exchange with the larger Lynn of Lorn (Tett *et al.* 2003; Laurent *et al.* 2006), a dynamic individual mussel growth model (Grant and Bacher 1998), and economic models for an idealised marina, written by the author, and a mussel farm. The phytoplankton model is described in greater detail in chapter 10.

Mussel Model

The mussel growth component of the ESE model was programmed into EXTEND-SIM 7 by the other modeller working on the Firth of Clyde study site; Fiona Culhane. This model was based on a dynamic energy balance model developed by Grant and Bacher (1998). This calculated the growth of an individual mussel resulting from inputs of available carbon from both phytoplankton and particulate organic matter. The model assumed the mussels were grown according to the typical Scottish practise where wild spat are allowed to seed onto ropes suspended in the top 15-20 metres of water and harvested after two years. (Tett *et al.* 2011 in press). The ropes are attached to a line which is suspended by a series of buoys and is capable of yielding 25 tonnes of fresh mussels when harvested. The model assumed that there were 12 lines in the simulated mussel farm with one third being harvested, one third holding first year mussels and the final third being prepared for seeding annually.

Economic Models

The economic models used for both the marina and the mussel farm were, in essence, very similar. Costs such as employee salaries, taxes and depreciation were deducted from the net revenues obtained from the rental of berths, a chandlery and various yachting services in the case of the marina and the sale of mussels in the case of the farm. As mentioned earlier , to maintain simplicity the model was set up to consider one idealised marina and one typical mussel farm both of which could increase in size indefinitely. This necessitated including scalars for the employee numbers within the model. The number of workers employed at the marina was based on sets of 250 berths with each set employing ten full time staff plus between 0 and 10 seasonal staff depending on the proportion of berths occupied. Each overnight stay in a berth is estimated to generate between £125 and £150 (McKenzie Wilson 2006), a figure which includes spending on berth rentals, services and meals.

In the case of the mussel farm it was estimated that the farm would employ one employee for each 0.25 lines. Mussels were assumed to fetch £2.40 per kilogram (wet weight)(price based on figures supplied by a local mussel farm). When the businesses were operating profitably the model re-invested a percentage of the revenue back into the business capital. In this way the businesses were kept in a steady state during each scenario. At the end of each simulation the model output two indicator values for each business; Total annual salaries paid to employees and net revenue. As long as the revenues remained positive it was assumed that the business was economically sustainable while the salaries were assumed to be proportional to the amount of money entering the local community from each business. These indicators provided a useful means of comparing the economic health of these two industries as well as their contribution to the local economy.

Output step

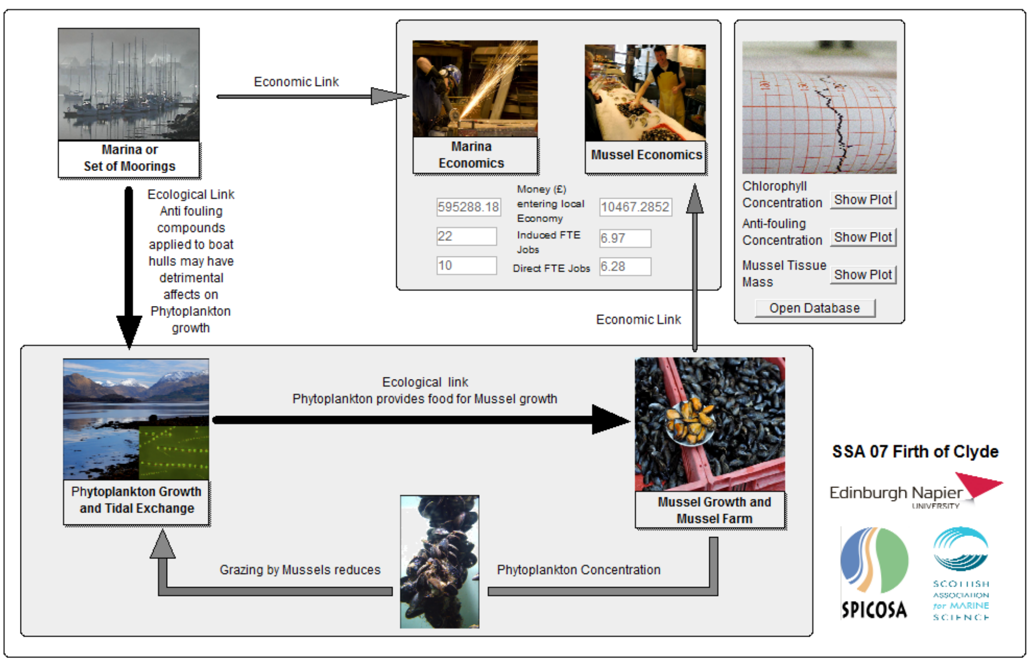


Figure 11.4: Diagram of the final user interface of the Firth of Clyde study site ESE model. Different aspects of the model can be accessed by clicking on the relevant picture. This opens boxes for the input of data, such as the number of occupied berths in a marina, or drop down lists allowing the selection of anti-fouling compound, uncertainty factor, etc. Buttons allow graphs of various output to be displayed and these can be changed according to the wishes of the stakeholders.

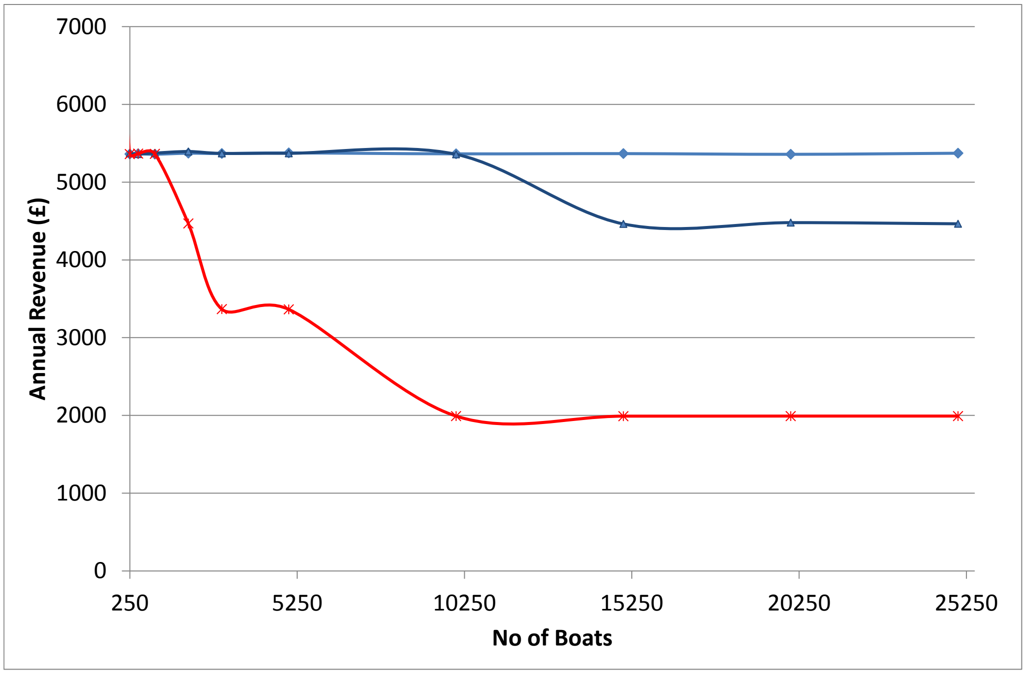


Figure 11.5: Plot showing the affect on a mussel farms revenue when different uncertainty factors are applied to the toxicity of anti-fouling compound present in the loch.

As previously mentioned, at the beginning of the project it had proved difficult to engage stakeholders from the wider civil society, instead it was officials from the Argyll and Bute council, The Scottish Environment Protection Agency (SEPA) and the Firth of Clyde Scottish Sustainable Marine Environment Initiative (SSMEI) who proved willing to participate. Working at the ”operational” level of governance Tett *et al.* (2011 in press) more accurately described them as policy-stakeholders.

The output step is intended to allow concerned stakeholders to see the results of the SAF process and in the Firth of Clyde study site this was carried out by organising a stakeholder forum. It is important to ensure that the language and terminology used during a forum be pitched at a level that is comprehensible to everyone attending. In this case the lack of representatives from civil society and the presence of officials who already shared a common frame of reference with the scientists presenting the results allowed the stakeholder forum to proceed in a relaxed and informal manner. It was therefore possible to present the conceptual and mathematical models in a very detailed way allowing the underlying assumptions, gaps in data and uncertainties inherent in the model to be discussed.

This is not a trivial point. As an aside the meeting was attended by a relatively new member to the study site team whose background was in law and sociology. After the meeting she admitted that she found a large part of the discussion around the model was rather too technical and expressed dismay that during a discussion on the models appraisal it was pointed out that it explained approximately 60%-70% of the variability in the loch, a figure which she assumed was far too low to be of any good.

It was also pointed out that while individual components of the ESE model were scientifically robust its primary use was not as a predictive model but rather as a tool to enable stakeholders to quickly explore different aspects of a particular problem or policy issue, (Indeed the model has been used in a similar way throughout the investigation into the phytoplankton community in Loch Creran), this has allowed the outcome of different scenarios to be studied, (see example figure 11.5), while providing a focus for further informed debate. During stakeholder meetings this promoted a long and fruitful conversation about the model, its possible uses and yielded some constructive ways in which it could be improved and possibly enhanced in the future. Figure 11.4 shows the user interface of the completed model. The design of this interface was largely due to the input given by stakeholders during the forum.

Although coastal management by the Argyll and Bute Council favoured spatial planning, which the model in its present form could not address, all of the policy-stakeholders gave very positive feedback about the model. As Tett *et al.* (2011 in press) notes this may have been due in part to their familiarity in using models in their own decision making process. The representative from SEPA was particularly impressed by the models conservative approach and felt it would be useful in situations where a cut-off point had to be determined, for example, if the minimum distance between a marina and a mussel farm, had to be stipulated.

It was interesting that although the policy-stakeholders showed a great deal of curiosity towards the underlying assumptions and functioning of the model they also made it clear that they had no wish to be heavily involved in the actual modelling process. Rather they preferred to leave this task to scientists who they felt they could trust to construct a reliable and scientifically robust model.

11.4 Discussion

Many of the problems associated with coastal zone management are complex and will generally involve a large and diverse group of participants or stakeholders. The gestalt of each of these members will vary greatly and will tend to diverge as the number and complexity of the involved participants increases. The implications for the environment, economy and society posed by many of these problems often means that some resolution must be arrived at. Decisions have to be made regardless of their overall efficacy or acceptability. If there is to be any chance of agreement or at the very least a working compromise it is necessary to engage each of these stakeholders, try to understand and share with the other participants their world view and attempt to address at least some of their concerns. Providing this is done sympathetically it may in many cases, significantly improve the probability of an acceptable outcome.

Arriving at a point where stakeholders can accept or at least recognise one another's different points of view may at times appear unlikely or even impossible, however the very act of involving them in the process of decision making, helping to negate their feelings of disenfranchisement can make a successful outcome more likely. While the nature of the solution to a problem may hold significance it is being included in the process that is often most important to the stakeholder.

Getting to grips with the complex interactions of a group of stakeholders may be daunting but to ignore one or several of them can be disastrous. A stakeholder who feels left out may in turn seek out ways of undermining or sabotaging even the best intentioned decisions. As Conklin (2005) points out "*Social complexity can be understood and used effectively, but it can be ignored only at great peril*".

The intricate nature of coastal zone interactions will make it unlikely that a simple *one solution suits all* answer will ever be arrived at. The evolving characteristics of an ecosystem and the varied and changing interactions within a diverse number of users requires constant vigilance. It is important therefore to involve stakeholders during and after the decision making process. After all they are often the ones who will be called upon to change their behaviour.

In terms of the SPICOSA experiment the very act of mapping and engaging a group of stakeholders has introduced a large social aspect into the process. The model itself - its functionality, appearance and possible future improvements, such as the introduction of a spacial aspect - arose from ongoing discussions with stakeholders over the issue.

The literature is replete with examples where the top down approach has failed

(Anderies *et al* 2006; Bruen 2008; Espinosa *et al*. 2008), fisheries management in particular appears to be plagued by the inability of managers to integrate or even in some cases understand the social behaviour of fishermen (Blyth *et al.* 2002), and include this in their management plans. One of SPICOSA's strengths appears to lie in its determination to involve stakeholders from the very beginning whether the issue has been raised by them or not and continue to include them throughout the process.

Dilemmas facing the coastal zone manager such as water quality, erosion, pollution and conflict resolution between the numerous different users of coastal zone resources may, initially, appear relatively simple but can in reality involve a myriad of interlinked problems embedded in the social framework of the involved communities.

Given the social complexity involved in integrated coastal zone management it could be argued that many of the issues faced by coastal zone managers today can be considered as *wicked problems*. As Conklin et al (2007) state "Social complexity is inseparable from problem wickedness".

In the 1970's Horst Rittel a professor of the science of design and Melvin Webber a professor of city planning, both working at the University of California became disillusioned with what they described as first generation systems analysis which, due to its linear nature was prone to failure when confronted with the socially complex types of problem that were increasingly being encountered by city planners. They suggested that wicked problems can be identified by ten different characteristics; see (Rittel and Webber 1973). Dr Jeff Conklin, a software engineer and now director of the CogNexus Institute recognised that Rittel and Webbers definition mainly related to planning and policy and in an attempt to redefine the concept for a wider application identified six characteristics of wicked problems; i.e.

The problem cannot be understood until after it has been formulated. Different social groups may see a problem in quite distinct ways depending on their frame of reference. It is often only when a problem has been defined, in relation to the different world views of the stakeholders, that it can properly be understood.

They lack a stopping rule

They have no right or wrong answer. Again the solution depends on the different frames of reference held by different stakeholders.

Each problem is unique.

Each solution is a one off. Often the opportunity to learn by trial and error does not exist. For example, once the seas are empty of fish it is too late to go back and try and do things differently.

They have no given alternative solutions. There may be no discrete solution from which to choose or there may be too many to choose. Stakeholders have to collectively decide on the way to resolve the issue.

Anyone with experience of working in large projects or institutions, particularly those with a wide range of different participants will undoubtedly recognise at least some of the above characteristics.

In an attempt to address the difficulty presented by wicked problems various approaches have been tried including; the Creative approach, the Entrepreneurship and Innovation approach, the Systems approach and the Collaborative approach. SPICOSA has tended to concentrate on the latter two methods.

By formulating a systems approach framework and combining it with the collaborative approach favoured by Conklin and others, SPICOSA has created a framework well suited for addressing a wide range of wicked problems. Systems' thinking has moved on from the simple GAFI (Gather information, Analyse, Formulate answer, Implement answer) approach so disliked by Rittel and Webber in the 1970's and now lends itself to complex problems containing multi interdependent linkages. Kreuter et al (2004) suggest that by providing an easily accessible visual language that includes the use of conceptual maps and diagrams to aid understanding amongst stakeholders, by taking a more holistic approach considering not just the individual components of the system but also the whole system and the connections inherent within it, by allowing a fuller examination and enquiry and by adding precision, systems thinking can reduce the ambiguities and aid in better communication amongst stakeholders.

Combining these techniques with a collaborative approach where stakeholders are first identified through stakeholder mapping techniques and then actively involved in ongoing discussion further reduces the degree of wickedness. As Conklin and his colleagues point out, wicked problems aren't really solved, one merely helps stakeholders to negotiate a shared understanding and a shared meaning, (Conklin et al 2007).

While the combination of these two methods provides a powerful tool for working with complex problems the coastal manager is faced by one further dilemma. Given the complex social interactions, the vested interests, the difficult political arena and the glare of the media, any decisions made involving the coastal zone will have to be scientifically robust. While professionals may recognise a wicked problem, politicians, managers and the general public want answers. The media demand black and white solutions to issues, uncertainty will rarely be tolerated.

SPICOSA takes this necessity for scientific rigour by introducing modelling to its extensive toolbox. As Rittel pointed out in his paper ”One cannot build a freeway to see how it works”, (Rittel and Webber 1973). However computer modelling has come a long way since the 1970's allowing highly complex systems to be modelled in a variety of different ways depending on the desired outcome. While many of the problems may have a high level of wickedness associated with them, an analysis of the system will often reveal areas that lend themselves to classical linear analysis resulting in an acceptable answer.

In the past models have usually been conceived of as being predictive, concerned with determining the outcome of a pre-determined set of starting conditions. It is true that many, possibly all, of the models developed through the SPICOSA project have a strong predictive element, at least in part. Indeed it is this predictive quality and the uncertainty analysis associated with it that give it much of its robustness. However when converted into the combined ecological, social and economic model which is presented to stakeholders these models become more useful as tools that can be used to explore the system.

As Brugnach *et al.* (2008) state, when dealing with complex systems it may not be possible to determine the exact outcome of certain actions but simply show that certain outcomes may be possible and highlight some of the implications associated with those outcomes. When this is the case uncertainty in some parts of the system doesn't need to be accounted for but can be included as a range of scenarios. An example of this can be seen in the Firth of Clyde study site model where uncertainty in the possible effects of anti-fouling compounds on phytoplankton growth is presented via a series of drop down buttons.

The SPICOSA approach of combining systems thinking, collaboration and modelling, ideally in an integrated multidisciplinary team consisting of a sociologist, an economist, a modeller and an ecologist, and liaising with stakeholders provides a very powerful way of coming to terms with complex problems. In terms of running an experiment many of the wicked problems in SPICOSA have actually been dealt with by being tamed.

Wicked problems can of course be tamed in a variety of ways. The approach used in the Firth of Clyde study site, before shifting the focus to Loch Creran, was to take the general question regarding the effects of an increase in leisure boating in the Firth of Clyde - scarily complex, and reformatting it so that it first became the effect of anti fouling compounds applied to the hulls of leisure boats on phytoplankton growth and mussel aquaculture in the Firth of Clyde and then further restricting the boundaries to encompass only Loch Fyne, thus turning what was a wicked problem into one much easier to handle. (This may, in part, account for the reduced number of stakeholders who stayed with the project).

In conclusion the SPICOSA framework, combining techniques for stakeholder mapping and stakeholder collaboration with systems analysis and modelling, particularly the exploratory ESE models provides a very powerful set of tools for dealing with the type of complex problems increasingly facing coastal zone managers.

Chapter 12

Summary and Conclusions

This study had two main aims. The first was to try to determine whether or not, anecdotal evidence of changes to the phytoplankton community in Loch Creran had any foundation, and the second, if significant changes to the phytoplankton community in the loch were found, was to attempt to identify the reasons behind them. Fortunately the loch had been extensively studied during the 1970's and this provided a convenient baseline against which the state of the loch in the late 2000's could be measured.

12.1 PCI

Rather than try to consider each species of phytoplankton separately, it was deemed more practical to consider them as lifeforms (Margalef 1978; Tett *et al*. 2008), with the exception of *Skeletonema spp.* This species of chain forming diatom was ubiquitous in the loch during the 1970's and early 1980's, and as can be seen in chapter 2, figure 2.9, constituted a large proportion of the diatom biomass during the spring bloom in this period.

From the results in chapter 2 it is clear that there have indeed been marked changes in the abundance of the different phytoplankton lifeforms extant in the loch. While ciliates show little change in their numbers throughout the year there was a significant increase in their numbers around the time of the spring bloom which, during 2008-09, occurred two to three weeks later in the year than it had during the 1970's.

Pelagic diatoms (see figure 2.7), small flagellates (see figure 2.15) and to a lesser extent dinoflagellates (see figure 2.12) all showed a significant reduction in their numbers. It should be noted however, that while pelagic diatom numbers vary quite considerably throughout the year, these changes are largely confined to the early months of the year, especially around the time of the spring bloom in March and April. In particular *Skeletonema spp.* (see figure 2.10) showed a marked decline. At the same time however, (see figure 2.11), numbers outside the loch, in the larger Lynn of Lorn, showed no significant change in abundance throughout the year. This suggests that the cause for the decline lay in the conditions within the loch itself.

12.2 Anti-Foulants

Once it had become evident that the changes in the abundance of these lifeforms in the loch was indeed significant it was decided to look at the possibility that the decline in phytoplankton was caused by an increase in anti-fouling compounds entering the loch from the hulls of leisure craft.

The decision to look, in the first instance, at the effects of anti-foulants in the loch rather than nutrient concentrations was prompted partly by a need to satisfy the studentships funding body and study site requirements and partly because recent studies in the loch between 2003 and 2006 had found no evidence of any significant changes to nutrient concentrations in the loch.

As a lack of appropriate resources made direct measurement of anti-fouling concentrations in the loch difficult it was decided to approach the problem by adapting an existing assimilative capacity model, the dCSTT model (Laurent 2006) as described in chapter 10. This was then combined with output from the existing MAMPEC model (Van Hattum *et al.* 2002) designed to determine the chemical fate of a compound in the marine environment.

It soon became clear, from the modelled results (see figures 6.1 and 6.2) and from personal observations, that the number of boats using Loch Creran, both recreationally and commercially, was not high enough to have any significant impact on the water quality within the loch. It is true that the model dealt rather simplistically with these compounds only calculating concentrations for one anti-foulant at a time and thus avoiding synergistic affects, but lack of peer reviewed toxicological studies made anything more ambitious impossible. It was also evident that the large number of boats combined with the high uncertainty factor needed to simulate any deleterious effects from the anti-fouling compounds made it extremely unlikely that these compounds were responsible for the observed decline in phytoplankton in the loch.

12.3 Grazing

One of the more surprising aspects of the decrease in phytoplankton abundance in Loch Creran was the drop observed in small flagellates. The rapid growth rate of small protists usually enable them to keep pace with the exponential growth rates of phytoplankton species and it is generally accepted that they are responsible for a large part of the predation on primary producers in the sea (Sherr and Sherr 2002; Calbet and Landry 2004).

On first inspection (see figures 2.7 and 2.10), the observed drop in pelagic diatom numbers in spring could be taken as indicative of an increase in grazing pressure. If this was true, it would be reasonable to expect that the decline in pelagic diatoms during the spring would be accompanied by an increase in the numbers of their predators, such as small flagellates. Clearly however, this is not the case. It may be that instead, the decline in diatoms has meant less food for small phagotrophic flagellates which have declined accordingly.

Of course pressure could also come from an increase in grazing from bivalves and other filter feeders within the loch. Oysters (*Crassostrea gigas*) and mussels (*Mytilus edulis*) began to be grown commercially in Loch Creran in the 1990's and table 8.1 in chapter 8 summarises the production levels for farmed bivalves in Loch Creran during 2009.

Nonetheless, even assuming that bivalves can selectively graze on phytoplankton (Bougrier *et al.* 1997; Rouillon & Navarro 2003; Ward *et al* 2003), conservative estimates of the clearance rates to be expected do not account for the drop in phytoplankton numbers observed in the loch. Indeed Trottet, *et al.* (2007) found evidence that mussel farms may actually enhance phytoplankton productivity.

However, grazing pressure does not arise solely from farmed bivalves. Segueira et al. (2007) have estimated that wild populations of benthic filter feeders in Loch Creran would be capable of clearing 40% of the volume of the loch per day. While this could significantly reduce the levels of phytoplankton in the loch (see figure 8.1), there is no evidence that the numbers of wild benthic filter feeders in the loch have significantly changed over the past four decades (Black *et al.* 2000; Moore 1996). If that is the case, it would be reasonable to suppose that this ”background” grazing is not playing any significant role in the observed recent decline in phytoplankton numbers.

12.4 Water Temperatures

In chapter 9 there is evidence that water temperatures in the loch have risen since the 1970's. Higher water temperatures could, potentially, increase heterotrophic processes within the system. In a sea loch such as Loch Creran, where the onset of the spring bloom is controlled by the amount of light available in the early part of the year, this can potentially lead to a mismatch between the abundance of grazers and phytoplankton present in the loch at any particular time. Sommer *et al.* (2007) carrying out mesocosm experiments noticed a significant increase in the numbers of ciliates and other protozoans when water temperatures were raised. This was also accompanied by an earlier onset of growth.

Interestingly the results from chapter 3, in which a phytoplankton community index developed by Tett *et al* (2008) was used to study the phytoplankton community in Loch Creran, indicated significant changes to its structure. These included a significant increase in the abundance of ciliates relative to pelagic diatoms (figure

3.3), dinoflagellates (figure 3.5) and small flagellates (figure 3.6). Again most of these changes occurred in the early part of the year, in the months preceding the start of the spring bloom.

Ciliates have been found to play an important part in microplankton food webs (Hansen *et al.* 1997; Kamiyama and Arima 2001) with reported clearance rates second only to larger calanoid copepods. Nielsen and Kiorboe (1994) studying ciliates in the Kattegat estimated that they could consume 49% of the annual primary production. They did however, make the assumption that all of the ciliates observed at their study site were heterotrophic. Nonetheless, the increase in ciliate abundance observed in Loch Creran, although significant during the spring, still lies mainly within the 5th and 95th percentile envelope created from the 1970's data. It is possible however, that increased grazing pressure, from elevated numbers of ciliates, appearing slightly earlier in the year, has a part to play in the observed reduction in phytoplankton, particularly if this community is experiencing stress from other factors.

It is also possible that rising water temperatures could affect the zooplankton in the loch, particularly if the water temperature was higher during the winter months. Wiltshire *et al*. (2008) observed that at Helgoland Roads and the German Bight raised water temperatures led to a delay in the onset of the spring bloom. They surmised that this may be because more herbivores were able to survive into the autumn and early winter. Nielsen and Kiorboe (1994) in their study on ciliates concluded that ciliate numbers were largely controlled by predation from copepods. Could a change in the species composition of the larger zooplankton community in the loch be relieving some of this pressure on ciliates and allowing their numbers to grow? Unfortunately no attempt was made to record either zooplankton species or numbers in the loch during 2008 and 2009 and so the affects of any changes in either zooplankton species composition or numbers in Loch Creran can again, only be speculative.

Given the complexity of marine food webs, it is very difficult to explain the decreased abundance of pelagic diatoms, dinoflagellates and small flagellates in terms of predator/prey interactions. Although grazing can have a significant impact on the concentration of phytoplankton in a semi-enclosed water body such as Loch Creran, the levels of grazing from farmed bivalves do not appear to be high enough to account for all of the changes observed.

12.5 Nutrient Concentrations

In 2009, access to the research vessels RV Serpula and RV Calanus, both operated by the Scottish Association for Marine Science, Dunstaffnage, allowed the investigation in Loch Creran to be extended to nutrients. These were collected in the Lynn of Lorn and in the main basin of the loch. A comparison of the concentrations measured during 2009 with those made in the 1970's (see figure 4.1), revealed no significant changes in either dissolved inorganic nitrogen (DIN) or dissolved silicon (DSi). DIN levels were however found to be elevated during March and April of 2009.

The availability of suitable concentrations of nitrogen and, in the case of diatoms, silicon, plays a vital part in the growth of phytoplankton. Once the intensity of available light has risen above a certain threshold in the spring it is generally assumed that phytoplankton growth will continue until the supply of available nitrogen in the surface stratified layers of the water column has been exhausted. A decline in phytoplankton productivity could be easily explained if there was found to be a lack of available nitrogen in the system. Clearly this is not the case.

Figure 4.1 does however reveal significantly lower levels of dissolved inorganic phosphorus (DIP) in 2009 compared with the 1970's. The mean concentrations of DIP measured in the main basin of the loch during March 2009 ranged between 0.55 and 36.24 μg l^{-1} (see table 4.2), with a mean value of 10.35 μg l^{-1}. Reynolds (2006) notes that the onset of phosphorus *famine* in phytoplankton cells usually occurs when concentrations in the surrounding water drop to around 3.0 μg l^{-1}, so it is possible that, at times, a lack of phosphorus is reducing the productivity in the loch. Nonetheless, luxury uptake of phosphorus by phytoplankton, during periods when it is abundant, can probably sustain between 2 and 4 further generations before the cell becomes exhausted (Reynolds 2006). Given the relatively high, mean concentration of phosphorus in the loch it seems that, while it may account for some of the reduced productivity in the loch, it is unlikely to explain the large reduction observed in the abundance of phytoplankton.

12.6 Rainfall

Perhaps more interesting is the pattern observed in the spring, of elevated nitrogen and lowered phosphorus levels. This could be indicative of an increase in freshwater flowing into the loch and one likely source of this extra water would be rainfall. This raises the question; have rainfall levels risen in the Loch Creran catchment area relative to the 1970's? This was addressed in chapter 9 where it was shown that although there was no significant difference between the precipitation levels for the entire year, there was a significant difference at certain times of the year, particularly between January and April. Not only had the levels of rainfall during this period risen, but the general pattern of precipitation, as evidenced from a comparison of the climatologies for the 1970's and the late 2000's, had changed, with heavier rainfall occurring 2 to 3 weeks later than in the past.

These periods of heavy rainfall could affect the state of the loch in several different ways. An increase in freshwater flowing into the loch could potentially increase the flushing rate, altering the amount of water displaced through tidal exchange and increasing the rate that phytoplankton are washed out of the loch (Ross *et al*. 1994; Su *et al*. 2004; Lionard *et al*. 2008). Tett *et al*. (1986) observes, that the level of rainfall would need to be greater than three times the mean value for this to be a possibility. It can be seen from figure 9.14 that although there were days when less rain fell during 2008-2009 than in the past, these are outnumbered by the number of days when rainfall was much greater than the 1977-81 levels. It is also clear that there are a considerable number of days that exceed mean 1977-1981 values by more than a factor of three. It seems reasonable to assume then that the rate of washout in the loch has increased during the spring months.

Although the exact mechanism, by which the phytoplankton population in the loch is inoculated, is not well understood, McQuoid and Godhe (2004) carrying out mesocosm experiments in Gulmar Fjord in Sweden found that resting stages and cysts from pelagic diatoms (including *Skeletonema* spp.) and dinoflagellates respectively played a large part in providing the next years seed population, largely determining the species composition in any given year. They also concluded that the successful propagation of the various resting stages was particularly sensitive to changes in environmental factors such as day length, temperature and mixing.

It is possible then that the change in the pattern and intensity of precipitation around

Loch Creran, combined with a drop in wind speeds, has altered the conditions under which resting stages are mixed into the water column.

An increase in freshwater inflowing to the loch should also increase the level of nutrients entering the surface layers of the loch. This could account for the higher levels of nitrogen observed during the spring. However, if anything, an increase in nutrients would be expected to increase the productivity of the loch not reduce it.

12.7 CDOM

Perhaps the most influential outcome of an increase in rainfall would be an associated rise in turbidity in the loch and elevated levels of chromophoric dissolved organic materials (CDOM), both of which could change the amount of light penetrating the upper layers of the water column. Devlin *et al*. (2009) found that in areas where there was a high level of freshwater inflow, such as fjords, CDOM had a greater influence on light attenuation in the water column than suspended particulates. Although no direct measurements of CDOM were carried out in Loch Creran during 2008-09, salinity levels were recorded during each of the transects carried out along the length of the loch. McKee *et al.* (2002), working in Loch Etive and Binding and Bowers (2003), studying the Clyde Sea, found a high level of correlation between salinity and CDOM and so it was decided to use a salinity proxy to substitute for actual CDOM measurements.

As discussed in chapter 9, a high correlation was found between levels of rainfall and CDOM concentrations in the surface layer of the loch. However, perhaps unexpectedly, heavy rainfall preceded peaks in CDOM concentration by 7 days. This is rather longer than the two to three days often reported in the literature for run-off to enter local rivers and lochs, nevertheless much depends on the topography, type of soils and perhaps most importantly for the west coast of Scotland, their saturation levels. Kostka and Holko (2003) studying run-off events in North Slovakia found delays of between 3 and 9 days between rainfall and water entering the local waterways. Although much of Glen Creran cuts through steeply sided hills, a large part of the main basin in Loch Creran is surrounded by relatively flat, arable land while, approximately 50% of the water entering the loch flows in from river Creran to the upper basin. This then enters the main basin through the restricted narrows beneath Creagan bridge. The general topography and the passage of water through this upper basin may well account for the observed delay.

12.8 Light Limitation

It is generally assumed that phytoplankton growth is limited by low levels of light during the winter months until a threshold is reached in spring, after which its growth becomes controlled by the availability of nutrients. If this was the case then the levels of CDOM in the surface layer of the loch would have very little affect on productivity. It was necessary then to determine whether light played any part in controlling productivity or not.

Unfortunately the presence of phytoplankton in the water column can, in itself, influence the amount of light available for growth. As the concentration of phytoplankton cells increase they can begin to shade their neighbours and increase the rate of attenuation in the upper layers of the water. Figure 9.19 in chapter 9 illustrates the result of regressing light attenuation against the concentration of chlorophyll present in the top 3-12 metres. It is clear that there is a strong relationship between the amount of phytoplankton in the water and the observed rate of attenuation.

In an attempt to reduce the possibility that the available light was actually a function of the existing chlorophyll concentration, it was decided to use the light available immediately below the water surface. Figure 9.16 illustrates the concentration of chlorophyll measured in the surface layer of the loch and this has been plotted alongside the irradiance found immediately below the waters surface. The lines on the plot are included to illustrate the general trends in the data. It seems clear that there is evidence of a relationship and indeed on analysis a significant correlation, $r = 0.636$, p o.o47, was found between light availability and the chlorophyll concentration.

The original premise was that increased amounts of precipitation would raise the levels of CDOM in the loch and that this would have a detrimental affect on the productivity in the loch. Figure 9.21 illustrates the result of a regression of chlorophyll concentration against CDOM in the top 3-12 metres of the loch. While it seems clear that there is a relatively strong relationship between the presence of CDOM and the concentration of chlorophyll in the loch, it is also evident that it is not the only factor influencing the growth of phytoplankton. Indeed regressing the available light against CDOM in the top 3-12 metres (see figure 9.22), shows a very weak correlation. Suspended particulates, self shading and attenuation by the water itself will, most likely, also have a role to play.

It is interesting that CDOM is also known as ”Gelbstoff”, or yellow stuff due its colour, and as McKee *et al.* (2002) note, effectively forms a yellow filter in the surface layer of the water column. Vahatalo *et al.* (2005) point out that this will filter wavelengths between 500 and 600 nm, a range particularly important for photosynthesis. This may mean that increasing the levels of CDOM in the loch could have a greater effect than simply attenuating the amount of light available for growth. Unfortunately no attempt was made to differentiate between the different wavelengths of light in the loch when measurements were made during 2008-09.

In conclusion, while the abundance of pelagic diatoms, dinoflagellates and small flagellates in Loch Creran have significantly decreased since the 1970's and the composition of the phytoplankton community in the loch has markedly altered, there appears to be no obvious, single cause. Instead the changes observed are most likely the result of an accumulation of different factors.

As water temperatures have risen this may have been accentuated by an increase in the numbers of herbivorous protozoans, ciliates and a possible change in the community structure of the larger zooplankton present in the loch. In addition the phytoplankton community in the loch has, since the 1990's been under increased pressure from grazing by farmed bivalves in the loch.

The extra rainfall has also increased the levels of CDOM entering the water column. This has affected the amount and quality of light available in the water column to phytoplankton with, at least some detrimental affects on their growth.

The most prominent of the factors affecting the phytoplankton community in Loch Creran is the change in local weather patterns. These have altered the intensity and pattern of precipitation in Loch Creran's catchment area and there is a strong likelihood that this has, at least sporadically, increased flushing rates and therefore increased the numbers of phytoplankton being lost to washout from the loch. These changes have also affected mixing regimes in the loch undoubtedly leading to losses of phytoplankton due to disentrainment and subsequent stratification.

12.9 Future Work

As is often the case with field based, ecological studies, this investigation seems to have raised more questions than it has answered. Very little is known about the community of zooplankton in Loch Creran. Studies of phytoplankton generally focus on the availability of light and nutrients, relegating herbivory to a steady state constant. However if water temperatures continue to rise, an understanding of the structure of the zooplankton community in the loch may allow a better understanding of any changes that may be expected to arise in the future.

The mechanisms by which the loch gains its seed population also remain largely unknown. It is not known whether cells lie dormant on the bed of the loch to overwinter, are introduced from the Lynn of Lorn or, most likely, are introduced through a combination of both methods. And finally it would be instructive to investigate the affect of CDOM on phytoplankton growth in the loch? Again a better understanding of these processes may allow better predictions regarding the future trajectories of the fate of the phytoplankton communities, not only in Loch Creran but in other Scottish sea lochs.

Chapter 13

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Appendices

Appendix A

A.1 Chlorophyll Measurements

Table A.1: Chlorophyll (Chl)(μg/l) and Pheopigment (Pheo)(μg/l) concentrations measured in Loch Creran, Loch Fyne and the Lynn of Lorn during 2008 and 2009. BP represents measurements from the pier at Barcaldine, Loch Creran. LY1 represents the station adjacent to the Greag Isles in the Lynn of Lorn. C1 to C6 refer to stations in Loch Creran (see table 2.4).

Date	Station	Depth(m)	Mean Chl.($\mu g/l$)	SD.	Pheo.($\mu g/l$)	SD.
01/03/08	BP	1	0.35	0.25	0.33	0.14
09/03/08	BP	1	0.12	0.03	0.14	0.06
23/03/08	BP	1	0.08	0.02	0.10	0.05
28/03/08	BP	1	0.19	0.01	0.16	0.03
02/04/08	C4	1	0.91	0.04	0.45	0.02
02/04/08	C4	10	0.51	0.28	0.71	0.19
02/04/08	C5	10	0.60	0.21	0.50	0.05
02/04/08	C5	1	0.48	0.14	0.31	0.00
02/04/08	C3	10	0.53	0.11	0.40	0.03
02/04/08	C3	1	0.64	0.22	0.29	0.11
02/04/08	LY1	10	0.67	0.09	0.34	0.05
02/04/08	LY1	1	0.41	0.05	0.22	0.05
06/04/08	BP	1	0.37	0.07	0.17	0.04
12/04/08	BP	1	0.36	0.07	0.12	0.06
20/04/08	BP	1	2.15	0.32	0.06	0.00
24/04/08	C5	10	0.63	0.13	0.23	0.08
24/04/08	C5	1	0.43	0.08	0.25	0.09

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Date	Station	Depth(m)	Mean Chl.($\mu g/l$)	SD.	Pheo.($\mu g/l$)	SD.
24/04/08	C3	1	1.34	0.50	0.37	0.03
24/04/08	C3	10	1.44	0.79	0.37	0.20
24/04/08	LY1	1	2.30	1.40	0.53	0.19
24/04/08	LY1	10	3.32	1.82	0.60	0.35
24/04/08	CU	10	0.37	0.04	0.16	0.04
24/04/08	CU	1	0.36	0.00	0.11	0.01
24/04/08	BP	1	1.02	0.05	0.34	0.01
04/05/08	BP	1	0.51	0.08	0.34	0.11
11/05/08	BP	1	1.39	0.15	0.79	0.04
13/05/08	BP	1	0.20	0.09	0.13	0.05
19/05/08	BP	1	0.37	0.05	0.14	0.03
24/05/08	BP	1	1.52	0.15	0.19	0.01
24/05/08	BP	1	1.42	0.00	-	-
02/06/08	BP	1	0.85	0.02	0.10	0.04
22/06/08	BP	1	1.25	0.20	0.64	0.00
12/07/08	BP	1	1.29	0.30	0.41	0.27
04/08/08	BP	1	1.11	0.19	0.58	0.20
14/09/08	BP	1	1.71	0.63	0.28	0.14
03/11/08	BP	1	0.13	0.09	0.06	0.03
01/12/08	BP	1	0.12	0.03	0.11	0.05
01/03/09	BP	1	0.36	0.00	0.17	0.00
09/03/09	BP	1	0.30	0.07	0.23	0.07
15/03/09	BP	1	0.26	0.08	0.12	0.03
25/03/09	LY1	40	0.11	0.00	0.08	0.00
25/03/09	C5	15	0.22	0.01	0.17	0.01
25/03/09	C5	2	0.88	0.05	0.62	0.02
25/03/09	C6	2	1.10	0.05	0.56	0.04
25/03/09	C3	8	0.58	0.03	0.29	0.01
25/03/09	C2	12	0.39	0.03	0.20	0.01
25/03/09	C6	18	0.17	0.01	0.20	0.01
25/03/09	LY1	40	0.11	0.00	0.08	0.00
25/03/09	C5	15	0.22	0.01	0.17	0.01
25/03/09	C5	2	0.88	0.05	0.62	0.06
25/03/09	C6	2	1.10	0.05	0.56	0.07
25/03/09	C3	8	0.58	0.03	0.29	0.03
25/03/09	C2	12	0.39	0.03	0.20	0.02
25/03/09	C6	18	0.17	0.01	0.20	0.01
08/04/09	LY1	40	0.15	0.00	0.14	0.01

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Date	Station	Depth(m)	Mean Chl.($\mu g/l$)	SD.	Pheo.($\mu g/l$)	SD.
08/04/09	LY1	2	2.28	0.12	0.44	0.15
08/04/09	C2	10	1.11	0.02	0.24	0.00
08/04/09	C2	2	1.09	0.02	0.22	0.03
08/04/09	C5	15	0.79	0.01	0.29	0.02
08/04/09	C5	2	0.85	0.02	0.30	0.04
08/04/09	C6	15	0.39	0.03	0.28	0.04
08/04/09	C6	2	0.80	0.09	0.33	0.02
13/04/09	BP	1	1.68	0.18	0.24	0.02
19/04/09	BP	1	2.89	1.75	1.08	0.51
27/04/09	BP	1	0.67	0.24	0.18	0.12
05/05/09	BP	1	2.46	1.11	0.28	0.08
19/05/09	C3	24	0.55	0.21	0.33	0.21
19/05/09	C3	1	2.88	0.45	1.29	0.35
19/05/09	LY1	10	1.16	0.21	0.16	0.03
19/05/09	C6	1	1.68	-	0.67	0.30
27/05/09	BP	1	1.33	0.49	1.07	0.08
22/06/09	LY1	5	2.86	0.33	0.38	0.15
22/06/09	C5	5	2.95	0.58	0.24	0.11
22/06/09	C3	5	3.09	0.21	0.29	0.11
13/07/09	BP	1	1.94	0.32	0.25	0.32
21/07/09	C3	5	2.10	1.15	0.47	0.04
21/07/09	C5	5	4.43	0.11	0.57	0.23
21/07/09	LY2	5	1.28	0.19	0.63	0.13
19/08/09	C5	5	1.40	0.33	0.31	0.18
19/08/09	C3	5	1.56	0.16	0.04	0.07
19/08/09	LY1	5	0.32	0.06	0.09	0.03
07/09/09	BP	1	0.80	0.39	0.28	0.09
22/09/09	BP	1	1.71	0.26	0.16	0.04
25/09/09	LY1	5	0.19	0.09	0.14	0.02
25/09/09	C3	5	0.78	0.04	0.20	0.02
25/09/09	C5	5	0.81	0.07	0.14	0.02
30/10/09	LY1	5	0.07	0.00	0.05	0.00
30/10/09	C5	5	0.14	0.00	0.07	0.01
12/03/10	BP	1	0.69	0.07	0.01	0.02

Appendix B

B.1 Nutrients

Table B.1: Mean concentration of nitrate (mg/l) recorded in Loch Creran and the Lynn of Lorn during 2009. BP refers to measurements made from the pier at Barcaldine, Argyll. LY1 is located in the Lynn of Lorn adjacent to the Greag Isles. SD = standard deviation.

Date	Location	Depth (m)	Mean Concentration (mg/l)	SD
01/03/09	BP	1	0.02857	0.03088
09/03/09	BP	1	0.03586	0.03295
12/03/09	BP	1	0.02376	0.02597
25/03/09	C5	15	0.10493	0.01459
25/03/09	C6	18	0.10482	0.02391
25/03/09	C1	12	0.08609	0.02774
25/03/09	C3	8	0.06211	0.02644
08/04/09	C2	10	0.07920	0.03325
08/04/09	C5	2	0.06302	0.03419
08/04/09	LY1	40	0.08579	0.02443
19/04/09	BP	1	0.00745	0.01125
27/04/09	BP	1	0.01196	0.01460
05/05/09	BP	1	0.00417	0.00683
19/05/09	C3	1	0.00238	0.00476
19/05/09	C6	20	0.02094	0.01532
19/05/09	LY1	10	0.04309	0.02490
22/06/09	C3	5	0.00329	0.00383
22/06/09	C5	5	0.00030	0.00060
22/06/09	C6	20	0.00844	0.01388

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Date	Location	Depth (m)	Mean Concentration (mg/l)	SD
22/06/09	LY1	5	0.00595	0.01036
13/07/09	BP	1	0.00714	0.01273
21/07/09	C3	5	0.00090	0.00114
21/07/09	C5	5	0.00541	0.00693
21/07/09	LY1	5	0.00149	0.00297
19/08/09	C3	5	0.01018	0.01189
19/08/09	LY1	5	0.00568	0.00698
25/09/09	C5	5	0.00839	0.00975
25/09/09	LY1	5	0.01736	0.02023
30/10/09	C5	5	0.05487	0.02606
30/10/09	LY1	5	0.01970	0.01880

Table B.2: Mean concentration of phosphate (mg/l) recorded in Loch Creran and the Lynn of Lorn during 2009. BP refers to measurements made from the pier at Barcaldine, Argyll. LY1 is located in the Lynn of Lorn adjacent to the Greag Isles. SD = standard deviation.

Date	Location	Depth (m)	Mean Concentration (mg/l)	SD
01/03/09	BP	1	0.00602	0.00238
09/03/09	BP	1	0.00259	0.00109
12/03/09	BP	1	0.00055	0.00044
25/03/09	C5	15	0.03624	0.00159
25/03/09	C6	18	0.01456	0.00402
25/03/09	C1	12	0.00000	0.00000
25/03/09	C3	8	0.01249	0.00202
08/04/09	C2	10	0.00014	0.00028
08/04/09	C5	2	0.00020	0.00026
08/04/09	LY1	40	0.01315	0.00396
19/04/09	BP	1	0.00117	0.00169
27/04/09	BP	1	0.00339	0.00207
05/05/09	BP	1	0.00124	0.00067
19/05/09	C3	1	0.00022	0.00043
19/05/09	C6	20	0.00091	0.00028
19/05/09	LY1	10	0.00121	0.00139
22/06/09	C3	5	0.00174	0.00135
22/06/09	C5	5	0.00271	0.00043
22/06/09	C6	20	0.00490	0.00245
22/06/09	LY1	5	0.00035	0.00069
13/07/09	BP	1	0.00188	0.00031
19/07/09	C3	5	0.00068	0.00065
21/07/09	C3	5	0.00043	0.00055
21/07/09	C5	5	0.00055	0.00078
21/07/09	LY1	5	0.00000	0.00000
19/08/09	LY1	5	0.00014	0.00027
25/09/09	C5	5	0.00083	0.00082
25/09/09	LY1	5	0.00000	0.00000
30/10/09	C5	5	0.00271	0.00329
30/10/09	LY1	5	0.00007	0.00014

Table B.3: Mean concentration of silicate (mg/l) recorded in Loch Creran and the Lynn of Lorn during 2009. BP refers to measurements made from the pier at Barcaldine, Argyll. LY1 is located in the Lynn of Lorn adjacent to the Greag Isles. SD = standard deviation.

Date	Location	Depth (m)	Mean Concentration (mg/l)	SD
01/03/09	BP	1	0.37323	0.37675
09/03/09	BP	1	0.17651	0.03677
12/03/09	BP	1	0.39699	0.26183
25/03/09	C5	15	0.34743	0.39008
25/03/09	C6	18	0.32008	0.17961
25/03/09	C1	12	0.30134	0.12960
25/03/09	C3	8	0.28600	0.11421
08/04/09	C2	10	0.30279	0.09639
08/04/09	C5	2	0.21266	0.04974
08/04/09	LY1	40	0.27581	0.10216
19/04/09	BP	1	0.15471	0.03080
27/04/09	BP	1	0.14828	0.06977
05/05/09	BP	1	0.14354	0.11463
19/05/09	C3	1	0.88695	1.69633
19/05/09	C6	20	0.19278	0.10921
19/05/09	LY1	10	0.18078	0.07880
22/06/09	C3	5	0.23106	0.12710
22/06/09	C5	5	0.13277	0.06510
22/06/09	C6	20	0.20201	0.05746
22/06/09	LY1	5	0.19061	0.03283
13/07/09	BP	1	0.12147	0.05971
21/07/09	C3	5	0.14101	0.06699
21/07/09	C5	5	0.98771	1.65580
21/07/09	LY1	5	0.19932	0.10302
19/08/09	C3	5	0.24279	0.14687
19/08/09	LY1	5	0.15626	0.07333
25/09/09	C5	5	0.22846	0.08292
25/09/09	LY1	5	0.27362	0.08155
30/10/09	C5	5	0.28148	0.26451
30/10/09	LY1	5	0.19106	0.11360

Appendix C

C.1 Irradiance

Table C.1: Irradiance (W hr m^2) measured at Dunstaffnage, Argyll, during 1978. Day = day of the year. Data provided courtesy of the BADC. (BADC 2011).

Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
1	300	2	388	3	611	4	573	5	397
6	174	7	404	8	536	9	552	10	331
11	609	12	859	13	290	14	490	15	586
16	465	17	1377	18	879	19	357	20	747
21	295	22	292	23	198	24	1012	25	1222
26	403	27	641	28	339	29	577	30	1096
31	732	32	401	33	744	34	399	35	796
36	698	37	565	38	895	39	1002	40	1958
41	2069	42	2002	43	1895	44	1212	45	2033
46	1897	47	1890	48	2436	49	2480	50	2443
51	2319	52	451	53	662	54	474	55	677
56	431	57	541	58	1932	59	1349	60	519
61	932	62	854	63	3032	64	2130	65	538
66	823	67	3044	68	701	69	1081	70	562
71	1515	72	1641	73	1263	74	1968	75	2902
76	3706	77	2111	78	1135	79	1897	80	3053
81	2029	82	1379	83	2467	84	1886	85	2609
86	2960	87	1599	88	2337	89	2214	90	2923
91	881	92	2476	93	2822	94	4787	95	4250
96	4055	97	3181	98	2536	99	2628	100	5448
101	3001	102	5044	103	2829	104	4965	105	3337

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Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
106	2933	107	5624	108	2681	109	3625	110	1578
111	3124	112	4224	113	3806	114	2355	115	4208
116	4018	117	2725	118	1030	119	3376	120	4875
121	6897	122	5288	123	1821	124	909	125	4149
126	4851	127	4458	128	6528	129	7708	130	3079
131	1693	132	3198	133	2637	134	6174	135	5072
136	5019	137	6915	138	4473	139	7482	140	7082
141	6935	142	2701	143	3062	144	7312	145	3494
146	2254	147	4790	148	6480	149	7692	150	6842
151	6532	152	6776	153	6939	154	5923	155	6358
156	4648	157	3895	158	3283	159	3805	160	3514
161	5882	162	2302	163	6458	164	8337	165	6301
166	3349	167	5518	168	8659	169	8170	170	3965
171	2349	172	2214	173	2818	174	2497	175	7040
176	4415	177	5702	178	2147	179	2374	180	3432
181	3467	182	2132	183	3015	184	4726	185	4118
186	7015	187	7531	188	1680	189	4801	190	6954
191	8268	192	2101	193	3631	194	1827	195	2503
196	4051	197	6467	198	3292	199	3363	200	2858
201	6426	202	5410	203	1844	204	3691	205	3419
206	2419	207	2125	208	3473	209	2907	210	1291
211	6212	212	6819	213	4917	214	4409	215	995
216	718	217	3807	218	3885	219	4812	220	4278
221	1402	222	4649	223	5638	224	2291	225	2544
226	2495	227	4191	228	3648	229	3714	230	2808
231	1385	232	3593	233	1326	234	1833	235	2481
236	2610	237	5942	238	4895	239	3420	240	2866
241	1511	242	4758	243	1744	244	2699	245	1904
246	4359	247	3770	248	423	249	4165	250	2459
251	3036	252	874	253	1676	254	2458	255	4477
256	1246	257	2552	258	2672	259	1232	260	3006
261	1740	262	1645	263	1501	264	702	265	466
266	1573	267	2139	268	2060	269	2092	270	2653
271	629	272	1082	273	1108	274	2047	275	1441
276	2375	277	2457	278	981	279	1092	280	2023
281	1276	282	1658	283	1390	284	2222	285	2445
286	1861	287	404	288	689	289	1432	290	2192
291	964	292	985	293	1458	294	377	295	1271

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Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
296	439	297	781	298	292	299	918	300	791
301	502	302	356	303	477	304	644	305	1390
306	1000	307	311	308	392	309	371	310	914
311	581	312	710	313	641	314	284	315	223
316	371	317	633	318	489	319	342	320	398
321	330	322	382	323	256	324	324	325	322
326	167	327	466	328	532	329	364	330	915
331	713	332	846	333	245	334	118	335	319
336	186	337	363	338	531	339	443	340	293
341	248	342	183	343	213	344	268	345	165
346	405	347	327	348	779	349	726	350	488
351	668	352	465	353	413	354	616	355	212
356	230	357	368	358	383	359	245	360	270
361	401	362	325	363	808	364	843	365	890

Table C.2: Irradiance (W hr m^2) measured at Dunstaffnage, Argyll, during 2009. Day = day of the year. Data provided by the British Atmospheric data centre (BADC 2011).

Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
1	551	2	468	3	286	4	295	5	598
6	62	7	273	8	114	9	451	10	60
11	396	12	396	13	525	14	360	15	130
16	390	17	390	18	382	19	406	20	151
21	625	22	509	23	311	24	528	25	390
26	482	27	466	28	807	29	147	30	382
31	279	32	805	33	807	34	291	35	406
36	877	37	1164	38	1291	39	1015	40	243
41	1499	42	1565	43	329	44	458	45	625
46	704	47	386	48	502	49	585	50	509
51	404	52	604	53	381	54	501	55	311
56	1097	57	843	58	585	59	1269	60	528
61	668	62	562	63	2181	64	1969	65	320
66	564	67	1043	68	1349	69	3144	70	482
71	1548	72	1489	73	497	74	1287	75	466
76	2941	77	3356	78	3616	79	3464	80	807
81	1299	82	3094	83	914	84	1929	85	147
86	2001	87	3508	88	2489	89	1850	90	166
91	1422	92	4144	93	4426	94	1579	95	279
96	1931	97	1690	98	2274	99	911	100	805
101	3454	102	3889	103	4052	104	1561	105	807
106	5277	107	5589	108	4971	109	6035	110	291
111	2817	112	4531	113	4796	114	1259	115	237
116	1305	117	1797	118	3508	119	1572	120	877
121	3520	122	5926	123	4807	124	1648	125	1164
126	1838	127	3743	128	3229	129	2639	130	1291
131	7479	132	7640	133	7718	134	5598	135	1015
136	3065	137	4840	138	2482	139	5182	140	1505
141	2786	142	7096	143	2146	144	1890	145	1499
146	5226	147	3624	148	1549	149	6358	150	1565
151	7831	152	7792	153	7000	154	8030	155	329
156	6647	157	3777	158	8302	159	7182	160	458
161	7769	162	6972	163	7991	164	4409	165	647
166	3738	167	5163	168	2767	169	4503	170	704

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Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
171	3966	172	2062	173	2313	174	7743	175	386
176	7590	177	6968	178	3046	179	4087	180	502
181	5647	182	2079	183	3931	184	874	185	585
186	6921	187	3218	188	4207	189	5668	190	1560
191	8248	192	7809	193	4621	194	4369	195	404
196	5092	197	5682	198	4071	199	2982	200	604
201	6475	202	2671	203	4831	204	5896	205	381
206	7372	207	3122	208	5145	209	3253	210	501
211	3929	212	2576	213	2909	214	4081	215	641
216	2703	217	5224	218	4160	219	5093	220	1097
221	3080	222	5533	223	2020	224	3207	225	843
226	940	227	2756	228	2688	229	3181	230	585
231	1017	232	3104	233	4813	234	4110	235	1269
236	4950	237	3213	238	1226	239	1718	240	1444
241	2366	242	2090	243	1344	244	2942	245	668
246	1167	247	3756	248	393	249	1653	250	562
251	1042	252	3013	253	3128	254	4162	255	2181
256	2819	257	3217	258	1480	259	4152	260	1969
261	924	262	2321	263	1923	264	573	265	1610
266	2095	267	686	268	1008	269	1492	270	564
271	574	272	829	273	1805	274	1961	275	1043
276	1813	277	2238	278	1065	279	2160	280	1349
281	2206	282	453	283	939	284	1437	285	3144
286	494	287	950	288	1096	289	2263	290	533
291	1121	292	646	293	668	294	1496	295	1548
296	875	297	530	298	252	299	1178	300	1489
301	982	302	308	303	170	304	780	305	497
306	492	307	511	308	941	309	916	310	1287
311	798	312	932	313	761	314	1105	315	808
316	557	317	736	318	409	319	519	320	2941
321	441	322	495	323	110	324	172	325	3356
326	258	327	346	328	103	329	258	330	3616
331	193	332	691	333	689	334	638	335	3464
336	256	337	418	338	438	339	380	340	2918
341	270	342	266	343	215	344	147	345	1299
346	520	347	454	348	293	349	571	350	3094
351	368	352	211	353	163	354	267	355	914
356	388	357	465	358	678	359	515	360	1929

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Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2	Day	W hr m^2
361	534	362	265	363	356	364	313	365	2191

Appendix D

D.1 Precipitation

Table D.1: Mean Precipitation between 1971 and 1981 measured at Dunstaffnage, Argyll. Data provided by the BADC (BADC 2011). DOY = Day of the year, SD = Standard deviation.

DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
1	5.1	6.9	2	4.1	4.2	3	10.7	13.1
4	4.0	7.9	5	9.9	9.6	6	5.0	4.9
7	5.1	5.0	8	4.1	6.7	9	6.4	8.4
10	6.5	6.7	11	8.2	8.8	12	6.1	9.7
13	4.1	3.9	14	5.0	5.9	15	3.6	5.0
16	4.3	4.9	17	3.0	4.4	18	5.6	13.9
19	5.5	7.6	20	7.6	6.8	21	4.6	5.0
22	9.2	8.4	23	4.9	5.0	24	5.1	5.7
25	5.4	5.9	26	5.4	5.7	27	4.7	6.5
28	3.9	2.7	29	6.4	9.7	30	7.6	8.7
31	4.8	4.7	32	2.4	1.9	33	2.6	5.3
34	5.3	5.8	35	1.7	2.5	36	3.2	4.2
37	2.9	4.7	38	1.7	2.6	39	2.6	2.4
40	3.7	5.5	41	6.5	8.4	42	3.6	4.0
43	5.7	6.6	44	4.2	5.8	45	1.9	2.6
46	5.3	6.3	47	1.6	2.3	48	2.3	5.6
49	1.9	3.1	50	4.1	5.2	51	3.4	4.2
52	2.6	3.7	53	4.0	3.2	54	5.1	6.6
55	0.9	1.3	56	3.9	7.4	57	1.5	2.2
58	4.1	8.7	59	1.9	2.6	60	3.4	3.9

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
61	5.8	6.4	62	9.5	12.9	63	3.7	3.8
64	4.0	5.9	65	6.5	6.9	66	6.2	6.6
67	5.5	6.9	68	3.7	6.8	69	3.2	4.2
70	3.7	4.7	71	2.7	3.4	72	3.7	5.6
73	1.9	2.8	74	0.7	1.3	75	2.5	4.3
76	1.1	2.7	77	2.6	3.5	78	1.2	1.5
79	2.3	5.0	80	2.3	3.5	81	6.6	8.5
82	2.7	4.4	83	1.4	2.8	84	6.1	6.1
85	3.6	4.3	86	1.8	2.5	87	4.4	4.2
88	2.3	3.3	89	6.6	10.5	90	7.9	12.1
91	5.8	7.9	92	3.0	2.6	93	5.0	11.7
94	3.9	6.3	95	3.9	6.1	96	2.7	3.4
97	2.6	3.5	98	1.0	1.8	99	1.4	3.6
100	1.7	2.0	101	2.4	4.3	102	4.5	4.2
103	2.3	2.2	104	1.8	2.1	105	2.4	3.2
106	1.4	2.3	107	1.8	4.1	108	0.9	1.3
109	1.0	1.8	110	1.4	2.3	111	2.5	4.2
112	3.3	6.9	113	3.1	7.3	114	0.6	1.4
115	0.9	2.7	116	0.2	0.5	117	1.1	2.7
118	1.7	3.0	119	1.6	2.9	120	5.8	8.5
121	3.9	7.8	122	2.6	4.1	123	1.2	2.6
124	2.9	4.9	125	0.9	2.0	126	0.5	1.2
127	2.8	5.0	128	0.7	1.4	129	1.5	2.7
130	4.1	6.8	131	2.8	2.0	132	3.3	3.1
133	5.0	8.2	134	1.3	1.9	135	2.8	6.2
136	0.4	0.9	137	3.3	6.9	138	4.7	8.9
139	2.5	4.9	140	1.4	1.2	141	1.3	2.1
142	2.3	4.0	143	2.0	2.6	144	1.8	2.8
145	0.2	0.3	146	2.9	4.6	147	4.1	11.2
148	2.1	3.3	149	0.8	1.8	150	3.0	5.7
151	1.8	3.8	152	0.9	1.4	153	2.6	2.9
154	1.8	2.3	155	2.1	3.0	156	4.4	5.4
157	8.4	11.6	158	3.8	4.3	159	3.2	5.5
160	3.1	4.6	161	1.9	3.5	162	2.4	4.6
163	2.5	5.6	164	3.3	6.2	165	1.0	1.5
166	3.2	4.2	167	3.8	5.6	168	1.4	1.9
169	3.4	4.2	170	7.8	9.9	171	2.4	3.8
172	5.0	5.8	173	4.1	6.1	174	4.5	5.3

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
175	3.1	4.9	176	2.2	3.1	177	1.0	2.1
178	0.8	2.2	179	2.2	2.6	180	2.2	2.9
181	2.7	2.7	182	2.6	4.2	183	4.4	9.3
184	1.6	1.8	185	0.6	2.4	186	1.9	4.0
187	3.9	4.8	188	1.8	3.8	189	1.8	2.1
190	2.2	3.8	191	2.0	4.2	192	3.3	4.2
193	1.8	2.3	194	2.2	2.6	195	5.3	6.4
196	3.8	4.9	197	5.8	6.3	198	2.0	3.7
199	2.0	4.2	200	3.8	4.4	201	5.4	9.0
202	1.6	2.3	203	4.1	6.1	204	7.9	7.6
205	7.3	8.9	206	4.4	7.6	207	2.7	4.3
208	4.5	6.3	209	6.5	8.9	210	2.1	2.7
211	2.1	4.6	212	1.0	2.3	213	1.3	3.6
214	2.3	2.9	215	2.6	2.9	216	4.1	5.9
217	7.1	7.0	218	6.4	9.7	219	4.5	5.7
220	1.3	2.4	221	3.8	3.9	222	2.5	4.4
223	1.1	2.2	224	3.6	5.4	225	3.4	4.3
226	2.9	4.7	227	4.8	5.7	228	4.4	4.7
229	2.2	3.5	230	2.9	6.5	231	2.1	3.8
232	2.0	3.2	233	5.8	5.6	234	2.9	3.6
235	4.1	6.8	236	2.3	2.9	237	2.4	4.3
238	1.2	2.5	239	0.9	3.2	240	1.5	4.0
241	3.6	4.3	242	2.2	4.1	243	5.5	9.3
244	4.1	6.9	245	4.1	4.4	246	4.9	5.5
247	5.4	6.3	248	4.7	4.9	249	9.1	9.1
250	4.4	6.3	251	6.4	12.4	252	8.4	10.2
253	9.7	10.3	254	5.1	4.6	255	2.8	3.7
256	9.6	14.2	257	4.0	3.8	258	5.4	7.7
259	1.3	1.9	260	7.8	6.4	261	5.1	8.0
262	1.9	2.7	263	4.3	5.8	264	4.2	5.0
265	5.7	6.3	266	7.0	6.9	267	4.2	6.1
268	9.6	12.7	269	4.9	5.1	270	7.1	6.7
271	7.6	8.7	272	7.2	10.5	273	6.0	7.9
274	4.0	6.2	275	4.5	4.1	276	2.7	5.3
277	6.2	6.4	278	9.0	9.1	279	4.3	6.5
280	5.3	9.0	281	7.8	9.3	282	7.5	6.7
283	4.2	5.9	284	1.6	6.5	285	4.2	7.2
286	2.3	3.8	287	1.4	2.0	288	3.2	6.6

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
289	1.9	5.6	290	1.0	3.2	291	2.9	8.1
292	5.1	10.7	293	3.5	5.0	294	2.4	5.0
295	3.4	18.1	296	2.6	2.2	297	7.6	6.8
298	5.0	6.3	299	3.4	4.6	300	1.8	2.4
301	5.0	6.6	302	3.9	6.4	303	4.9	5.5
304	8.2	10.4	305	6.5	8.1	306	5.8	5.6
307	12.9	11.3	308	6.9	9.1	309	8.2	7.4
310	5.7	5.1	311	5.0	8.0	312	6.5	9.4
313	5.8	5.2	314	7.9	10.1	315	8.1	8.9
316	9.9	9.0	317	5.7	6.6	318	7.6	9.3
319	10.1	12.5	320	6.3	4.5	321	5.7	6.9
322	9.7	11.5	323	6.8	6.1	324	5.5	6.8
325	5.0	6.5	326	7.9	10.0	327	6.3	5.8
328	5.6	5.8	329	7.6	8.2	330	5.4	5.5
331	5.3	6.8	332	7.0	7.8	333	7.9	9.3
334	5.6	5.3	335	7.8	9.4	336	6.0	6.6
337	2.6	3.6	338	2.9	3.6	339	5.1	6.7
340	3.7	4.6	341	4.7	5.5	342	6.3	5.3
343	4.8	4.5	344	5.7	4.8	345	11.3	12.5
346	6.1	3.5	347	7.6	8.8	348	7.4	7.1
349	3.2	4.2	350	6.7	9.1	351	5.8	7.0
352	6.1	6.6	353	3.5	6.2	354	4.3	9.3
355	2.5	4.5	356	2.3	3.6	357	5.7	7.4
358	5.4	9.8	359	7.8	8.6	360	9.0	10.2
361	5.9	6.9	362	5.1	5.0	363	6.1	8.2
364	5.5	5.0	365	8.8	9.5			

Table D.2: Mean Precipitation between 2002 and 2009 measured at Dunstaffnage, Argyll. Data provided by the BADC (BADC 2011). DOY = Day of the year, SD = Standard deviation.

DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
1	2.3	3.4	2	2.2	2.7	3	4.4	7.9
4	2.7	2.8	5	5.6	4.8	6	10.3	16.2
7	8.2	11.3	8	9.0	10.8	9	9.8	9.0
10	7.9	6.9	11	13.1	11.0	12	8.7	7.2
13	9.7	8.2	14	8.8	7.3	15	5.8	2.0
16	4.9	4.3	17	6.5	3.8	18	12.6	5.6
19	10.7	8.2	20	9.6	5.6	21	5.1	9.1
22	5.1	6.2	23	5.0	5.6	24	5.4	9.2
25	5.1	6.9	26	2.9	6.7	27	2.4	3.4
28	2.0	2.9	29	2.7	4.3	30	4.1	4.5
31	4.5	4.4	32	4.7	6.1	33	6.4	11.9
34	2.7	2.9	35	5.8	7.1	36	1.6	1.8
37	3.7	3.8	38	6.9	7.7	39	6.2	8.0
40	5.7	10.9	41	4.3	4.2	42	5.3	6.8
43	8.3	7.9	44	2.3	2.1	45	3.7	6.7
46	5.6	8.0	47	3.0	6.4	48	2.8	2.8
49	1.2	3.0	50	2.1	4.8	51	2.0	2.4
52	3.0	5.7	53	2.2	3.6	54	1.3	1.8
55	0.9	1.0	56	2.3	4.0	57	3.5	6.2
58	7.5	11.3	59	5.7	10.2	60	3.2	4.1
61	2.6	3.3	62	6.5	11.3	63	6.2	5.3
64	6.3	6.8	65	6.0	7.2	66	6.3	4.6
67	6.0	4.6	68	8.6	10.2	69	3.9	3.8
70	6.2	5.3	71	3.5	4.3	72	3.7	4.5
73	5.8	10.3	74	5.0	7.8	75	6.5	6.0
76	8.2	11.8	77	2.3	3.3	78	2.2	4.2
79	1.1	1.6	80	6.6	9.3	81	1.8	2.2
82	1.4	1.8	83	2.0	2.7	84	0.8	1.2
85	3.7	6.3	86	2.8	4.0	87	1.2	2.0
88	2.3	2.7	89	1.6	2.1	90	1.7	1.7
91	3.9	7.2	92	3.1	7.4	93	1.8	2.5
94	5.0	7.5	95	2.7	3.7	96	2.5	4.7
97	2.3	3.2	98	2.2	3.5	99	1.2	1.4
100	1.3	2.6	101	5.6	7.0	102	1.8	2.4

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
103	0.9	1.1	104	2.3	3.8	105	2.8	5.9
106	4.8	7.8	107	2.2	4.6	108	3.1	4.2
109	0.6	1.1	110	2.0	3.8	111	5.0	6.3
112	6.7	8.7	113	3.6	6.2	114	4.4	3.3
115	3.4	2.6	116	4.4	5.5	117	6.3	6.8
118	3.4	5.7	119	0.8	1.6	120	5.0	4.9
121	4.8	5.5	122	4.7	5.1	123	2.2	2.2
124	7.5	9.3	125	7.1	6.4	126	6.7	6.9
127	6.4	6.0	128	4.3	6.1	129	3.8	6.0
130	4.7	6.2	131	1.0	2.4	132	1.3	3.4
133	1.3	2.2	134	1.5	3.1	135	1.8	2.8
136	3.1	3.0	137	3.1	3.6	138	5.4	3.4
139	5.9	6.0	140	1.2	0.9	141	3.7	5.9
142	3.4	4.1	143	6.0	6.0	144	6.3	6.5
145	5.9	6.9	146	2.7	3.2	147	3.3	4.6
148	0.7	0.7	149	2.3	3.1	150	1.8	2.6
151	2.0	3.9	152	2.4	5.7	153	4.5	5.9
154	5.5	10.1	155	3.5	6.6	156	0.4	0.6
157	2.1	4.4	158	2.0	4.0	159	4.1	5.3
160	0.5	1.2	161	3.4	5.3	162	2.1	2.2
163	3.2	2.9	164	7.0	5.9	165	4.9	9.0
166	2.6	3.8	167	1.2	1.3	168	7.4	7.4
169	7.3	6.9	170	3.9	3.8	171	6.0	5.4
172	5.7	5.3	173	4.4	3.0	174	1.7	3.7
175	2.9	4.1	176	1.0	1.9	177	1.3	2.3
178	4.5	6.5	179	3.0	4.3	180	2.2	2.5
181	6.8	5.7	182	3.2	3.7	183	3.9	5.4
184	5.8	8.8	185	1.1	1.3	186	1.0	1.3
187	2.8	3.9	188	1.9	2.3	189	2.6	2.5
190	3.9	9.2	191	1.6	2.5	192	1.9	2.8
193	1.3	1.3	194	0.4	0.5	195	4.2	5.4
196	1.1	1.6	197	0.9	1.3	198	2.7	3.7
199	2.6	4.4	200	4.0	4.9	201	6.5	6.3
202	3.9	5.0	203	2.4	4.3	204	3.4	4.0
205	1.5	1.7	206	4.2	4.9	207	5.2	7.6
208	1.4	1.7	209	4.8	5.3	210	4.0	5.7
211	5.4	12.0	212	4.0	5.1	213	4.6	6.2
214	4.5	5.7	215	4.7	7.4	216	4.8	5.9

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
217	2.7	3.0	218	3.0	4.6	219	0.9	1.1
220	0.8	1.2	221	3.6	4.1	222	8.8	20.5
223	9.5	11.3	224	4.3	3.5	225	3.6	4.9
226	5.8	6.8	227	4.5	5.8	228	1.1	1.9
229	9.8	15.5	230	3.6	3.6	231	8.3	11.0
232	4.3	10.0	233	5.4	6.5	234	1.9	3.1
235	6.3	8.9	236	1.7	4.0	237	2.4	3.7
238	2.3	2.1	239	7.9	8.0	240	5.0	6.9
241	2.8	3.0	242	6.3	8.7	243	6.2	9.3
244	3.9	6.7	245	0.9	1.2	246	4.9	5.2
247	1.5	2.5	248	11.2	13.7	249	4.2	3.7
250	5.5	5.8	251	3.3	8.3	252	1.6	2.8
253	1.9	4.9	254	1.2	2.3	255	6.1	6.9
256	7.3	9.6	257	8.3	12.7	258	1.0	1.9
259	1.3	2.5	260	7.5	8.4	261	5.1	6.6
262	8.2	7.9	263	8.0	11.9	264	11.3	10.4
265	5.4	4.6	266	1.7	2.0	267	3.4	4.0
268	3.9	4.4	269	1.8	2.5	270	2.4	3.5
271	3.7	4.1	272	4.2	3.7	273	1.1	1.3
274	3.8	5.1	275	4.2	3.0	276	6.6	8.0
277	2.8	3.1	278	3.3	4.6	279	12.6	9.1
280	2.5	4.0	281	1.7	2.0	282	8.1	9.2
283	0.6	0.7	284	6.1	5.3	285	6.7	10.7
286	1.0	1.7	287	0.9	2.0	288	2.8	5.4
289	1.7	4.1	290	1.4	2.6	291	2.2	2.3
292	1.7	2.1	293	5.1	7.3	294	2.8	4.9
295	4.4	9.4	296	1.8	2.3	297	6.7	7.7
298	12.7	17.4	299	2.6	3.5	300	9.4	15.8
301	3.7	3.7	302	5.0	4.9	303	4.7	6.3
304	4.1	7.1	305	5.6	7.4	306	6.1	5.4
307	7.5	6.8	308	4.2	3.5	309	3.5	3.3
310	5.9	7.8	311	5.8	4.7	312	4.5	4.4
313	2.8	3.7	314	12.0	8.8	315	8.9	7.2
316	6.0	6.0	317	5.5	5.7	318	3.2	3.3
319	6.5	6.8	320	9.0	8.0	321	5.6	7.5
322	6.4	10.8	323	8.4	10.2	324	8.1	8.8
325	7.2	8.0	326	3.3	4.0	327	5.8	7.2
328	5.8	10.2	329	8.8	8.0	330	5.3	5.3

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
331	8.6	8.3	332	2.6	4.3	333	6.8	5.4
334	9.9	10.0	335	3.4	2.9	336	3.4	3.2
337	9.6	15.6	338	6.4	6.8	339	5.7	8.8
340	3.6	4.4	341	4.5	5.9	342	3.0	3.2
343	3.1	4.4	344	12.5	19.0	345	2.2	2.8
346	3.8	6.6	347	12.3	20.1	348	7.4	8.4
349	4.6	6.2	350	1.8	2.4	351	2.6	3.2
352	2.3	3.5	353	3.3	5.2	354	5.8	5.3
355	8.0	11.3	356	3.1	4.0	357	9.5	8.3
358	4.8	6.0	359	3.4	5.6	360	5.1	6.8
361	5.0	5.9	362	2.9	4.4	363	4.3	5.9
364	4.6	5.8						

Table D.3: Mean Precipitation between 1977 and 1980 measured at the Strath of Appin, Dungrianach, Argyll. Data provided by the BADC (BADC 2011). DOY = Day of the year, SD = Standard deviation.

DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
1	6.1	9.2	2	8.4	12.1	3	9.5	9.1
4	5.5	7.9	5	10.4	8.2	6	7.6	7.0
7	7.0	8.5	8	1.8	1.8	9	7.7	5.4
10	3.9	3.7	11	2.6	5.0	12	2.8	3.8
13	3.1	4.4	14	6.0	8.9	15	5.7	6.1
16	2.3	4.0	17	5.6	11.5	18	0.4	0.8
19	2.6	4.1	20	4.0	4.0	21	2.4	2.9
22	7.1	7.4	23	3.0	2.8	24	2.3	2.5
25	2.6	2.6	26	3.8	6.2	27	1.5	2.5
28	3.2	3.5	29	2.9	2.7	30	5.8	6.8
31	6.9	8.6	32	4.5	4.0	33	8.6	8.2
34	9.1	9.0	35	5.0	5.2	36	3.4	3.3
37	5.2	7.3	38	6.0	7.4	39	5.2	9.1
40	0.2	0.3	41	3.0	5.2	42	1.8	2.6
43	3.4	4.7	44	6.0	8.2	45	0.9	1.2
46	5.3	6.3	47	0.5	0.8	48	0.6	1.3
49	4.1	6.7	50	6.2	8.4	51	1.0	2.3
52	0.5	1.1	53	5.4	5.6	54	3.6	5.3
55	0.5	1.1	56	2.4	5.5	57	2.3	3.2
58	6.3	12.4	59	2.5	2.5	60	2.6	3.9
61	8.0	8.6	62	14.5	16.8	63	5.1	6.7
64	5.1	8.3	65	6.7	7.0	66	10.0	9.1
67	14.8	12.0	68	6.0	7.4	69	6.3	3.1
70	8.5	6.5	71	3.6	1.7	72	5.2	7.0
73	3.9	4.1	74	1.0	1.5	75	4.4	7.5
76	1.6	3.6	77	3.3	3.0	78	4.0	4.2
79	2.8	3.5	80	4.5	4.4	81	2.6	3.1
82	1.4	3.1	83	4.0	6.8	84	12.0	8.5
85	6.0	6.0	86	2.7	3.3	87	2.9	4.0
88	4.4	5.9	89	2.1	4.5	90	6.0	7.0
91	6.6	8.9	92	5.0	5.2	93	2.5	3.4
94	0.6	1.2	95	0.0	0.0	96	0.2	0.4
97	0.0	0.0	98	1.0	0.9	99	0.3	0.7

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
100	0.6	0.8	101	1.2	1.5	102	2.3	2.5
103	3.0	3.7	104	1.5	2.8	105	1.6	2.5
106	1.6	2.5	107	0.9	1.6	108	0.3	0.7
109	0.6	1.2	110	2.5	3.8	111	4.6	7.9
112	7.3	12.5	113	7.0	10.1	114	4.0	7.7
115	1.2	2.7	116	2.1	3.1	117	1.8	2.9
118	4.9	4.1	119	0.6	0.3	120	2.5	3.9
121	0.1	0.2	122	0.4	0.7	123	1.9	2.9
124	3.6	2.9	125	0.9	0.8	126	0.1	0.2
127	7.1	11.9	128	2.3	3.7	129	0.4	0.7
130	0.9	1.7	131	1.8	1.7	132	5.8	7.0
133	1.8	1.4	134	1.8	2.2	135	5.6	7.6
136	0.4	0.6	137	3.9	4.1	138	2.3	3.7
139	0.8	1.9	140	1.1	2.4	141	1.9	2.4
142	1.5	2.4	143	0.9	1.1	144	2.9	5.1
145	1.0	1.9	146	0.5	1.2	147	0.9	0.9
148	1.1	1.5	149	1.6	2.1	150	1.4	2.6
151	0.7	1.4	152	1.3	2.4	153	0.5	1.1
154	0.5	0.7	155	3.7	5.0	156	6.2	4.6
157	6.4	7.7	158	5.9	4.3	159	5.5	6.7
160	8.2	9.2	161	3.5	4.2	162	0.3	0.6
163	0.0	0.1	164	4.4	9.8	165	5.2	8.0
166	2.2	3.0	167	6.1	8.7	168	1.6	3.1
169	2.2	4.7	170	1.0	1.7	171	3.0	5.9
172	8.1	7.6	173	5.8	5.8	174	5.0	6.5
175	0.7	1.5	176	0.7	1.0	177	0.2	0.5
178	0.7	1.2	179	5.6	5.5	180	1.9	1.7
181	5.7	5.5	182	2.7	3.3	183	2.8	2.6
184	4.5	3.3	185	1.0	2.0	186	6.0	7.6
187	3.5	4.8	188	6.2	9.6	189	1.8	1.8
190	7.7	11.1	191	0.2	0.3	192	2.4	5.3
193	0.9	1.3	194	1.9	2.7	195	3.7	5.4
196	0.8	1.7	197	8.8	11.2	198	5.4	7.5
199	6.2	7.8	200	6.5	7.4	201	5.7	5.4
202	4.5	5.2	203	5.2	4.4	204	12.1	14.8
205	9.3	9.3	206	4.2	2.9	207	5.7	6.8
208	8.9	12.8	209	11.2	10.2	210	3.5	4.8
211	0.3	0.8	212	1.9	4.2	213	2.8	4.7

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
214	2.4	3.6	215	3.1	2.6	216	3.9	4.5
217	6.6	7.9	218	7.3	14.6	219	1.0	2.3
220	0.3	0.4	221	0.1	0.2	222	0.3	0.7
223	3.1	4.7	224	6.0	8.8	225	3.5	5.8
226	4.3	4.2	227	4.1	2.3	228	4.6	6.1
229	3.0	4.2	230	3.2	5.0	231	3.6	3.4
232	5.2	5.9	233	7.1	6.3	234	6.9	5.9
235	4.4	8.3	236	0.5	0.6	237	2.2	3.1
238	0.5	0.9	239	0.4	0.5	240	0.0	0.0
241	4.5	5.6	242	1.1	1.2	243	5.8	7.8
244	5.0	10.1	245	8.1	9.1	246	12.0	12.1
247	8.8	10.1	248	10.2	11.3	249	11.5	11.4
250	6.6	10.6	251	9.3	11.7	252	8.8	13.8
253	18.4	22.2	254	16.0	7.5	255	7.8	6.2
256	14.8	17.6	257	5.4	3.8	258	9.2	11.8
259	3.0	3.7	260	6.7	4.2	261	14.1	12.4
262	5.5	3.8	263	9.7	9.5	264	6.5	6.6
265	9.8	11.4	266	6.7	9.7	267	13.8	13.7
268	6.2	7.4	269	7.8	5.6	270	10.7	6.3
271	10.4	5.4	272	11.4	12.8	273	10.6	14.5
274	7.0	6.6	275	7.6	6.1	276	3.0	3.5
277	7.2	3.1	278	14.0	11.2	279	4.6	5.6
280	6.1	6.8	281	9.2	9.6	282	11.7	9.4
283	5.9	7.0	284	3.5	3.5	285	7.4	7.9
286	3.4	4.6	287	0.8	1.1	288	5.3	10.0
289	1.8	2.9	290	3.3	3.6	291	2.7	2.6
292	6.9	8.9	293	7.9	4.8	294	2.5	2.0
295	4.0	5.0	296	2.6	2.9	297	10.0	7.9
298	4.3	1.9	299	3.6	4.6	300	3.7	4.1
301	11.0	6.4	302	9.6	8.1	303	10.5	6.2
304	16.2	10.9	305	13.3	12.1	306	6.3	3.8
307	20.1	14.0	308	7.6	7.0	309	5.7	5.9
310	4.7	7.3	311	6.4	10.0	312	7.7	15.0
313	4.5	4.1	314	13.1	16.2	315	9.3	10.9
316	4.9	9.2	317	5.8	8.2	318	10.2	12.9
319	13.0	15.4	320	7.0	4.8	321	10.3	9.1
322	15.5	10.3	323	7.5	5.2	324	13.1	12.7
325	9.9	4.4	326	21.1	13.3	327	11.6	2.7

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
328	7.1	3.4	329	8.6	10.4	330	11.9	11.9
331	4.0	7.1	332	7.3	7.5	333	3.9	5.8
334	7.7	8.7	335	1.8	3.5	336	2.6	3.6
337	1.5	2.2	338	7.6	8.5	339	3.6	5.1
340	2.2	2.4	341	1.4	1.6	342	4.5	6.2
343	3.4	5.8	344	9.5	6.2	345	12.7	20.1
346	5.8	5.2	347	5.2	6.0	348	4.5	4.3
349	5.7	7.0	350	5.8	12.3	351	4.0	8.2
352	4.4	5.4	353	3.7	6.5	354	2.5	2.7
355	1.1	1.4	356	0.2	0.2	357	5.0	7.3
358	6.1	9.8	359	6.0	9.1	360	6.0	5.7
361	8.0	8.5	362	1.1	0.9	363	6.5	9.5
364	3.3	4.3	365	6.2	9.9			

Table D.4: Mean Precipitation between 2005 and 2009 measured at the Strath of Appin, Dungrianach, Argyll. Data provided by the BADC (BADC 2011). DOY = Day of the year, SD = Standard deviation.

DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
1	9.0	10.2	2	6.0	7.7	3	8.5	8.4
4	5.3	6.6	5	4.2	3.2	6	10.8	16.2
7	19.1	14.2	8	10.3	12.3	9	7.9	9.4
10	11.5	13.1	11	20.7	13.4	12	14.2	10.2
13	11.5	7.6	14	5.7	7.3	15	8.4	7.6
16	6.9	1.5	17	6.3	0.9	18	11.7	8.7
19	17.5	12.3	20	13.4	5.4	21	8.8	2.1
22	2.8	4.7	23	1.5	3.0	24	2.2	2.2
25	2.2	4.0	26	2.6	4.2	27	1.1	1.5
28	1.5	2.0	29	0.5	0.9	30	0.3	0.5
31	7.4	8.1	32	1.1	1.7	33	1.8	1.2
34	5.6	8.1	35	5.5	6.6	36	5.8	6.2
37	1.3	1.1	38	7.0	9.0	39	10.5	11.1
40	4.1	6.1	41	6.1	10.7	42	1.7	2.2
43	10.9	11.7	44	4.4	4.9	45	6.3	10.7
46	3.9	6.5	47	7.7	8.9	48	5.4	6.1
49	1.6	2.1	50	0.6	1.0	51	0.7	0.8
52	9.0	15.3	53	7.7	11.9	54	4.8	8.0
55	6.7	12.4	56	2.7	3.2	57	7.6	15.0
58	4.8	5.9	59	13.6	24.5	60	8.3	5.8
61	5.6	9.3	62	6.9	7.6	63	7.8	7.0
64	4.5	4.5	65	6.5	12.7	66	6.2	5.8
67	8.1	7.8	68	8.9	8.9	69	6.8	5.0
70	3.6	1.6	71	8.6	7.4	72	6.8	7.7
73	4.7	4.2	74	5.1	5.3	75	6.8	10.5
76	7.4	10.9	77	16.6	28.4	78	2.9	4.4
79	0.6	1.3	80	1.7	3.8	81	2.6	1.9
82	2.1	2.2	83	1.4	1.8	84	4.3	6.9
85	5.7	7.9	86	3.7	5.1	87	3.3	3.7
88	4.1	4.8	89	2.5	2.7	90	1.9	2.5
91	1.2	1.3	92	3.7	6.8	93	1.8	2.9
94	3.1	3.7	95	5.3	5.0	96	4.6	5.2
97	5.2	4.6	98	5.5	6.5	99	2.1	2.7

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
100	4.7	4.7	101	3.7	5.1	102	4.2	4.3
103	3.6	4.9	104	2.3	3.8	105	0.7	1.4
106	3.3	3.9	107	1.0	1.7	108	3.8	6.6
109	2.6	3.7	110	0.4	0.9	111	2.0	2.4
112	6.5	13.9	113	9.0	10.7	114	4.4	5.4
115	7.6	7.2	116	3.0	4.0	117	8.1	9.9
118	2.4	3.2	119	4.0	8.6	120	0.8	0.9
121	6.5	7.7	122	4.2	4.4	123	4.7	6.8
124	3.5	4.1	125	5.9	8.8	126	6.5	4.7
127	7.1	7.6	128	8.7	8.9	129	2.6	3.9
130	3.5	4.9	131	2.4	5.3	132	0.4	0.7
133	0.6	1.4	134	0.2	0.5	135	1.2	2.1
136	1.8	3.9	137	5.5	7.0	138	4.6	6.5
139	7.8	4.7	140	4.0	4.9	141	4.6	6.1
142	1.3	1.7	143	2.7	3.1	144	4.9	5.0
145	5.3	4.9	146	10.1	12.3	147	7.6	9.9
148	2.3	2.4	149	3.8	6.5	150	3.7	5.3
151	0.7	1.5	152	1.3	1.3	153	5.9	11.6
154	6.8	11.6	155	1.2	2.3	156	0.2	0.4
157	2.6	2.9	158	2.8	5.5	159	1.2	2.0
160	0.8	1.4	161	0.1	0.3	162	0.1	0.1
163	2.2	2.7	164	2.1	3.3	165	0.2	0.3
166	5.7	7.5	167	6.4	8.8	168	7.1	8.4
169	9.1	8.1	170	14.8	7.8	171	3.7	4.3
172	14.0	16.6	173	7.1	4.7	174	2.8	3.1
175	1.1	1.3	176	0.0	0.0	177	1.7	3.4
178	2.7	3.8	179	0.7	1.3	180	3.2	5.3
181	2.8	4.5	182	4.6	7.5	183	3.9	6.0
184	4.0	2.9	185	7.7	13.3	186	4.3	4.5
187	2.3	3.7	188	2.8	1.7	189	2.7	3.0
190	8.6	13.7	191	0.7	1.1	192	3.8	7.4
193	1.3	1.7	194	1.2	1.5	195	4.6	6.9
196	1.8	2.2	197	1.8	4.0	198	3.1	4.7
199	6.1	6.5	200	4.4	3.0	201	8.8	7.4
202	3.1	4.5	203	1.7	3.8	204	1.4	2.6
205	1.2	2.0	206	0.6	1.3	207	4.8	6.8
208	1.7	2.5	209	1.4	1.7	210	3.4	5.7
211	1.6	1.6	212	2.9	5.0	213	14.7	12.4

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
214	3.9	3.3	215	15.9	25.2	216	5.7	6.1
217	5.2	5.7	218	6.0	7.5	219	3.0	5.1
220	1.5	1.4	221	1.2	1.4	222	5.0	3.8
223	2.7	2.8	224	10.3	11.7	225	3.6	6.1
226	5.5	9.2	227	7.1	11.7	228	5.0	6.6
229	1.3	1.0	230	12.9	22.6	231	7.3	9.1
232	14.0	26.0	233	3.4	7.1	234	6.4	7.3
235	4.7	4.6	236	6.4	9.9	237	3.5	3.2
238	7.7	5.8	239	6.7	4.1	240	7.7	4.5
241	10.4	12.7	242	2.0	2.2	243	6.5	7.3
244	12.9	12.0	245	3.6	2.2	246	3.9	3.9
247	4.5	5.1	248	4.4	5.0	249	14.0	22.0
250	2.5	4.1	251	7.7	12.3	252	1.6	2.8
253	1.9	2.5	254	5.4	10.3	255	5.4	5.5
256	5.9	7.0	257	9.5	12.3	258	2.6	3.3
259	7.5	15.1	260	7.3	7.3	261	2.0	1.8
262	11.0	13.1	263	11.0	8.2	264	15.4	26.4
265	7.9	11.8	266	4.0	5.0	267	7.2	5.3
268	3.8	2.8	269	0.2	0.3	270	4.5	7.4
271	6.4	5.4	272	8.3	10.2	273	2.9	2.4
274	7.4	9.6	275	3.2	3.2	276	5.9	6.5
277	5.4	6.8	278	5.1	8.1	279	6.1	8.3
280	1.5	1.9	281	8.6	11.9	282	12.8	8.6
283	5.9	9.9	284	16.2	12.0	285	5.4	3.9
286	1.2	0.6	287	3.3	2.3	288	0.8	0.7
289	6.1	10.3	290	3.9	5.0	291	1.5	1.2
292	2.8	3.7	293	2.3	2.1	294	14.2	13.9
295	5.8	11.7	296	4.2	4.7	297	7.2	10.3
298	20.1	14.8	299	10.5	9.2	300	11.7	8.8
301	17.9	16.2	302	4.3	4.7	303	6.6	6.5
304	6.1	6.5	305	10.6	102.4	306	7.4	12.1
307	7.4	8.9	308	6.4	5.5	309	3.3	3.3
310	1.8	3.3	311	6.7	5.1	312	7.0	11.5
313	5.6	5.6	314	13.6	12.9	315	12.9	11.8
316	12.8	9.8	317	6.0	6.0	318	6.2	3.7
319	11.5	7.2	320	10.9	6.7	321	5.6	5.6
322	10.0	10.9	323	9.2	8.9	324	9.7	14.6
325	18.7	24.5	326	2.2	1.8	327	5.3	7.4

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DOY	Rain(mm)	SD	DOY	Rain(mm)	SD	DOY	Rain(mm)	SD
328	6.6	1.2	329	17.1	12.0	330	17.9	16.7
331	6.8	7.9	332	6.5	5.8	333	3.1	3.8
334	7.4	11.0	335	13.7	24.6	336	4.6	1.0
337	12.7	17.0	338	6.7	12.7	339	9.1	6.8
340	4.6	5.2	341	3.3	3.5	342	4.3	6.9
343	6.9	7.3	344	10.3	8.4	345	5.9	11.6
346	3.4	6.7	347	6.7	11.0	348	19.1	26.1
349	1.2	1.0	350	2.4	5.4	351	3.3	4.7
352	3.5	4.8	353	6.7	9.8	354	4.6	4.5
355	7.4	9.6	356	13.1	17.2	357	0.8	0.9
358	3.3	5.8	359	0.8	0.9	360	2.5	4.5
361	2.3	3.5	362	5.1	5.8	363	6.9	11.3
364	4.6	5.9	365	9.0	11.2			

Appendix E

E.1 Wind speeds

Table E.1: Mean wind speed (Knots) measured at Tiree between 1972 and 19788. SD = standard deviation. Data provided by the British Atmospheric data centre (BADC 2011).

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
1	16.25	5.17	2	19.14	8.30
3	19.27	7.46	4	17.95	8.91
5	17.19	9.25	6	18.35	5.88
7	18.45	5.81	8	19.37	9.09
9	15.25	4.11	10	23.66	7.72
11	23.08	5.20	12	24.26	6.89
13	20.10	5.68	14	21.41	6.51
15	20.32	5.02	16	16.08	6.55
17	15.14	7.84	18	23.48	8.44
19	26.42	7.70	20	26.14	10.58
21	22.83	8.99	22	20.69	5.69
23	23.43	6.99	24	22.13	5.56
25	18.54	4.42	26	17.59	5.72
27	17.07	7.06	28	23.84	13.61
29	21.57	10.72	30	20.30	9.48
31	17.09	5.81	32	18.86	9.54
33	17.66	8.13	34	19.48	5.72
35	16.20	3.50	36	15.81	4.01
37	16.89	5.18	38	12.77	6.44
39	15.02	5.84	40	17.52	7.06
41	19.55	6.46	42	17.17	5.95
43	16.51	7.44	44	15.54	7.36

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Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
45	13.27	5.38	46	15.74	4.74
47	20.14	7.87	48	16.22	6.36
49	13.44	3.68	50	16.68	7.78
51	18.31	5.60	52	16.61	5.71
53	20.26	8.45	54	15.65	7.77
55	18.27	4.53	56	15.33	6.23
57	12.19	6.57	58	17.47	5.97
59	20.30	6.54	60	19.71	5.01
61	16.19	5.52	62	16.02	6.60
63	18.34	9.43	64	16.51	7.36
65	21.06	4.52	66	21.65	6.30
67	18.95	5.62	68	15.43	5.19
69	17.94	6.48	70	14.46	6.28
71	12.12	3.88	72	10.23	5.20
73	12.88	5.77	74	19.30	6.07
75	15.92	5.42	76	17.50	8.33
77	14.79	4.57	78	13.45	6.45
79	14.30	7.34	80	19.97	8.95
81	15.67	5.16	82	15.32	4.27
83	16.72	7.85	84	14.47	5.26
85	14.44	4.62	86	19.12	7.03
87	17.94	6.02	88	17.58	6.87
89	18.15	7.89	90	19.23	5.21
91	18.44	5.85	92	15.64	7.69
93	15.30	9.03	94	14.34	8.57
95	12.24	5.76	96	15.16	9.03
97	16.04	10.65	98	12.76	9.81
99	14.35	7.72	100	16.39	7.49
101	15.84	7.86	102	15.19	6.86
103	14.94	7.81	104	13.59	7.89
105	12.36	6.97	106	11.40	4.64
107	12.36	6.15	108	11.79	5.88
109	13.29	6.81	110	10.38	5.78
111	8.92	4.64	112	10.78	5.37
113	11.37	5.13	114	10.65	4.37
115	12.05	8.37	116	11.50	5.63
117	13.02	5.47	118	12.93	6.45
119	14.84	8.46	120	15.03	5.60

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Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
121	13.59	4.28	122	13.70	3.89
123	10.75	2.53	124	9.18	2.29
125	9.87	2.23	126	10.89	5.58
127	12.82	6.18	128	15.56	4.97
129	17.54	7.08	130	15.79	6.40
131	14.61	3.35	132	17.44	4.49
133	14.58	4.66	134	12.15	5.79
135	14.90	6.15	136	14.91	4.57
137	12.96	7.83	138	11.09	3.17
139	10.55	3.73	140	11.80	5.37
141	11.48	5.00	142	12.04	5.68
143	13.51	4.48	144	16.29	6.29
145	14.24	5.64	146	11.96	6.10
147	11.81	5.47	148	11.49	7.33
149	11.71	4.10	150	14.19	5.33
151	14.12	3.97	152	12.19	4.97
153	13.55	9.17	154	12.86	5.75
155	12.68	4.55	156	15.41	2.86
157	14.00	5.79	158	13.61	3.44
159	12.79	4.21	160	12.72	4.15
161	14.81	4.83	162	17.92	5.40
163	13.89	5.22	164	12.55	3.46
165	14.24	2.57	166	13.02	2.26
167	11.31	3.13	168	11.65	3.18
169	14.08	5.95	170	14.96	4.02
171	11.03	3.39	172	10.23	5.21
173	10.92	6.01	174	12.59	6.41
175	10.82	3.39	176	11.62	3.86
177	12.25	4.59	178	12.07	3.11
179	11.42	4.21	180	10.55	4.30
181	10.92	2.76	182	13.38	4.71
183	13.89	4.60	184	10.52	3.88
185	12.50	6.55	186	11.23	5.84
187	11.61	4.66	188	9.39	1.76
189	11.33	3.49	190	9.80	4.36
191	10.62	5.09	192	11.53	5.14
193	10.87	3.32	194	11.16	3.85
195	10.22	2.19	196	14.09	3.18

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Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
197	12.89	6.60	198	9.72	6.04
199	10.95	2.05	200	13.62	4.10
201	13.82	3.84	202	12.67	5.05
203	12.75	6.42	204	11.05	6.01
205	13.93	5.44	206	13.03	4.90
207	11.72	3.18	208	10.28	3.96
209	10.95	4.89	210	11.13	3.10
211	9.56	2.23	212	12.15	3.66
213	13.35	2.80	214	11.72	3.61
215	11.45	3.52	216	10.33	3.63
217	11.59	3.28	218	12.43	5.17
219	11.84	4.89	220	13.20	6.62
221	8.82	3.83	222	8.98	3.75
223	10.48	4.27	224	10.94	4.21
225	11.51	4.55	226	10.23	4.76
227	10.52	5.31	228	11.29	3.30
229	10.70	4.34	230	11.23	6.37
231	11.52	3.57	232	13.55	6.18
233	11.59	5.47	234	9.88	3.61
235	10.09	5.46	236	13.59	4.58
237	12.05	4.87	238	11.88	6.20
239	10.07	2.40	240	14.74	6.98
241	13.82	5.16	242	11.63	6.15
243	12.64	4.18	244	13.02	6.65
245	11.52	6.21	246	10.86	5.78
247	12.50	6.24	248	13.23	4.00
249	11.22	4.14	250	13.34	2.93
251	13.68	3.49	252	12.12	5.06
253	15.10	9.10	254	13.70	5.96
255	14.32	6.05	256	12.88	2.37
257	16.93	3.08	258	15.55	6.63
259	14.00	7.88	260	10.84	6.53
261	10.14	4.14	262	12.47	6.29
263	13.00	8.68	264	15.74	6.48
265	14.86	8.04	266	15.36	5.92
267	15.87	6.73	268	16.69	4.54
269	15.45	4.40	270	12.56	4.75
271	15.80	7.99	272	18.26	6.86

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Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
273	16.65	6.93	274	14.44	8.31
275	13.37	7.20	276	15.42	5.76
277	16.46	6.16	278	15.60	7.22
279	14.83	5.41	280	18.61	10.74
281	15.05	4.41	282	14.01	5.06
283	12.50	4.77	284	17.21	5.82
285	15.27	8.46	286	14.11	6.89
287	14.17	7.28	288	12.39	5.63
289	14.40	7.32	290	12.36	5.82
291	14.73	6.51	292	17.97	6.97
293	17.06	7.42	294	15.98	4.92
295	19.57	6.89	296	20.43	4.06
297	18.77	4.65	298	17.33	5.59
299	18.76	4.80	300	20.08	10.48
301	19.23	7.80	302	18.06	6.97
303	20.19	6.11	304	14.43	7.51
305	17.05	5.19	306	17.99	3.66
307	17.97	3.15	308	17.05	5.50
309	15.70	5.23	310	16.44	7.08
311	19.45	6.37	312	17.77	4.71
313	19.83	6.16	314	19.72	8.28
315	22.84	10.11	316	21.33	6.66
317	16.78	5.95	318	18.52	9.10
319	20.48	6.40	320	19.74	7.14
321	18.71	8.93	322	15.80	5.03
323	16.34	7.72	324	16.52	6.23
325	13.86	8.38	326	17.16	6.04
327	18.46	7.55	328	17.88	6.87
329	16.19	6.66	330	13.37	4.66
331	17.20	6.35	332	16.65	7.46
333	18.95	10.02	334	15.60	3.11
335	17.46	6.42	336	23.69	8.99
337	19.42	10.33	338	20.50	9.16
339	20.79	7.47	340	21.60	9.65
341	21.40	8.18	342	15.23	8.15
343	15.62	7.05	344	19.12	6.01
345	17.95	6.67	346	19.98	8.75
347	18.51	7.26	348	19.17	9.33

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Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
349	18.00	6.06	350	20.14	4.70
351	17.99	10.45	352	18.74	6.39
353	19.27	7.56	354	18.14	6.62
355	19.49	6.47	356	17.65	6.88
357	17.05	8.28	358	19.17	2.42
359	16.34	4.54	360	19.19	8.56
361	21.26	6.40	362	22.39	2.48
363	17.93	3.87	364	20.91	6.53
365	18.18	3.65			

Table E.2: Mean wind speed (Knots) measured at Tiree between 2004 and 2008. SD = standard deviation. Data provided by the British Atmospheric data centre (BADC 2011).

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
1	18.30	5.20	2	16.74	3.80
3	15.40	8.69	4	16.00	7.93
5	20.89	5.53	6	16.82	5.18
7	13.73	9.11	8	10.04	8.49
9	13.56	13.03	10	12.60	11.87
11	11.27	10.23	12	13.51	11.69
13	12.37	9.64	14	18.61	6.50
15	18.06	8.76	16	14.18	4.33
17	14.82	6.20	18	16.48	3.68
19	20.22	6.27	20	18.50	8.32
21	11.36	2.40	22	13.87	5.47
23	16.52	2.48	24	15.92	3.86
25	13.77	10.25	26	15.07	4.67
27	14.36	6.62	28	16.47	6.50
29	13.03	2.16	30	13.35	1.47
31	17.48	4.42	32	11.45	6.68
33	11.83	7.54	34	10.87	9.92
35	9.35	6.84	36	13.10	1.14
37	10.82	6.62	38	14.12	9.83
39	14.73	8.56	40	16.26	7.44
41	17.78	7.37	42	17.29	8.27
43	14.78	5.61	44	14.91	9.70
45	11.47	5.86	46	14.39	7.18
47	15.56	6.45	48	9.30	1.63
49	10.71	6.93	50	13.67	7.60
51	15.19	7.46	52	13.89	4.64
53	17.48	7.62	54	15.03	5.69
55	15.72	2.80	56	14.07	7.61
57	18.59	8.30	58	17.01	7.41
59	16.42	7.34	60	17.61	7.76
61	16.37	10.42	62	15.98	5.09
63	16.74	2.04	64	18.59	8.35
65	10.96	9.01	66	15.64	4.78
67	13.64	4.64	68	17.05	5.25
69	15.65	3.97	70	21.61	1.96

Continued from previous page

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
71	23.61	10.20	72	23.24	8.75
73	15.43	3.24	74	17.69	4.02
75	16.15	6.61	76	16.41	3.12
77	16.51	9.33	78	14.35	8.20
79	15.75	7.58	80	13.34	3.13
81	19.14	6.59	82	18.27	7.12
83	17.17	3.33	84	13.54	4.62
85	11.52	4.50	86	9.75	1.22
87	11.43	4.02	88	13.28	5.74
89	13.40	5.24	90	10.85	4.24
91	9.93	3.89	92	13.81	4.95
93	14.06	3.36	94	12.57	3.77
95	14.39	3.86	96	16.98	5.01
97	18.89	7.42	98	17.96	8.57
99	15.55	2.24	100	13.07	3.26
101	12.86	5.19	102	12.34	4.70
103	11.97	6.85	104	13.75	4.33
105	13.25	2.77	106	11.66	3.08
107	17.95	6.02	108	12.88	4.41
109	14.00	4.16	110	11.22	4.88
111	14.02	7.69	112	14.06	3.68
113	11.25	2.66	114	11.74	7.63
115	9.81	6.99	116	12.66	3.74
117	11.86	5.45	118	13.79	5.02
119	12.48	7.41	120	11.44	4.65
121	11.03	2.91	122	12.77	6.55
123	13.20	5.23	124	13.61	2.32
125	16.10	4.65	126	12.87	6.34
127	12.68	4.93	128	14.10	3.98
129	11.42	3.47	130	10.16	3.62
131	7.86	2.75	132	10.45	3.98
133	9.26	3.26	134	10.50	3.36
135	9.23	2.84	136	10.45	6.12
137	7.94	4.03	138	12.95	5.34
139	14.05	7.79	140	13.58	2.97
141	12.73	2.68	142	13.03	5.78
143	11.81	4.33	144	11.88	4.40
145	10.10	1.75	146	13.03	3.50

Continued from previous page

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
147	12.98	2.71	148	17.41	4.16
149	12.29	4.05	150	8.82	4.54
151	9.56	5.53	152	9.94	1.88
153	11.27	4.29	154	10.13	4.41
155	8.97	2.88	156	9.05	3.27
157	9.70	2.55	158	6.83	1.96
159	7.62	2.05	160	10.14	3.09
161	12.44	3.83	162	13.84	5.20
163	13.94	6.58	164	12.31	2.07
165	11.84	4.75	166	9.71	1.92
167	9.96	1.90	168	10.59	1.98
169	10.58	4.09	170	12.69	3.66
171	12.37	6.74	172	14.70	7.76
173	11.16	4.00	174	10.74	2.58
175	10.30	4.95	176	9.35	7.79
177	13.64	9.41	178	11.58	5.40
179	12.43	1.62	180	10.77	1.79
181	11.66	3.65	182	13.35	1.86
183	13.92	6.77	184	11.63	3.32
185	7.35	2.98	186	7.90	2.67
187	7.80	2.79	188	10.32	2.49
189	11.84	3.05	190	10.44	2.15
191	9.17	4.19	192	11.41	3.51
193	10.97	4.71	194	10.55	3.08
195	8.84	2.67	196	9.01	2.11
197	11.88	3.45	198	13.17	3.58
199	10.46	4.33	200	10.11	2.89
201	11.44	4.08	202	10.75	4.06
203	9.69	3.09	204	11.64	2.62
205	12.12	2.77	206	9.25	1.35
207	8.49	2.64	208	8.33	2.41
209	10.13	5.20	210	10.17	6.46
211	10.14	3.71	212	10.92	4.52
213	13.15	2.37	214	13.80	3.53
215	11.19	2.31	216	11.95	4.77
217	11.48	3.62	218	10.45	1.16
219	10.02	6.15	220	11.92	5.38
221	11.66	5.56	222	10.75	5.09

Continued from previous page

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
223	8.00	2.01	224	11.47	4.61
225	11.89	2.40	226	9.36	2.45
227	9.19	2.29	228	10.89	5.61
229	8.83	3.28	230	11.59	2.76
231	14.85	5.72	232	10.23	6.10
233	9.71	5.65	234	10.70	3.14
235	12.33	5.60	236	8.32	1.77
237	13.24	5.17	238	14.17	2.88
239	14.11	3.86	240	11.93	2.42
241	12.92	5.35	242	13.24	3.20
243	10.73	3.49	244	11.46	2.74
245	12.33	3.22	246	13.74	4.93
247	8.34	2.73	248	9.20	3.95
249	9.13	2.09	250	10.04	3.79
251	10.69	3.89	252	9.36	4.34
253	12.80	4.97	254	14.70	5.94
255	17.65	6.74	256	14.15	4.34
257	12.36	6.75	258	10.70	2.09
259	16.00	4.66	260	15.93	4.84
261	16.42	5.31	262	15.70	4.22
263	17.79	5.38	264	16.69	5.62
265	16.76	4.61	266	16.75	4.88
267	10.64	3.96	268	15.57	6.15
269	16.22	5.86	270	15.34	5.59
271	12.40	3.91	272	11.64	5.35
273	12.27	5.41	274	13.70	4.52
275	16.25	3.72	276	14.79	3.63
277	15.58	7.62	278	16.70	3.19
279	18.89	2.94	280	12.67	4.98
281	14.53	5.14	282	10.99	4.83
283	10.84	5.35	284	15.99	2.92
285	13.93	6.56	286	15.08	5.00
287	16.19	4.82	288	13.47	2.86
289	14.74	3.19	290	15.27	2.80
291	8.43	2.34	292	9.62	6.25
293	10.50	5.25	294	15.14	8.65
295	15.54	6.22	296	12.91	8.05
297	14.46	8.11	298	12.75	9.45

Continued from previous page

Day of year	Wind (Knots)	SD	Day of year	Wind (Knots)	SD
299	17.68	12.17	300	14.52	8.64
301	10.63	9.48	302	12.71	8.33
303	14.61	6.93	304	16.68	6.73
305	14.12	4.81	306	11.33	6.18
307	11.57	4.26	308	12.63	5.72
309	15.95	7.14	310	16.82	5.55
311	12.12	4.92	312	11.87	8.49
313	15.98	6.63	314	23.40	6.97
315	20.55	12.02	316	15.10	11.35
317	14.48	8.56	318	13.57	6.54
319	11.99	5.88	320	10.75	6.91
321	15.58	4.10	322	10.80	1.94
323	16.16	6.04	324	16.71	8.02
325	18.51	6.91	326	16.54	7.48
327	19.09	6.84	328	22.37	8.80
329	22.10	6.33	330	13.58	5.13
331	17.25	9.21	332	15.57	6.17
333	11.29	4.39	334	9.50	6.37
335	8.77	2.60	336	13.64	6.80
337	16.84	7.26	338	17.17	7.37
339	15.52	7.05	340	17.71	5.92
341	15.29	6.07	342	16.82	3.66
343	18.08	3.47	344	18.41	5.48
345	13.99	7.87	346	17.90	7.93
347	21.55	5.64	348	21.41	4.46
349	17.06	5.59	350	17.97	7.62
351	18.87	4.36	352	14.80	3.37
353	14.11	7.25	354	15.86	3.69
355	20.48	3.85	356	17.95	3.55
357	15.33	7.27	358	15.32	6.90
359	13.00	6.41	360	15.07	4.42
361	15.67	9.55	362	15.76	10.99
363	15.60	9.70	364	11.30	6.80

Appendix F

F.1 Species and Life Forms

Table F.1: Phytoplankton Species List and Life form designation taken from Tett *et al.* (2005)

Species Name	Life Form designation
Skeletonema spp.	1
Thalassiosira large spp.	1
Thalassiosira nordenskioldii	1
Thalassiosira rotula/gravida	1
Thalassiosira spp.	1
Thalassiosira decipiens	1
Coscinosira spp.	1
Eucampia zodiacus	1
Ditylium brightwellii	1
Cerataulina pelagica	1
Chaetoceros large spp.	1
Chaetoceros subgenus Chaetoceros	1
Chaetoceros decipiens	1
Chaetoceros compressum	1
Chaetoceros didymum	1
Chaetoceros laciniosum	1
Chaetoceros Curviseta	1
Chaetoceros small spp.	1
Lepcyndrus spp.	1
Leptocylindrus danicus	1
Leptocylindrus minimus	1
Guinardia flaccida	1

Continued from previous page

Species Name	Life Form designation
Dactyliosolen spp.	1
Lauderia borealis	1
Schroedella	1
Rhizosolenia small spp.	1
Rhizosolenia delicatula	1
Rhizosolenia fragilissima	1
Rhizosolenia stolterfothii	1
Rhizosolenia large spp.	1
Rhizosolenia shrubsolei	1
Rhizosolenia setigera	1
Asterionella japonica	1
Asterionella gracillima	1
Striatella spp.	1
Thalassiothrix /Thalassionema spp.	1
Licmorphora spp.	1
Grammatophora spp.	1
Tabellaria spp.	1
Bacxillaria spp.	1
Unidentified diatom	1
Nitzschia spp.	2
Nitzschia closterium	2
Nitzschia delicatissima	2
Nitzschia seriata	2
Phaeodactylum tricornutum 1	2
Phaeodactylum tricornutum 2	2
Pseudo-Nitzschia	2
Coscinodiscus spp.	3
Navicula spp.	3
Pleuorisgma/Gyrosigma spp.	3
Prorocentrum micans	11
Exuviella	11
Dinophysis spp.	11
Katodinium	11
Gymnodinium spp. (Photosynthetic)	11
Gyrodinium aureolum	11
Heterocapsa (-Peridinium) triquetra	11
Scrippsiella trochoidea	11
Gonyaulax spp.	11

Continued from previous page

Species Name	Life Form designation
Gonyaulax small spp.	11
Gonyaulax large spp.	11
Gonyaulax spinifera/digitale	11
Gonyaulax triarantha	11
Gonyaulax polyedra	11
Gonyaulax diegensis	11
Gonyaulax tamarensis group	11
Very small dinoflagellate	11
Ceratium Spp.	12
Ceratium lineatum/minutum	12
Ceratium furca	12
Ceratium fusus	12
Ceratium tripos	12
Ceratium longipes	12
Pyrocystis spp.	13
Small flagellates	20
Other small flagellates	20
Unidentified Flagellates	20
Euglenoids /Eutreptiella spp.	21
Dinobyron spp.	22
Silico-flagellate	22
Tear drop flagellates	23
Chrysochromulina/Prymnesuim	24
Colonial flagellate	26
Chattonella -like	27
Mesodinium spp.	31
Diplopsalis	101
Perduniumi ovatum	101
Peridinium depressum	101
Peridinium pallidum/pellucidum	101
Peridinium large spp.	101
Minuscula bipes	101
Unidentified Dinoflagellates	101
Gymnodinium/Gyrodinium spp.	101
Phalacroma spp.	101
Polykrikos spp.	101
Peridinium spp.	101
Parasite on *Leptocylindrus*	102

Continued from previous page

Species Name	Life Form designation
Parasite on *Dachylosolen*	102
Parasite on *Skeletonema* spp.	102
Chaonoflagellates	103
Diaphanoeca- like	103
Ciliates & Tintinnids	105
Oral ciliate	105
Uniform ciliate	105
Tintinnids	105
Helliocostomella	105