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Eutrophication and phytoplankton in the Liffey Estuary and Dublin Bay

By

Tim O'Higgins

A Dissertation submitted to

Trinity College Dublin

in fulfillment of the requirements

for the degree of

Doctor of Philosophy

Department of Zoology

September 2005

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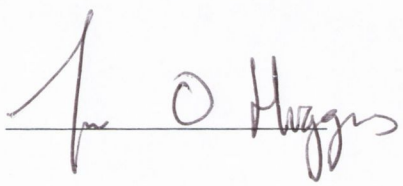


Eutrophication and phytoplankton in the Liffey estuary and Dublin Bay.
Tim O'Higgins

Abstract
Nutrients, chlorophyll and physical parameters were measured monthly in Dublin Bay and the Liffey estuary from 2000-2004. Nutrient and suspended solids concentrations were measured daily at the Ringsend sewage treatment plant over the same period. Two YSI 6600 sondes were deployed in the Liffey estuary in spring-summer 2004.
The Liffey estuary was found to be hypernutrified with respect to nitrogen and phosphorus throughout. The mean annual combined riverine and sewage area-normalised fluxes of nutrients to the estuary were 2309kg $N.m^{2}.y^{-1}$ and 311kg $P.m^{2}.y^{-1}$ for nitrogen and phosphorus respectively. These values are higher than the U.K. average and are considered moderately to highly eutrophic. Dublin Bay underwent seasonal nutrient limitation exhibiting a typical spring bloom pattern. Over the upgrade of the sewage treatment plant, the composition of the sewage effluent changed, with ammonia constituting 98% of the DIN in 2001 but only 26% in 2004 and this change was concurrent with an increase in TON.
In the upper estuary there was pronounced salinity stratification while in the lower estuary and the bay the water column was vertically well mixed. The vertical attenuation coefficient of PAR (k(PAR)) varied over the study area. Highest values for k(PAR) were found in the estuary and maximum light attenuation occurred off the Ringsend sewage treatment plant. This was attributed to the input of suspended particulates. There was a weak positive correlation between the natural log transformed data for mean chlorophyll *a* concentration and the ratio of the photic zone depth to mixed layer depth (Zp/Zm). The upper estuary had highest Zp/Zm values due to the shallow surface mixed layer caused by salinity stratification. Lowest chlorophyll and Zp/Zm values occurred off the Ringsend sewage treatment plant because high suspended solid concentrations increased light attenuation and the water column was vertically well mixed.
Highest maximum chlorophyll a concentrations occurred in the upper estuary (max=121.6mg chl*a*.m^{-3}) these high concentrations were associated with monospecific blooms of *Cryptomonas* sp. In summer 2004 a bloom of *Cryptomonas* sp. was detected in the upper estuary and lasted two weeks. This bloom acted as a significant source of carbon to the upper estuary (15mg.$C.m^{2}$) comparable in magnitude to the spring bloom in eutrophic systems. The termination of the bloom coincided with a drop in surface salinity. Modelled flushing times for the upper estuary indicate that flushing in this area is highly sensitive to river flow and flushing timescales are on the same timescale as phytoplankton growth. In the lower estuary and in Dublin Bay tidal flushing is of more significance than riverine flushing, effectively preventing proliferation of phytoplankton in the lower estuary.
During the spring bloom of 2004 a brief period of anoxia occurred off the Ringsend sewage treatment plant. The oxygen minimum coincided with the fluorescence maximum. At this time chlorophyll made up only 20% of the total phaeopigments. The thermal signature suggested that the peak in fluorescence came from a stratified offshore source. The anoxic event is attributed to a dieing phytoplankton bloom combined with organic loading from the Ringsend sewage treatment plant and thermal inputs form a local power station.
A persistent bloom of *Odontella aurita* in the bathing waters of north Dublin Bay was observed following the upgrade of the sewage treatment plant, the observation of this bloom coincided with the shift in nitrogen species from ammonia to oxidised forms.

SUMMARY

Temperature, salinity, nutrient and chlorophyll concentrations, and Secchi depth were measured monthly at 41 stations in the Liffey estuary and Dublin Bay from June 2000 to June 2004. Analysis of nutrient composition and suspended solid concentrations was made daily on sewage effluent from the Ringsend sewage treatment plant during the same period. During this time the plant was being upgraded from primary to secondary treatment (sequential batch reactors).

TON and PO_4 exhibited consistent linear behaviour with salinity within the estuary. Mean annual riverine TON flux from the River Liffey was 770 tonnes.y^{-1} the mean annual flux of NH_4 was 37 tonnes.y^{-1} while the mean annual PO_4 flux was 29 tonnes.y^{-1} but the fluxes of these nutrients were under the stochastic control of freshwater flow. The mean DIN input from the sewage treatment plant was 1941 tonnes.y^{-1} while the mean PO_4 flux from this source was 342 tonnes.y^{-1}. While the magnitude of the DIN flux from the sewage treatment plant remained relatively constant over the study period, the composition of the DIN in the sewage effluent changed over the study period with ammonia constituting 98% of the DIN in 2001 but only 26% in 2004 and this change was concurrent with an increase in TON. Considerations on nutrient abundances and ratios indicate that the estuary was hypernutrified throughout with N in particular being in oversupply. In Dublin Bay nutrient concentrations were reduced to below detection limits each year following a spring phytoplankton bloom. The dominant tidal currents in the bay result in the Liffey plume bringing elevated nutrient concentrations to the north of the Bay. Modelled nutrient inputs indicate that summer supply of TON at the 33.2 isohaline in the north of the bay (an area known to be susceptible to eutrophication) has doubled due to the change in sewage effluent composition.

The physical structure of the water column varies from a highly stratified area in the upper estuary to well mixed conditions in the lower estuary and in Dublin Bay. The diffuse attenuation coefficient of PAR (KPAR) also varied along the estuarine gradient with maximum values found in the lower estuary off the Ringsend sewage treatment plant. A statistically significant correlation was found between the natural log transformed mean chlorophyll a concentration and the natural log transformed ratio of the photic zone depth to mixed layer depth (Zp/Zm). Highest mean chlorophyll a concentrations were found in the stratified part of the upper estuary due to shallow mixing depth while lowest values found off the Ringsend treatment plant

corresponded to high light attenuation and deep mixing depth. Residence time calculations indicated that the stratified upper estuary is sensitive to riverine flushing on the same timescales as those of phytoplankton growth. In the lower estuary tidal flushing is more important effectively preventing the proliferation of plankton in this area. Residence times in the bay are generally sufficiently long to allow phytoplankton growth however the temperature signal recorded in the bay suggests a stratified offshore source for Dublin Bay waters, thus patterns of phytoplankton are likely also to reflect this source.

The temporal patterns in phytoplankton biomass differ between the estuarine and bay areas. Generally chlorophyll distribution in the estuary conformed to a linear dilution model but, at times sporadic high chlorophyll events (max. 121.6 $mg.m^{-3}$) were found in the estuary and the linear dilution model was not applicable. High chlorophyll events corresponded to times when the salinity in the upper estuary was low, reflecting low river flow. These blooms were associated with the motile phytoplankton *Cryptomonas* spp. The occurrence of these blooms appears to represent a significant source of carbon to the upper estuary, of up to 15g $C.m^{-2}$. High frequency data indicated that one such bloom was terminated by increasing riverine flows.

In Dublin Bay the temporal pattern in phytoplankton biomass conformed to the typical pattern in coastal regions of the western Irish Sea with a long growth season and high spring bloom biomass. Diatoms were dominant in the waters of Dublin Bay throughout the study period and dinoflagellate biomass was consistently low compared to other parts of the western Irish Sea. In 2004 a short period of water column anoxia occurred in the lower estuary coinciding with peak spring bloom biomass with stoichiometric considerations indicating that an additional source of carbon (probably from the sewage treatment plant) was partly responsible for the brief anoxic period. In 2004 a persistent bloom of the diatom *Odontella aurita* caused discolouration of the bathing waters in the north of Dublin Bay. The occurrence of the bloom was coincident with the upgrade of the sewage treatment plant and the increased supply of oxidised forms of nitrogen to the north of the bay.

Nutrient and chlorophyll considerations indicated that the Liffey estuary is moderately to highly eutrophied. Flushing times in both the walled part of the estuary and the open bay help to limit the magnitude of the undesirable disturbances caused by nutrient overloading.

"Only for my short Brittas bed made is as snug as it smells it's out I'd lep and off with me to the slobs della Tolka or the plage au Clontarf to feale the gay aire of my salt troublin bay and the race of the saywint up me ambushure."

From Anna Livia Plurabelle

James Joyce

Table of Contents

ACKNOWLEDGEMENTS

I am very grateful to everybody who has helped and supported me through the course of this work. All the staff in the Central Laboratory, Aideen Carney, Dennis Morrisssey, Imelda Averill, James Hart and everybody else. Thanks also to the men of the Port and Docks Company who have been so professional throughout. To Jim Wilson, who raised the bar when it was necessary and inspired confidence when things seemed bad. Thanks to my wife and family for all the support for the endless bent ears.

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

CHAPTER 1: INTRODUCTION

1.0.1 Eutrophication

Eutrophication has been defined in a legislative context by the European Union as:

"*the enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus causing 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 the quality of the water concerned*" (EU, 2000).

The study of eutrophication grew out of concerns about the degradation of freshwater resources due to anthropogenic alteration of nutrient fluxes to the aquatic environment. In the 1960s and 1970s the impacts of phosphorus loading to lakes and rivers was a major theme in ecological studies and many freshwater environments were proven to show a linear response in phytoplankton biomass and photosynthesis due to the addition of phosphorus (eg. Dillon & Rigler, 1974; Smith, 1979). Evidence from sediment cores illustrates that the eutrophication phenomenon has been linked to human population growth for two centuries. As global population increases, so too does the anthropogenic disturbance of biogeochemical nutrient cycling (Bratton *et al.*, 2003). Existing nutrient fluxes from land are already significantly greater than they would be in unaltered conditions. In Europe and North America riverine fluxes to coasts have been elevated 6-fold and 3-fold respectively (Howarth, 1998). Increasing global populations have lead to a growing amount of land transformed by man. Such land transformed or degraded by human activity now constitutes 39%-50% of the Earth's surface (Vitousek *et al.*, 1997) and projected figures for global population growth will result in a 2.4 to 2.7-fold increase in nitrogen and phosphorus driven eutrophication in the next 50 years (Tilman *et al.*, 2001). As awareness of the eutrophication problem has grown the emphasis of research has shifted to include the effects of eutrophication on estuarine and coastal zones in addition to freshwater environments.

1.0.2 Estuarine and coastal eutrophication

Unlike limnological examples, no broadly applicable relationship has been found to relate increasing nutrient loads to estuaries and coastal seas with increasing primary producer biomass. Rather, eutrophication processes are controlled by complex interactions of many factors which include chemical (nutrient limitation), physical (mixing and advection) and biological (grazing and growth rates). The combinations of these factors are unique to any given study area. While the estuarine and coastal marine biomes are clearly different, the definition of their boundaries is not simple. Where does an estuary begin and the sea end? Many definitions have been posited to define estuarine boundaries often using environmental variables such as salinity (e.g Venice, 1958; EU, 1994). Other definitions emphasise the importance of tidal influence (e.g. Fairbridge, 1980). However the imposition of such boundaries requires an arbitrary decision on the part of the environmental scientist lending to a degree of inherent subjectivity (Elliott & McLusky, 2002). Elliott and McLusky (2002) suggest a pragmatic "Expert Judgement Checklist Approach" based on available physical and biological information. Since the freshwater and saline end members of any estuary will have different ratios of nutrients, the issue of nutrient limitation varies from one end to the other. Generally estuarine and coastal eutrophication involve an increase in microalgal production due to increased nutrient loading. The increase in production can lead to extreme chlorophyll concentrations for instance the New River in North Carolina has displayed chlorophyll concentrations up to 379 $mg.m^{-3}$ (Mallin *et al.*, 2000) with a consequent reduction in water clarity reducing light penetration. This may result in a shift from macrophyte dominated primary production towards microalgal dominated production (Cloern, 2001). In summer anoxic or hypoxic conditions may occur as the excess organic matter decomposes (Wu., 2002). This in turn can lead to fish kills and reduction in macrofaunal diversity which may result in changes in ecosystem function. Estuarine eutrophication includes a broad range of discernible effects from primary level increase in algal biomass to a whole range of ecosystem dysfunctions while recognising that different estuaries have different capacities to undergo increased nutrient loading (see Cloern 2001 for review). The hydrographic complexity of marine environments also introduces similar unpredictability in the response of marine systems to nutrient loading. In general, in areas where cross-shelf advection

of nutrients dominates, eutrophication effects are less pronounced (Howarth, 1998). This means that semi- enclosed seas are often more susceptible to eutrophication. Well studied examples include the North Sea (Hydes et al, 1999), the Black Sea (Gordina *et al.*, 2001), and the Baltic Sea (Savchuk, 2005) while massive nutrient fluxes from the Mississippi have resulted in recurrent widespread hypoxia in the Gulf of Mexico (Rabalais *et al.*, 2001).

1.0.3 Phytoplankton Blooms

One feature common to many estuarine and marine eutrophied locations is the occurrence of prolonged or recurrent algal blooms (Hallegraeff, 1992; Takeoka, 2002). Generally blooms involve a simple seasonal increase in biomass of phytoplankton with a variety of species contributing; these may be naturally occurring events such as the diatomaceous spring bloom encountered annually throughout temperate shelf seas. In both estuaries and coastal shelf seas, intense blooms of phytoplankton may be sufficient to discolour the water column; the nature of the discolouration depending on the type of plankton present. High concentrations of dinoflagellates such as *Karenia mikimitoi* (Raine *et al.*, 2001) *Prorocentrum dentatum* (Gao & Song, 2005), which contain the pigment fucoxanthin may result in "red tides". The calcareous plates (or coccoliths) of the Coccolithophores may impart a milky white colour to the waters (Weeks *et al.*, 2004; Lessard *et al.*, 2005). Fucoxanthin the principle accessory pigment of the diatoms imparts a golden brown colour to the waters under bloom conditions. Other groups may also result in bloom events, for instance in Southampton Water, red tides are associated with the phototrophic ciliate *Mesodinium rubrum* (Crawford *et al.*, 1997) and blooms of the chrysophyte *Phaeocystis globosa* (which are often associated with the formation of unsightly foams) occur annually in the Irish Sea (Claustre *et al.*, 1990) and are considered problematic in the North Sea (Hamm & Rousseau, 2003). Blooms which are unsightly or inconvenient may be termed Nuisance Algal Blooms" (NABs). Harmful Algal Blooms (HABs) may include toxic species which impair fish health or pose a threat to human safety, either indirectly through consumption of filter feeders (e.g. *Prorocentrum minimum*) or directly by excretion of toxins (e.g. *Pfiesteria piscicida)* (Mallin *et al.*, 2000).

Monospecific blooms may be persistent for many years and can result in a complete change in the food web structure of an area. This was the case with the "brown tide" pelagophyte *Aureoumbra lagunensis* which has bloomed persistently since 1990 (Rhudy *et al.*, 1999; Liu *et al.*, 2001). Though the frequency of reporting of red tide events is increasing and there is undoubtedly a link between algal blooms and nutrients in estuarine and coastal waters, it is unclear to what extent eutrophication is driving the apparent increased frequency in algal bloom events (Hodgkiss & Ho, 1997). The increased frequency in reporting of algal blooms may be due to increased awareness of harmful algal bloom phenomena, though it appears that such blooms have occurred throughout history.[1]

While responses to nutrient loading vary between individual estuaries and between estuaries and shelf seas, a combination of diagnostic symptoms may be used to define the trophic status. A list of the pertinent parameters has been constructed by the United States group NEEA (National Estuarine Eutrophication Assessment) in the broadest single geographical study of estuarine eutrophication to date (Bricker *et al.*, 1999). A summary of the trophic status assigned to estuaries according to the various parameters measured is presented in Table 1.1. These indicative values were chosen to investigate estuarine eutrophication, and while the parameters necessary for measurement of eutrophication in the marine environment are the same, the concentrations of nutrients and chlorophyll defining marine eutrophication are typically much lower. For instance average concentrations >5 $mg.m^{-3}$ of chlorophyll *a* in a marine environment are considered to be indicative of hypernutrification (Smith *et al.*, 1999).

[1] "and all the waters that were in the river were turned into blood. And the fish that was in the river died; and the river stank, and the Egyptians could not drink the water of the river" Exodus 7 20:21. This passage from Exodus bears remarkable similarity to a red tide event producing anoxic conditions.

Table 1.1: Parameters used in assessment of eutrophication in estuaries adapted from Bricker *et al.*, (2003).

Parameter	Measurement	Value	Trophic status
Chlorophyll *a*	Surface conc	>60 >20,<60 >5,<20 0 and <5	Hypereutrophic High Medium Low
Turbidity	Secchi depth	<1 >1,<3 >3 Blackwater area	High Medium Low
Suspended solids	Concentration	Problem No Problem	
Nuisance algae	Cell concentrations	Occurrence	
Toxic algae	Cell concentrations	Problem No Problem	
Macroalgae	Coverage	Abundance	
Epiphytes	Coverage	Problem No Problem	
Nitrogen	Max dissolved surface conc	>1 $mg.l^{-1}$ >0.1,<1 mgl^{-1} >0 and <0.1 mg^{-1}	High Medium Low
Phosphorus	Max dissolved surface conc	>0.1 $mg.l^{-1}$ >0.01,<0.11 mgl^{-1} >0 and <0.01 mgl^{-1}	High Medium Low
Anoxia	Dissolved Oxygen Concentration.	0mgl^{-1}	
Hypoxia	Dissolved Oxygen Concentration.	>0,<2 $mg.l^{-1}$	
Biological stress	Dissolved Oxygen Concentration.	>2,<5 $mg.l^{-1}$	
Primary Productivity	Dominant producer	Pelagic, benthic, other	
Planktonic community	Dominant taxonomic group	Diatoms, flagellates etc	
Benthic Community	Dominant taxonomic group	Crustaceans Molluses etc	
Submerged Aquatic Vegetation	Spatial coverage		
Intertidal Wetlands			

1.0.4 The Study Area

The Liffey estuary runs 11 km through the city of Dublin (the largest city in Ireland with a population in the region of 1 million), from the weir at Islandbridge to the mouth of the Liffey at Poolbeg (Figure 1.1). The estuary is bounded on either side by man made walls. There are four main tributaries entering the estuary, the Poddle (a culverted river), the Camac, the Tolka and the Dodder as well as the Royal and Grand Canals and many small storm overflows also enter the estuary. In the upper reaches of the estuary (west of Butt Bridge) and for the most part of its length, the channel is no more than 100 m in width and at low tide approximately 1m in depth (depending on flow). At Butt Bridge the estuary broadens and deepens entering the Dublin Port area, here there are a number of shipping basins and docks with varied industrial uses. This part of the estuary is regularly dredged and the shipping channel is maintained at a depth of 7.8 m. The estuary is macrotidal (sensu Dyer, 1973) with mean highwater spring tides of 3.3 m and mean highwater neaps of 1.9 m. Previous hydrographic work has shown that the estuary is strongly salinity stratified at high tide throughout the narrow channel but more vertically mixed as the channel widens into the port area (Crisp, 1974; Wilson *et al.*, 1986). The estuary receives combined cooling and sewage wastewater effluent from the Ringsend sewage treatment plant and the Poolbeg thermal power station. At Poolbeg, the mouth of the estuary, the Liffey waters enter Dublin Bay.

Dublin Bay is a horseshoe shaped bay situated between the two headlands of Howth (to the north) and Dalkey (to the south), the bay is surrounded on the southern, northern and western sides by the conurbation of Dublin and open on the eastern side to the Irish Sea. The bay covers about 3375 ha in area and is shallow with maximum depths between the two major headlands of 15 m below chart datum, but with approximately half of the bay being under 10 m and the further half being below 5 m in depth. The bay is vertically well mixed by strong tidal currents (Crisp, 1974) which flow clockwise from south to north exiting in the north near Howth head with velocities of up to 0.5 $m.s^{-1}$ (ERU, 1992). The bottom sediments are composed of clean fine sands with very low silt clay fraction and organic content (ERU, 1992). The Liffey plume is known to extend northwards towards Howth head during ebbing tides but is undetectable in the area during flood tides or during periods of intensive

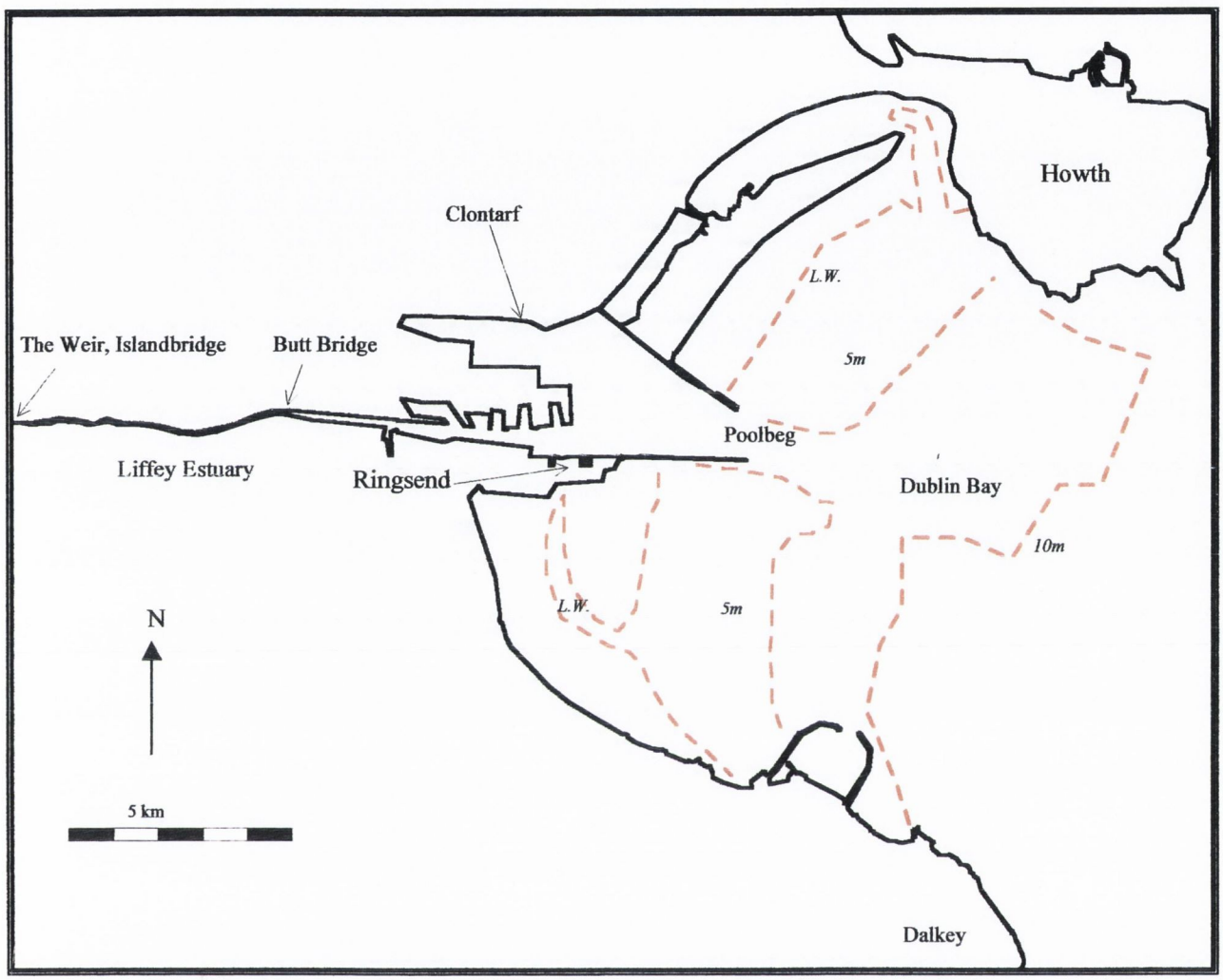


Figure 1.1: Map of the study area showing locations mentioned in the text. The black square marks the outflow of the Ringsend sewage treatment plant. The dashed red lines indicate the approximate position of the depth contours.

mixing due to wind stress and increased turbulence. Tidal exchanges are large (Wilson, 2005) and the tidal prism produces rapid flushing times in the order of three days. This rapid flushing has been cited as a reason that phytoplankton blooms have not been observed in the area (McMahon & Silke, 1998).

1.0.5 Eutrophication in the study area

Sewage from Dublin City has entered Dublin Bay through the River Liffey estuary since the city's foundation in A.D.988 but the main sewage system for the city was completed in 1906. This system carried sewage from around the city to Ringsend for primary treatment. The waste was pumped into settling tanks and the sewage effluent was released into the Liffey while the remaining sludge was transported to a designated dumping ground off Howth Head. The impact of anthropogenic nutrients on the local estuarine and marine environment are a major concern. The Liffey is known to carry large loads of nitrogen and phosphorus to the area (Brennan *et al.*, 1994). There is evidence of organic enrichment and anoxia in the sediments of the Liffey estuary with some areas showing a complete absence of macrofauna (Crisp, 1974; Jones & Jordan, 1979; Wilson *et al.*, 1986). The effects of eutrophication in Dublin Bay have been observed for almost a century. Adeney (1908) suggested that nitrogen might be the cause of the green "sewage algae" *Ulva* sp. in the Clontarf area in the north of Dublin Bay. At this time a link between sewage and green algae was emerging in other parts of the country (Letts & Richards, 1911). Subsequent studies (Jeffrey *et al.*, 1978, ERU, 1992; Jeffrey *et al.*, 1995) have described high concentrations of nitrogen and phosphorus in the northern intertidal areas of the bay and these have been linked to the annually recurring excessive growth of macroalgae particularly the ruderal green algae *Ulva* spp. and *Enteromorpha* spp. The major source of nutrients thought to support the high algal biomass are nitrogen rich particulate inputs from the cities municipal wastewater treatment plant at Ringsend. A further symptom of eutrophication has been excessive growth of the opportunistic brown alga *Ectocarpus siliculosis*, and its deposition on the shores of north Dublin Bay. This phenomenon was first noted in 1989 and thought to be related to the abundance of the filter feeding polychaete *Lanice concheliga* which was utilising nitrogen-rich particulates from the sewage treatment plant as a food source (Jeffrey *et al.*, 1993). These worms provided a hard substrate for the attachment of the algae and

may also have caused some remineralisation of the nutrients in those particulates increasing the macroalgal growth. Though the riverine and sewage fluxes of nutrients have been quantified for the year 1992-1993 (Brennan *et al.*, 1994) and annual winter nutrient monitoring has revealed elevated N:P ratios in the waters of Dublin Bay (McGovern *et al.*, 2002), there has been little study of the impacts of elevated nutrient concentrations on phytoplankton biomass in the estuary or the Bay. Chlorophyll measurements from Dublin Bay and the Liffey estuary (despite low frequency of sampling) have often yielded concentrations of over 10 $mg.m^{-3}$ (ERU, 1992; Brennan *et al.*, 1994), the concentration frequently taken to define a phytoplankton bloom (Iriate & Purdie, 2004).

1.0.6 Legislation and the Dublin Bay Project

The adverse effects witnessed in so many ecosystems from local scale to the scale of enclosed seas, combined with the increasing anthropogenic pressures on coastal and estuarine ecosystems has resulted in a number of programmes designed to monitor and limit anthropogenic nutrient inputs. In Europe the OSPAR convention (1992) was adopted in 1998 and involved the monitoring and regulation of discharges and the reduction of inputs of nutrients from urban, municipal, industrial, agricultural and other sources. One of the aims of this convention was to reduce nutrient inputs to the maritime environment such as to eradicate eutrophication by 2010. This is to be achieved under a number of existing EU regulations including the Water Framework Directive (WFD)(EU, 2000) which encompasses the Urban Waste Water Directive (UWWD)(EU, 1991a) and Nitrate Directive (EU, 1991b).

In addition to the nutrient parameters covered by the UWWD (which specifies the concentrations of N and P allowable for discharge from waste water treatment plants) the WFD requires that eutrophication be assessed in terms of undesirable disturbance to phytoplankton, macroalgae, angiosperms, benthic invertebrate fauna and fish fauna. High quality status is afforded to these parameters if they correspond with undisturbed conditions, good status is afforded if slight changes from an undisturbed condition are detected and moderate status is afforded if composition and/or abundance of these parameters differs moderately from undisturbed conditions.

The WFD aims to prevent further deterioration of aquatic ecosystems and promote sustainable water use. One of the obligations of this directive was the provision of secondary treatment to all urban wastewaters by the year 2000. The UWWD (EU, 1991a) legislation combined with the eutrophication problems observed in Dublin Bay prompted the overhaul of the city's wastewater treatment strategy. This €300 m project, known as "The Dublin Bay Project" involved the centralisation of the city's wastewater treatment system. The construction of a submarine wastewater pipeline began in 2001 and the upgrading of the existing primary treatment plant to a secondary system using aerobic sequential batch reactors followed. The secondary treatment plant was commissioned in June 2003. The data in this thesis were collected as part of the five year Dublin Bay Project in order to assess the changes in environmental parameters and to investigate compliance with effluent standards as a result of the upgraded sewage treatment plant. The emphasis is on the response of the phytoplankton in the Liffey estuary and Dublin Bay to nutrient loading. Though these areas mark distinct geographical locations, they also mark a transition from fresh to marine waters. Under the terms of the WFD, these waters encompass two different aquatic environments. The Liffey estuary is included under "transitional waters" defined as "*bodies of surface water in the vicinity of river mouths which are partly saline in character as a result of their proximity to coastal waters but which are substantially influenced by freshwater flows*" while Dublin Bay fits the following description of coastal waters "*surface waters on the landward side of a line, every point of which is a distance of one nautical mile on the seaward side from the nearest point of the baseline from which the breadth of territorial waters is measured extending where appropriate up to the outer limit of transitional waters*". Despite their different legislative definitions (which under the WFD may lead to different critical values for the indicators of trophic status), the estuary and the open bay are treated in this study as a continuum.

1.0.7 Aims

The aim of the study is to quantify the inputs of nitrogen and phosphorus from the River Liffey and the Ringsend sewage treatment plant into the Liffey estuary and Dublin Bay and explore the eutrophication effects these inputs have on phytoplankton biomass in the varying physical and chemical conditions along the estuarine gradient.

This was undertaken as follows.

- Characterisation of the nutrient fluxes and their temporal variability, relative magnitude and implications for nutrient limitation of phytoplankton growth for different locations in the study area. Hypothesis: That nitrogen is the limiting nutrient in Dublin Bay. That the river Liffey and the Ringsend sewage treatment plant are the major inputs of macronutrients to the Liffey estuary and Dublin Bay **Chapter 3**

- Characterisation of the physical environment its variability within the study area and its consequences for phytoplankton development with regard to light-climate and flushing time. Hypothesis: That tidal and riverine flushing as well as light availability may limit phytoplankton growth in the study area. **Chapter 4**

- Quantification and identification of patterns in phytoplankton response to nutrient loading and physical effects. Hypothesis: That anthropogenic nutrient inputs stimulate phytoplankton growth in the estuary and bay. **Chapter 5**

- Assessment of the eutrophication status of the study area. **Chapter 6**

CHAPTER 2: MATERIALS AND METHODS

2.0.1. Sampling programme and locations

Small working boats were used to sample 41 sites in the estuary and bay on a monthly basis (weather permitting). The sample sites stretched from the upper tidal reaches in the walled part of the estuary (at Butt Bridge) to the offshore waters in the open part of Dublin Bay encompassing the Liffey plume and the fully marine waters in the south of Dublin Bay. 17 sites were sampled in the walled part of the estuary (Figure 2.1) though stations 1 and 2 were frequently inaccessible due to tidal conditions. 24 stations were sampled in the open bay (Figure 2.2) though station 41 was sometimes inaccessible. For convenience, throughout this study stations 1-17 in the walled part of the estuary will be referred to as estuary and stations 18-41 in the open bay will be referred to as Bay stations based both on geography and on cluster analysis (O'Higgins & Wilson, 2005).

Each month from June 2000 until June 2004 two separate sampling cruises were undertaken, one dedicated to the walled part of the Liffey estuary and a second to the offshore waters in Dublin Bay. Sampling dates and the principle measurements taken on those dates are presented in Table 2.1. The sampling stations in the walled part of the estuary were located by reference to landmarks while in the bay stations were located during each cruise using a Global Positioning System (Garmin GPS 12XL). The latitudes and longitudes together with the Irish national grid coordinates are presented in Appendix I.

Additional sampling was conducted during the bathing season (May to September) of 2004. During this season 13 sites representing the intertidal zone around Dublin Bay were sampled on a weekly basis (Figure 2.2). The samples were collected by wading into the intertidal waters.

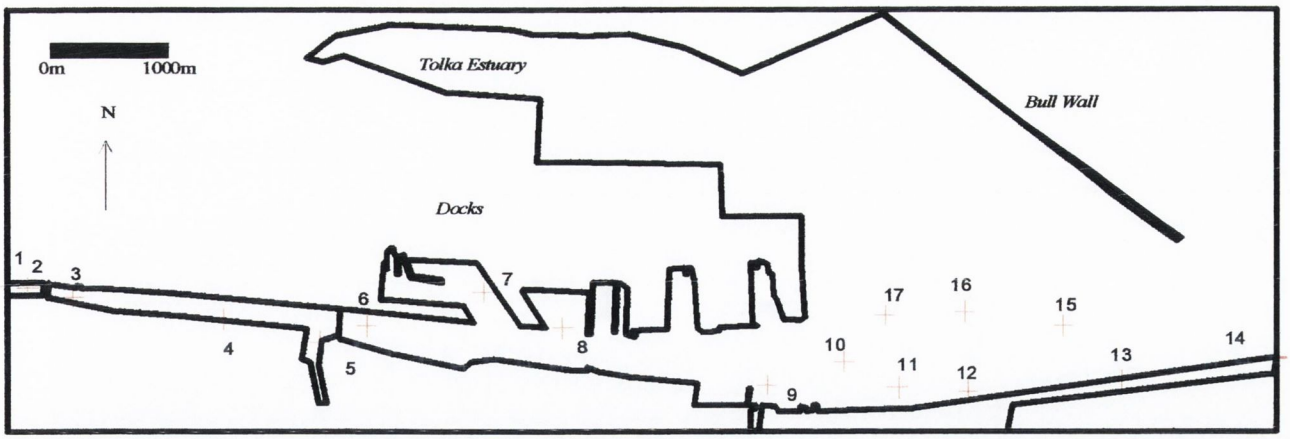


Figure 2.1. Map of sampling stations in the walled part of the Liffey estuary. The names of the sampling locations are presented below.

1. Butt Bridge
2. Customs House
3. Matt Talbott Bridge
4. Cardiff Lane
5. Dodder Outflow
6. Toll Bridge
7. Alexandra Basin
8. Ocean Pier
9. Old Treatment Works Outflow
10. Tanker Pier
11. New Treatment Works Outflow
12. Old Rathmines and Pembroke Outflow
13. Half Moon Club
14. Poolbeg Lighthouse
15. X15
16. X16
17. X17

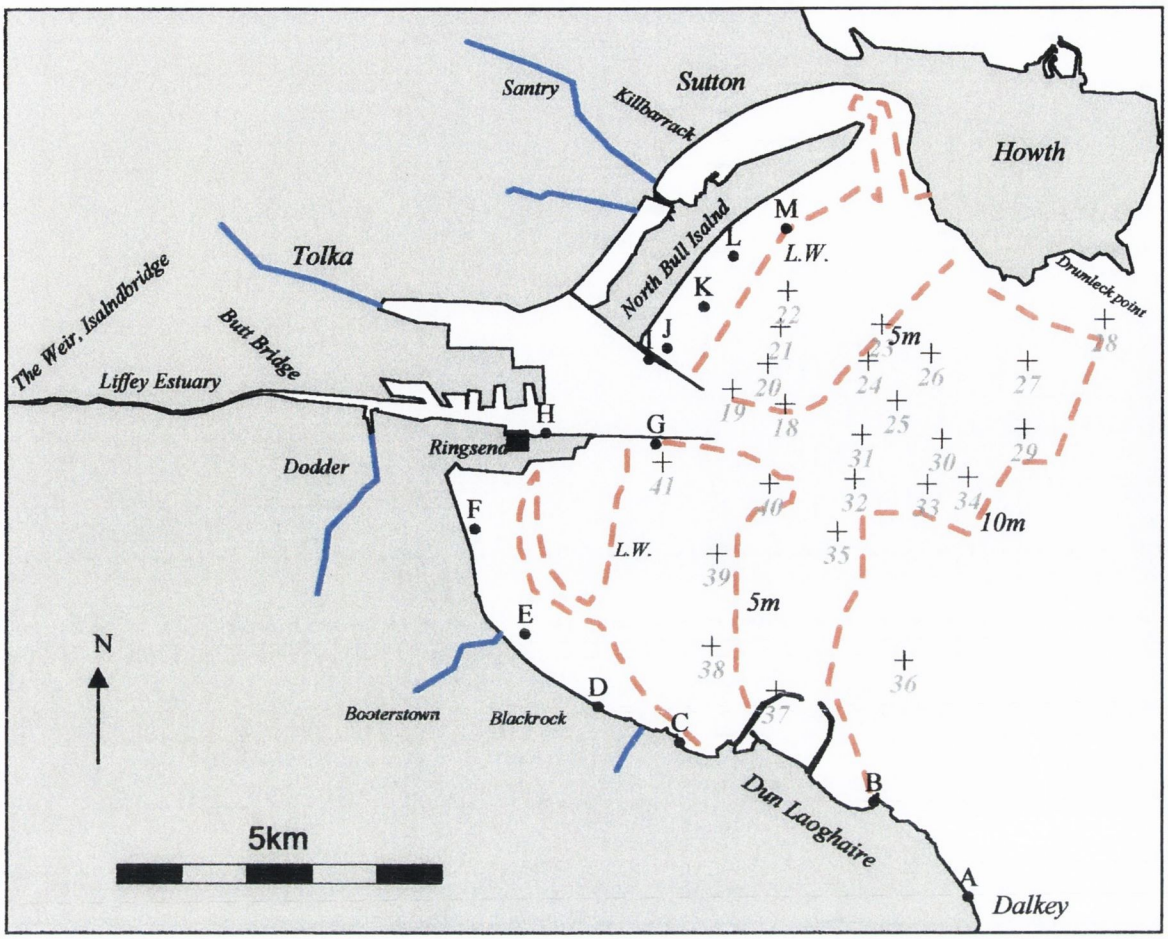


Figure 2.2: Map of the Liffey Estuary and Dublin Bay showing locations of sampling stations in the offshore water of Dublin Bay (crosses 18-41) and the intertidal sampling points for the bathing season 2004 (circles A-M). The names of the bathing water areas are given below. Bathymetry is marked in dashed red and major inflows are marked in blue. The large black square marks the location of the Ringsend sewage treatment plant.

A. Coliemore Harbour
B. Sandycove
C. Seapoint
D. Blackrock
E. Merrion Strand
F. Sandymount Strand
G. Half Moon Club
H. Bull Wall
I. Dollymount Strand South
J. Dollymount Bathing Zone
K. Dollymount Strand Middle
L. Dollymount Strand North

Table 2.1: Dates of sampling cruises in the bay and estuary, n number of stations sampled on each date, TON total oxidised nitrogen, PO_4 orthophosphate and Chl *a* chlorophyll *a*. y indicates the collection of a sample, n indicates parameter not measured,

Bay	n	TON	PO_4	Chl *a*	Estuary	N	TON	PO_4	Chl *a*
28-Jun-00	20	y	y	n	-	-	-	-	-
27-Jul-00	18	y	y	n	20-Jul-00	15	n	n	n
24-Aug-00	24	y	y	n	17-Aug-00	17	y	y	n
28-Sep-00	21	n	y	n	-	-	-	-	-
26-Oct-00	22	n	y	n	5-Oct-00	17	y	y	n
23-Nov-00	24	y	y	n	2-Nov-00	17	n	n	n
-	-	-	-	-	30-Nov-00	17	y	y	n
-	-	-	-	-	13-Dec-00	15	y	y	n
18-Jan-01	24	y	n	n	11-Jan-01	9	y	y	n
8-Feb-01	24	y	y	y	14-Feb-01	17	y	y	y
21-Feb-01	24	y	y	y	-	-	-	-	-
14-Mar-01	24	y	y	y	22-Mar-01	15	y	y	y
19-Apr-01	24	y	y	y	10-Apr-01	12	y	y	y
26-Apr-01	24	y	y	y	-	-	-	-	-
23-May-01	24	y	y	y	2-May-01	17	y	y	y
6-Jun-01	24	y	y	y	20-Jun-01	15	y	y	y
25-Jul-01	24	y	y	y	11-Jul-01	17	y	y	y
2-Aug-01	20	y	y	y	29-Aug-01	15	y	y	y
-	-	-	-	-	5-Sep-01	15	y	y	y
11-Oct-01	23	y	y	y	-	-	-	-	-
14-Nov-01	24	y	y	y	21-Nov-01	15	y	y	y
11-Dec-01	23	y	n	y	6-Dec-01	15	y	y	y
-	-	-	-	-	16-Jan-02	15	y	y	y
-	-	-	-	-	29-Jan-02	15	y	y	y
21-Feb-02	23	y	y	y	14-Feb-02	15	y	y	y
5-Mar-02	19	y	y	y	21-Mar-02	15	y	y	y
11-Apr-02	23	y	y	y	24-Apr-02	15	y	y	y
15-May-02	23	y	y	y	29-May-02	15	y	y	y
20-Jun-02	23	y	y	y	12-Jun-02	17	y	y	y
18-Jul-02	23	y	y	y	3-Jul-02	15	y	y	y
22-Aug-02	23	y	y	y	14-Aug-02	17	y	n	y
25-Sep-02	23	y	y	y	11-Sep-02	15	y	y	y
-	-	-	-	-	9-Oct-02	17	y	y	y
13-Nov-02	23	y	y	y	7-Nov-02	15	y	y	y
5-Dec-02	24	y	n	y	18-Dec-02	15	y	y	y
23-Jan-03	23	y	y	y	9-Jan-03	15	y	y	y
-	-	-	-	-	17-Feb-03	12	y	y	y
6-Mar-03	24	y	y	y	13-Mar-03	15	y	y	y
9-Apr-03	22	y	y	y	16-Apr-03	15	y	y	y
8-May-03	23	y	y	y	1-May-03	15	y	y	y
25-Jun-03	24	y	y	y	5-Jun-03	15	y	y	y
3-Jul-03	23	y	y	y	23-Jul-03	15	y	y	y
7-Aug-03	23	y	y		21-Aug-03	15	y	y	n
24-Sep-03	24	y	y	y	4-Sep-03	17	y	y	y
-	-	-	-	-	16-Oct-03	15	y	y	y
12-Nov-03	24	y	y	y	19-Nov-03	15	y	y	y
4-Dec-03	18	y	y	y	10-Dec-03	15	y	y	y
28-Jan-04	10	y	y	y	21-Jan-04	15	y	y	y
12-Feb-04	23	y	y	y	18-Feb-04	15	y	y	y
-	-	-	-	-	11-Mar-04	14	y	y	y
-	-	-	-	-	1-Apr-04	15	y	y	y
12-May-04	23	y	y	y	27-May-04	16	y	y	y
30-Jun-04	20	y	y	y	10-Jun-04	17	y	y	Y

2.1.0 Field sampling and measurements

Discrete surface and depth samples were taken using a weighted 2-litre PVC sampling bottle in the walled part of the estuary (stations 1-17). In the open bay (stations 18-41) surface samples only were taken by the same method. The following measurements and subsamples were taken from each of the bottles.

2.1.1 Salinity and temperature were measured from the sampling bottle using an electronic meter WTW LF197 fitted with a WTW Tetracon 325 probe calibrated against IAPSO seawater standards. A standard with known value 34.999 was used when sampling in the open bay and a standard with known value 30.002 was used for the brackish waters of the estuary.

2.1.2 Dissolved oxygen was measured from the sampling bottles using a WTW Oxi 197 meter fitted with a WTW CellOx 325 probe. The metre was calibrated regularly assuming 100% saturation in air. Sub-samples were taken from the bottle for nutrient analysis.

2.1.3 25 ml of sample were collected for total phosphorus determination. Samples for total phosphorus analysis were pipetted directly into acid washed (1molar HCL) glass bottles using a 10 ml pipette (Labosystems Finnpipette).

2.1.4 20 ml of sample for total nitrogen determination were pipetted using a 10 ml pipette (Labosystems Finnpipette) into glass bottles (pre-treated by digestion[2] at 125 °C and 103.4 kPa in an LTE Scientific series 225 autoclave) .

2.1.5 Samples for dissolved nutrients were collected in disposable "BD plastipak" plastic 50 ml syringes. The analyte was passed through a disposable 0.45 µm Acrocap® filter unit. Having rinsed the filter with sample in order to avoid contamination, 100 ml of the analyte were syringed into opaque Nalgene HDPE plastic sampling bottles.

[2] digestion solution with 10 g $K_2S_2O_8$, 6g H_2BO_3, 3 g NaOH made up to 1liter with deionised water in a volumetric flask.

2.1.6 1-litre subsamples were taken for chlorophyll *a* and phaeopigment determination and stored in the dark until their return to the lab.

2.1.7 Subsamples for phytoplankton were collected in opaque Nalgene HDPE plastic sampling bottles. The samples were preserved with a few drops of Lugol's Iodine and stored in darkness on return to the lab.

2.1.8 Secchi depth was measured using a 20 cm diameter black and white secchi disk, the rope was marked at 0.5 m intervals.

2.1.9 Water samples were collected from the intertidal zone for chlorophyll a and phaeopigment determination using 1 litre plastic sampling bottles, the samples were collected from the surface of the water column in the intertidal area. Samples were stored in darkness until their return to the lab. A 100 ml subsample was then poured from each bottle into an opaque Nalgene HDPE plastic sampling bottle and preserved with a few drops of Lugol's Iodine for phytoplankton enumeration and identification.

2.2.0 YSI sondes

YSI 6600 multiprobe sondes are electronic instruments which can measure temperature, salinity, fluorescence, dissolved oxygen and depth (Figure 2.1.9). These instruments are battery operated. The time interval of sampling affects battery life and depending on sampling frequency the sondes may be left sampling unattended for up to three months. Data collected by the sonde were downloaded via a cable into a desktop PC for analysis. The sondes have 384 kilobyte internal memory (allowing storage of 150,000 readings).

Temperature and conductivity measurements are made with the YSI6560 temperature and conductivity probe. The temperature element of the probe comprises a thermistor made of metallic oxide. The thermistor changes resistance predictably with changing temperature and the algortihhm for conversion to temperature in degrees Celsius is built into the sonde software, the constant relationship between the resistance and temperature means that this probe required no temperature calibration.

The conductivity element of the probe is made of four nickel electrodes, the voltage drop due to the water between electrodes is used to calculate conductivity. Salinity is calculated automatically by the sonde from the temperature and conductivity readings using algorithms from "Standard Methods for the Examination of Waste and Wastewater (Anon., 1989). Salinity was calibrated using IAPSO standard seawater (34.999 p.s.u.).

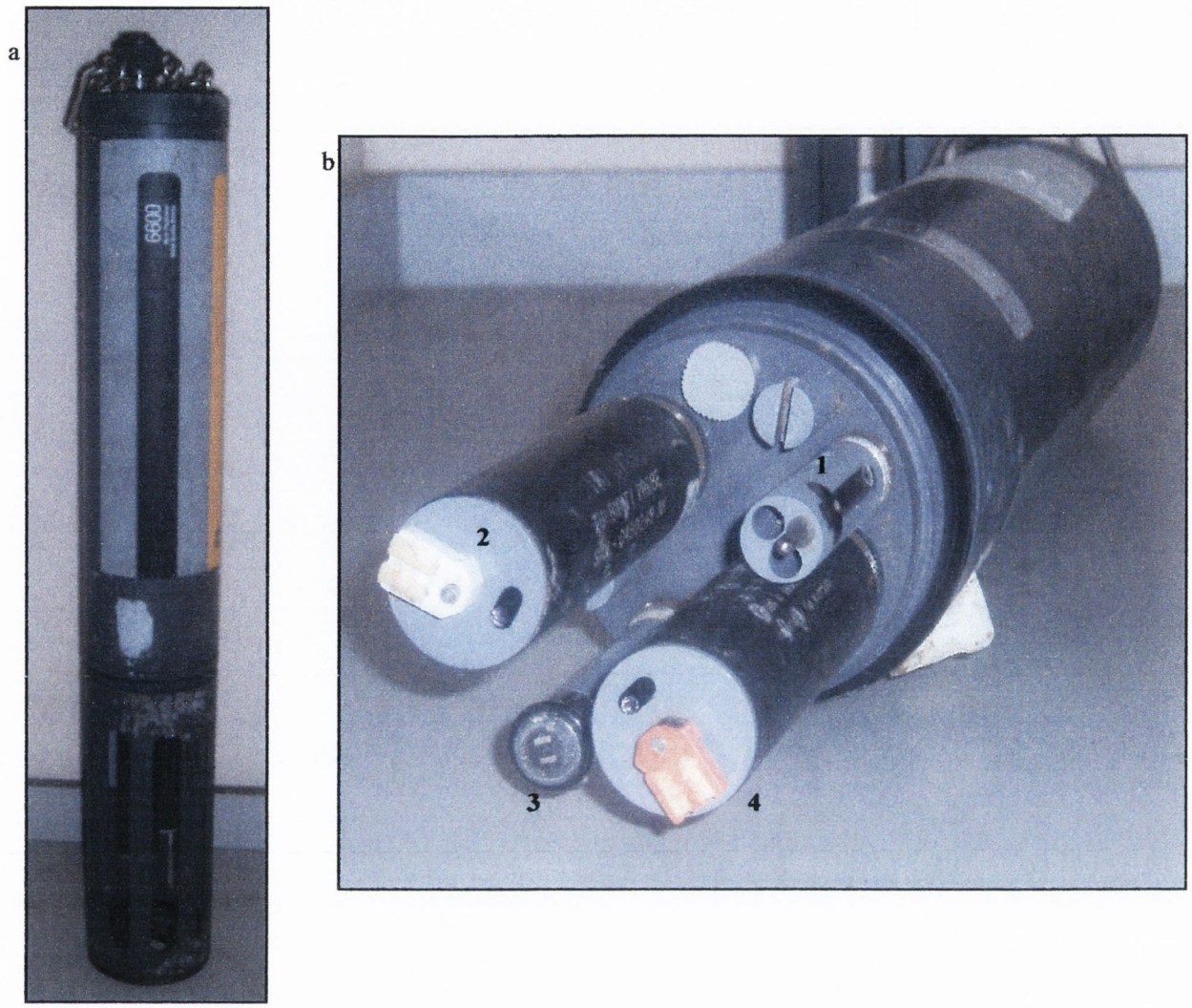


Plate 1: The YSI 6600 Multiprobe sonde. a) The sonde standing upright in its protective casing. Note the biofouling on the casing after a three month deployment. b) Close up of the sonde's probes. 1. Conductivity and temperature probe. 2. The fluorescence probe, the white element is the wiper which prevents biofouling. 3. The dissolved oxygen probe. 4. Turbidity probe (not used in this study).

Fluorescence is commonly used as a method of approximating phytoplankton chlorophyll concentration. The sonde's fluorescence probe (YSI 6025) measures the in vivo fluorescence signal of chlorophyll in water. This probe emits light at a wavelength of approximately 470 nm (visible as blue). This blue light stimulates the chlorophyll within phytoplankton cells to emit light (fluoresce) in the 650-700 nm region of the spectrum. The fluorescence is then measured by a highly sensitive photodiode which is screened by an optical filter which restricts backscatter of the 470 nm exciting light. In order to reduce the effect of biofouling of the fluorometer, the instrument is fitted with a wiper system to keep the photodiode clear of attached algae. Chlorophyll estimates derived from in-situ fluorescence are generally less accurate than in vitro determinations of actual pigment concentration because the photophysiological properties of the phytoplankton as well as the optical properties of the instrument effect the resulting measurement. Nevertheless these measurements allow much more frequent sampling intervals and are relatively inexpensive means (compared to laboratory based methods) of estimating phytoplankton biomass. Though the sondes have an inbuilt algorithm for the estimation of chlorophyll concentration further calibration was required due to in-situ variation in natural phytoplankton cell fluorescence, packaging effects and variable ratios of chlorophyll to phaeopigments.

The sonde's dissolved oxygen probe uses a Clarke type sensor which measures the current associated with the reduction of oxygen which diffuses through a Teflon membrane. The current is proportional to the partial pressure of oxygen in the surrounding seawater. Concentrations are measured with the sondes. Dissolved oxygen was calibrated in air and measured as percentage saturation.

2.2.1 Profiling deployment of sondes

The sondes were used on two occasions during routine sampling in the walled part of the estuary (stations 1-17) to create cross sectional profiles of temperature and salinity with depth along the estuary in order to establish the physical structure. The sondes were set to log data at four second intervals and deployed on a rope. The rope was lowered slowly over the edge of the boat at each of the sampling sites. When the rope

slackened the sondes were pulled slowly back to the surface in order to take as many measurements as possible. At each site the sonde was brought vertically through the water column several times in order to gain a more detailed profile of the water column given the relative infrequency of measurements.

2.2.2 In-situ time course deployment of sondes

Stations 3 and 16 in the walled part of the estuary were chosen for simultaneous deployment of two sondes for long term data recording. The two sondes were set to record temperature, salinity, dissolved oxygen, fluorescence and depth at intervals of 15 minutes. The sondes were deployed due east of station 3 and at station 16. Both sondes were deployed on the 1st of April 2004. The configuration of the deployment of the sondes was different at each site. The sonde at the North Bank Lighthouse was attached to a chain, hanging freely from the lighthouse until the 12th of May. The weight of the sonde and the fixed position of the lighthouse meant that the depth of the sonde varied over a tidal cycle and the data generated gave a vertical profile of the upper water column. The second sonde was hung from a floating marker buoy until the 10th of June. By attachment to the marker buoy it maintained a constant depth relative to the surface of the water. Since both chlorophyll a and its degredation products (phaeopigments) fluoresce and the ratio of chlorophyll to phaeopigments is highly variable, the fluorescence signal from the sonde was converted to an estimate of total phaeopigments. For this calibaration chlorophyll and phaeopigment data collected in Dublin Bay on the 1st of May were used. The mean measured total phaeopigment concentration was equated to the mean measured fluorescence signal.

$$\text{total phaeopigments } (mg.m^{-3}) = 3.09 * \text{fluorescence}$$

For the upper estuary the total phaeopigment concentration were converted to chlorophyll a concentration using the mean chlorophyll to phaeopigment ratio from monthly sampling trips (0.51). Net growth rates were calculated from the fluorescence signal using the equation

$$\mu = 1/(t_2 - t_1) * \ln(F_2/F_1)$$

where μ is the net growth rate; t_1 and t_2 are initial and final times respectively and F_1 and F_2 are the initial and final chlorophyll concentrations as measured by fluorescence.

2.3.0 Laboratory methods

2.3.1 Nutrient Analysis

Ammonia, phosphate, total oxidised nitrogen (TON) and nitrite were determined colorimetrically using a Zellweger analytics Lachat Flow Injection Analyser Quickhem FIA+ 800 series. The four parameters were determined simultaneously. For saline samples methods were based on Hansen & Koreleff (1999). The ranges and detection limits for measurement of each nutrient are shown in Table 2.2. All units of nutrient concentration are expressed as concentrations of elements rather than molecules. For example for TON 10 $\mu g.l^{-1}$ means 10 μg of N as TON per litre.

Nitrite (NO_2) was determined by diazotising the sample with sulphanilamide and coupling with N-1-Naphthylethylenediamine dihydrochloride. The resulting pink coloured dye was measured at 520 nm. total oxidised nitrogen (TON) was measured by reduction of nitrate (NO_3) to nitrite (NO_2) using a copperised cadmium column and measured in the same fashion as nitrite. Nitrate was determined by subtraction of the nitrite concentration from the TON concentration.

Table 2.2. Ranges and detection limits (D.L.) in $\mu g.l^{-1}$ of each nutrient measured with the flow injection analyser, for each type of sample analysed in the study.

	TON		NO_3		NO_2		NH_4		PO_4	
Sample type	Range	D.L.	Range	D.L.	Range	D.L.	Range	D.L.	Range	D.L.
Estuarine	0-1000	10	0-1000	10	0-200	2	0-1000	10	0-500	5
Open Bay	0-500	10	0-500	10	0-100	2	0-500	10	0-250	5
Sewage Effluent	0-1000	370	0-1000	370	0-250	5	0-1000	10	0-1000	10

For the determination of ammonia different methods were used in saline and freshwater samples.

In freshwaters, hypochlorite ions were generated by alkaline hydrolysis of sodium dichloroisocyanurate (DIC). These hypochlorite ions react with ammonia to produce monochloramine. The monochloramine reacts with salicylate ions to from a blue indophenol compound which was measured at 660 nm.

For saline samples the method was based on the Bertholet method. Ammonia reacted with hypochlorite ions in the presence of phenol and catalytic amounts of nitroprusside to from monochloramine giving indophenol blue. EDTA was added to the buffer to prevent formation and precipitation of calcium and magnesium hydroxides and carbonates.

Phosphate (PO_4) was determined by reaction with ammonium molybdate and potassium antimonyl tartarate in an acidic medium to from an antimonly-phosphomolybdate complex. This was reduced with ascorbic acid to yield an intense blue colour measured at 880nm. Throughout the text the term PO_4 refers to molybdate reactive phosphorus (MRP).

The ranges of measurements and the detection limits for all determinations are presented in Table 2.2.1. Detection limits were quantified as three times the standard deviation of 10 blank runs. The detection limits for TON and NH_4 were 10 $\mu g.l^{-1}$ and the detection limit for orthophosphate was 5 $\mu g.l^{-1}$ (where concentrations fell below the detection limits, nominal values of half the detection limits were used for calculation of averages and standard deviations).

Linear regressions of nutrient with salinity were carried out for the monthly samples in the bay and estuary when nutrient concentrations were above detection limits. The statistical significance p was calculated for correlation coefficients (r) of each regression. The riverine fluxes of nutrients were calculated by multiplication of the regressed nutrient concentrations for freshwater by the daily mean flow data for the particular sampling date. Flow data were provided by the EPA for the Liffey at Leixlip in County Kildare. At Leixlip the River Liffey flows represent 82% of the total catchment, these flows were multiplied by 1.21 to estimate total riverine flow in the Liffey estuary (McCarthaigh, 2000, 2001, 2002, 2003, 2004).

2.3.2 Suspended Solids

Suspended solid concentrations were measured for all sewage effluent samples. Whatmann GF/C glass fibre filters were placed on a filtration apparatus (electric pump and manifold) and washed with 100 ml of deionised water, suction was applied and maintained until all traces of water were removed. Filters were dried overnight in an oven at 105°C and stored in a desiccator. Filter papers were numbered with pencil and weighed on a Mettler AT 261 balance. The filters were placed on the filtration apparatus and 50 ml of the sewage effluent sample were filtered. The filter was removed to an oven and dried overnight at 105°C. Filters were cooled in a desiccator and weighed again on the Mettler AT 261 balance. The concentration of suspended solids per litre was calculated as

$$[(A-B)*1000]/ \text{ Sample volume (ml)}$$

Where A is the weight of the filter and suspended solids (mg) and B is the weight of the filter (mg).

2.3.3 Chlorophyll *a* and Phaeopigments

The 1-litre samples gathered during sampling trips were filtered onto Whatman GF/F filters (nominal pore size 0.45 μm) using an electric pump attached to a manifold (Pall Corp 15503). When glass manifold receptacles were used these were wrapped in tinfoil in order to avoid deterioration of the phaeopigments at other times dark tinted PVC receptacles were used to avoid these problems. Upon filtration the filters were folded in quarters using a tweezers taking care not to touch the filtered chlorophyll. The folded filters were then placed in glass vials graduated at 10 ml which were wrapped in tinfoil to prevent deterioration of the chlorophyll *a*. The vials were transferred to a freezer at –20 °C. The filters remained in the freezer for not more than 2 weeks.

Spectrophotometric analysis of the chlorophyll *a* and phaeopigments concentrations were carried out according to the method of Aminot and Rey (2000) using a Shimadzu UV 1601 spectrophotometer. The spectrophotometer was blanked using

Shimadzu UV 1601 spectrophotometer. The spectrophotometer was blanked using 90% acetone in both reference and sample cuvettes. Once a baseline correction was made the blank standard was examined at 665 nm and 750 nm wavelengths. If readings were greater than 0 the baseline correction protocol was repeated.

On removal from the freezer the vials containing the samples for chlorophyll analysis were transferred to an ice bath. A small amount of 97.8% acetone (~3 ml) was added to each glass vial and the filter was homogenized in the acetone for exactly one minute using an electrical homogeniser "Ultra-Turrax T8 IKA Labortechnik". After homogenisation the stirring rod of the homogeniser was washed down with a small amount of 97.8% acetone ensuring that any residue of the homogenate was retained in the graduated glass vials. The homogenized solution was made up to exactly 10 ml with 97.8% acetone. This solution was placed in a Whatman disposable 0.45 μm nylon membrane "Autovial" and filtered into a 20 mm cuvette. The surfaces of the cuvette were wiped thoroughly with soft lens tissue. The cuvette was placed in the spectrophotometer and the lid was closed. The absorbance was read at the 665 nm and 750 nm wavelengths. Following these readings, 0.1 ml of 1% by volume HCL was pipetted into the cuvette and after exactly 2 minutes the absorbance values at each wavelength were measured to determine total phaeopigment concentration. After each sample had been measured the cuvette was washed thoroughly with deionised water. The following equations were used to determine the concentration of chlorophyll *a* and phaeopigments in the sample

$$\text{Chlorophyll } a = 11*2.43*((A-B)*10)/(2 * V)$$

$$\text{Phaeopigments} = 11*2.43*(1.7*[C-D]-[A-B]*10)/(2*V)$$

Where A and B are the absorbencies at 665 nm and 750 nm respectively before acidification, V is the initial volume filtered and C and D are the absorbencies after acidification at 665 nm and 750 nm respectively. Total phaeopigments were calculated as the sum of Chlorophyll *a* and phaeopigments (Aminot & Rey, 2000).

2.3.4 Phytoplankton enumeration and identification

Phytoplankton samples were enumerated according to the method of Utermohl (1931), which involves the settling of a known volume of sample in a sedimentation chamber, the protocols used were based on those developed by the Helsinki commission monitoring and assessment group (HELCOM, 2001). Prior to sedimentation the sample bottles were gently rotated along all axes for one minute in order to distribute all cells evenly throughout the sample and to avoid bias against heavier cells, the sample was then poured directly into the chamber. The volume of sample settled for enumeration was determined by the total phaeopigment concentration in the sample according to Table 2.3.

Table 2.3: Determination of sample volume for settling in sedimentation chamber.

Total phaeopigment concentration ($mg.m^{-3}$)	Chamber volume (ml)
<1	25
>1,<10	10
>10	5

The sedimentation chambers were sealed with a thick circular coverslip and a thin layer of "Vaseline" petroleum jelly was applied in order to prevent air from entering the chamber. The samples were settled in darkness and away from vibration to avoid the production of convection currents and other processes which might result in deviations from a normal distribution of the plankton on the base of the sedimentation chamber. Settling time was determined by the length of the sedimentation chamber according to Table 2.4

Table 2.4: Appropriate settling time for sedimentation chamber of given volume

Volume of chamber (ml)	Sedimentation time (hours)
5	5
10	8
25	14

Phytoplankton were examined at x200 magnification using inverted phase contrast microscopy on a Nikon Eclipse TS100. Identification of phytoplankton was according to Dodge (1982) for dinoflagellates and Tomas (1997) and Sykes (1981) for diatoms and other groups. The cell was considered a single counting unit. At least 20 fields or 200 cells of the most abundant species were counted. The number of counting units per litre was determined by multiplying the number of fields counted by the coefficient C given in equation 1

Equation 1:

$$C = \frac{A \times 1000}{N \times a \times V}$$

Where

A = the cross section area of the top of the cylinder (491 000 000 μm^2)

N = number of fields counted

a = area of a single field

V = Volume of sample settled

Approximate 95% confidence limits were calculated using equation 2 (HELCOM, 2001)

Equation 2:

$$C.L. = n \pm 2 \times \frac{100}{\sqrt{n}}\%$$

Where n is the number of cells counted.

Cell carbon content was estimated for the most abundant phytoplankton species using biovolume calculations according to the method of Kovala and Larrance (1966). The mean dimensions of 20 cells were used for the calculation of the biovolumes.

2.4.0 Modelled Parameters

2.4.1 Tidal Currents

Mean tidal cycle current speeds were modelled from previously published data (ERU. 1992). Mean current speeds for a tidal cycle during spring and neap tides were plotted against tidal range for the day. The resulting linear equation (Figure 2.3) was applied to tidal range data from tidal predictions in Dublin Bay. The mean tidal current speeds were used to calculate a relative stratification parameter $1/u^3$ where u is the tidal current speed (Simpson and Pingree, 1978).

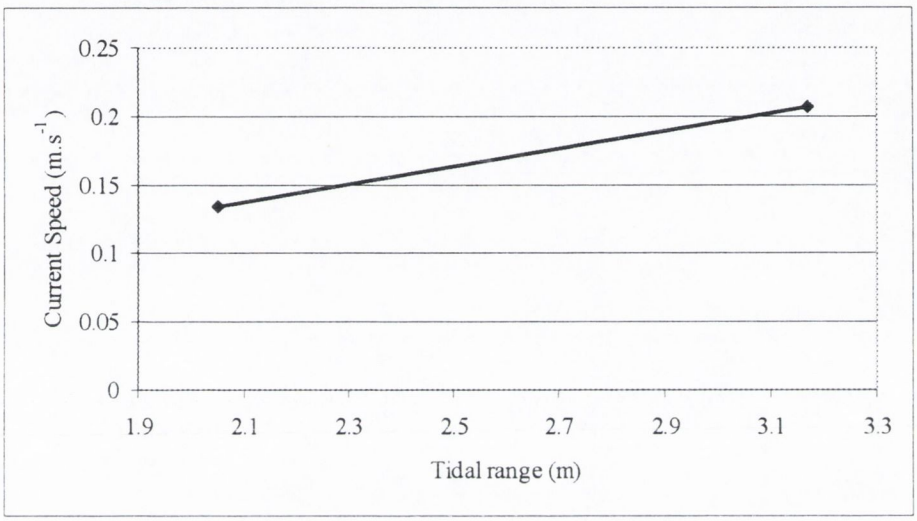


Figure 2.3: Maximum daily tidal range (x axis) plotted against mean current speed. Current Speed = 0.0644*Tidal range + 0.002 for 1st of October 1989 and 7th of October 1989 (data from ERU 1992).

2.4.2 Flushing time

Two methods were used for the calculation of flushing time. Flushing time of the Liffey estuary due to tidal forcing was calculated according to the tidal prism method of Dyer (1973). The volume of the estuary (V) m^3 was calculated using depth data from admiralty charts and the area of the channel. The tidal prism volume (P) (which varies over the spring neap cycle) was calculated using the local tide tables and areas from the admiralty charts. Flushing time was calculated as

$$[(V+P)/P]*t$$

where t is the time taken for a tidal cycle (12.42 hours). Flushing times in hours were calculated for mean and maximum spring tides and for mean and minimum neap tides. The resulting flushing times were then plotted against tidal range. Figure 2.4 illustrates the linear relationship between tidal range and flushing time. Flushing time due to the influence of river flow was calculated as

$$T_f=V/Q$$

Where T_f is flushing time, V is the volume of the estuary and Q is the daily averaged flux of water from the Liffey.

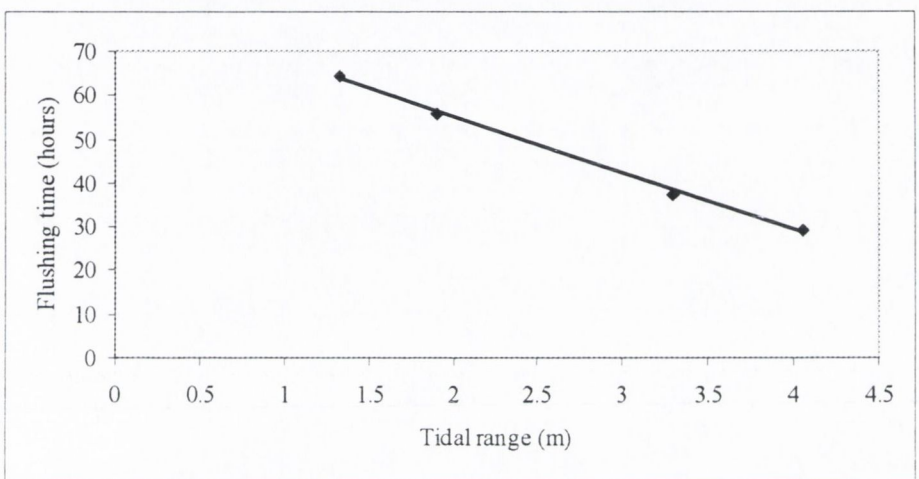


Figure 2.4: Modelled Flushing time plotted against tidal range .
Flushing time = -12.858 tidal range + 80.809

2.4.3 Light penetration

The diffuse attenuation coefficient of Photosynthetically Active Radiation (kPAR) was estimated from a published relationship between k (PAR) and secchi depth Z_{sd} in the Irish Sea (Bowers *et al.* 2002).

$$z_{sd} * k(PAR) = 1.41$$

and $$k(PAR) = 1.41 / z_{sd}$$

The euphotic zone may be defined as that part of the water column to which light penetrates and photosynthesis may occur. The compensation depth of water is the depth where there is sufficient light so that photosynthesis equals respiration (often taken as 0.1% of incident irradiation), this marks the bottom of the euphotic zone.

The depth of the euphotic zone can thus be calculated as

$$Z_p = 4.605 / k(PAR)$$

2.5.0 Flow data

Flow data were provided by the EPA from their measurement station at Leixlip. Flow at this point represents 82% of the Liffey catchment area. These flow data were adjusted by multiplication to account for 100% of the catchment. Where linear regressions were not statistically significant mean concentrations of the nutrient in the upper estuary were used for the calculation of fluxes. The river and estuarine fluxes of chlorophyll *a* were calculated in a similar fashion and converted to a carbon flux using a ratio of 1:40 (Jones, 1979).

2.6.0 Data analysis

Linear regressions and other simple statistical functions were carried out using the Microsoft Excel spreadsheet software package.

Maps of the distribution of the various parameters within the study area and vertical sections of the estuary were created using the Surfer 8 software package. The kriging method was used for interpolation of the spatial distributions.

CHAPTER 3: NUTRIENT STATUS

3.0.1 The Eutrophication problem

Human activity through changes in land use, agriculture, forestry and urbanisation has resulted in serious perturbations to biogeochemical cycles of carbon, nitrogen and phosphorus. Anthropogenic inputs of nitrogen to terrestrial ecosystems are now at least the same size if not greater than natural inputs, and are likely to continue increasing as global population continues to increase (Tilman *et al.*, 2001). One major result of these altered cycles is an increase in the amount of nutrients entering rivers, estuaries and coastal zones around the world (Smith *et al.*, 1999). The principle anthropogenic sources of nitrogen and phosphorus to river and estuarine systems are agriculturally derived runoff and wastewater inputs (Vitousek *et al.*, 1997). Many studies show direct linkages between land use and nutrient concentrations in rivers and estuaries (e.g. Howarth, 1998; Meeuwig, 1999; Tilman *et al.*, 2001; Nedwell *et al.*, 2002; Turner & Rabalais, 2003). While nutrient data representing undisturbed conditions for rivers and estuaries are not always available, nitrogen loading to these systems is thought to have increased by 6-50 times while loading in phosphorus is thought to have increased 18-180 times from baseline conditions (Conley, 2000). While the nitrogen load entering rivers, estuaries, continental shelves and the open ocean is sequentially reduced by denitrification (Galloway *et al.*, 2003), these nutrient inputs still have profound effects for ecosystem function in many systems.

Unlike limnological examples, the eutrophication process in estuaries is generally not a linear response in biomass to increase of the limiting nutrient. Since estuarine environments exhibit a diverse array of physical and chemical conditions, both within a given estuary and between estuaries, there is to date no universally applicable paradigm of estuarine eutrophication (Cloern, 2001). However the impacts of anthropogenic nutrient inputs have been well documented for numerous systems around the world. Bricker *et al.*, (1999) found evidence for moderate to high eutrophication in 67% of estuarine surface area studied on the East coast of the United States and coastal marine eutrophication has caused anoxia at times covering an area greater than 15,540 km^2 in the northern Gulf of Mexico associated with the highly eutrophied waters of the Mississippi outflow (Rabalais *et al.*, 2001, McIsaac *et al.*,

2001). Though a systematic assessment of estuarine eutrophication similar to that of Bricker *et al.* (1999, 2003) has not been carried out in Europe, many major European eutrophied rivers have been identified. Eutrophied European river systems include the rivers Scheldt, Rhine, Seine, Thames, Loire and Danube (Cabecadas *et al.*, 1999; Aminot *et al.*, 1998; Nedwell *et al.*, 2002; OSPAR, 2003; Abril *et al.*, 2003; Schreiber *et al.*, 2003). The classification of the eutrophication status of the Liffey estuary has recently been revised. Based on data from 1995-1999 the estuary was considered eutrophic but this has recently been revised to intermediate status (Toner *et al.*, 2005). In general semi-enclosed seas are more susceptible to eutrophication than the open ocean. In Europe eutrophication effects have been extensively studied in the North Sea (Hydes et al, 1999; Ducroty, 1999; Colijn *et al.*, 2002; Lacroix *et al.*, 2004); the Baltic Sea (Savchuk, 2005; Neumann & Schernewski, 2005) and the Black Sea (Gordina *et al.*, 2001; Turkoglu & Koray, 2002; Feidrich *et al.*, 2002)

The question of eutrophication in the Irish Sea is less clear cut. Allen *et al.* (1998) described an upward trend in nutrient concentrations in the Irish Sea from a long time series in Port Erin on the Isle of Man which was observed to coincide with a significant increase in chlorophyll a concentrations. Other authors attributed the apparent nutrient increase to climatic forcing (Gibson *et al.*, 1997). However a recent study comparing the long term time series from the Isle of Man with a second long term time series (from Menai Bridge) concluded that anthropogenic loading governs long term variations in nutrient concentrations in the Irish Sea (Evans *et al.*, 2003). Major U.K contributors to eutrophication in the Irish Sea carrying high nutrient loads include the Severn and the Mersey (Nedwell *et al.*, 2002). Despite recurrent high nutrient concentrations at the mouths of the rivers Liffey, Boyne and Slaney (McGovern *et al.*, 2002), none of the coastal or bay areas studied by the EPA for the period 1999-2003 in the Irish Sea are considered to be eutrophied (Toner *et al.*, 2005).

Liebig's law of the minimum states that the yield of plants can be limited by the nutrient that is present in the environment in the least quantity relative to plant demands for growth. The three principal macronutrients necessary for plant growth are C, N and P (though carbon is rarely if ever limiting in coastal marine and estuarine environments). For phytoplankton C:N:P requirements are generally accepted to be in the Redfield (1963) ratio 106:16:1, though exceptions do occur (Michaels *et al.*, 2001;

Hall *et al.*, 2005). Diatoms which account for 40% of primary production in the ocean (Sarthou *et al.*, 2005) have in addition a requirement for Si which makes up their frustules and may become limiting to them (e.g. Kristiansen *et al.*, 2001). In the freshwater environment P is generally considered limiting while in the marine environment N is generally thought to be the limiting nutrient (Cloern, 2001). Notable exceptions to N limitation in the marine environment include large areas limited by micronutrients particularly Fe (Michaels *et al.*, 2001). Since estuaries represent a transitional zone from freshwater to marine water the question of nutrient limitation from one end of the estuarine continuum to another also varies. Some estuaries display a seasonal shift from P limitation in spring to N limitation in summer (Conley, 2000) while in some eutrophied estuaries neither nutrient is limiting, a situation known as hypernutrification (Elliott and McLusky, 2002).

In the study area while annual nutrient loading of the system has been quantified in the past (Brennan *et al.*, 1994; Wilson, 2005) and considerable problems with excessive macrofaunal abundance have been observed, there has been no comprehensive study of nutrient limitation conditions along the length of the Liffey estuary and over the seasonal cycle.

3.1.0 Results

3.1.1 Nutrient Composition

Data from the monthly sampling cruises clearly demonstrate that higher concentrations of all nutrients are found in the walled part of the estuary and lower concentrations are found in the open part of the Bay (Figure 3.1). Mean concentrations of TON in the estuary are more than 7 times those in the Bay; mean ammonia concentrations are 7.3 times higher and orthophosphate concentrations in the estuary are 3.8 times those in the Bay. Throughout the study NO_3 was the principle form of nitrogen, making up on average 87% of DIN in the bay and 76% of DIN in the estuary. Table 3.1 summarises the nutrient data at all sampling stations.

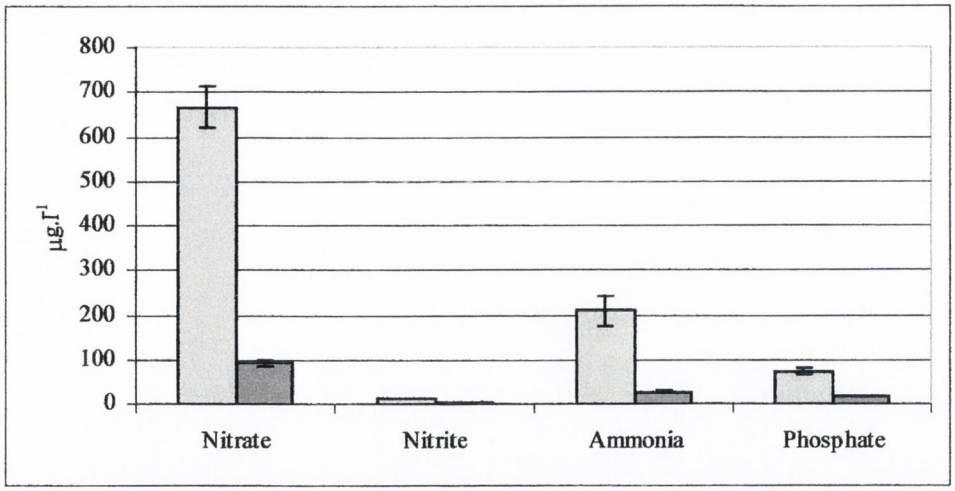


Figure 3.1: Mean nutrient concentrations for the period 2000-2004 in the walled part of the estuary (light grey) and in the open Bay (dark grey). Error bars are 95% confidence intervals

Figure 3.2 illustrates the typical spatial pattern of nutrients in the walled part of the estuary prior to the upgrading of the sewage treatment plant (commissioned, June 2003). TON concentrations decline steadily seawards. Highest concentrations are generally found at Station 1 and lowest concentrations at Station 14 at the mouth of the estuary. Distribution of PO_4 and NH_4 show a different pattern with large peaks at stations 11 and 12 off the Ringsend sewage treatment plant. Highest variability in nutrient concentrations was found at stations 9-11 for PO_4 and NH_4 reflecting the sporadic discharges of sewage effluent. TON variability was highest in the upper estuary reflecting variations in salinity. In the open bay stations 18-41 variability was low reflecting the essentially marine origin of the waters.

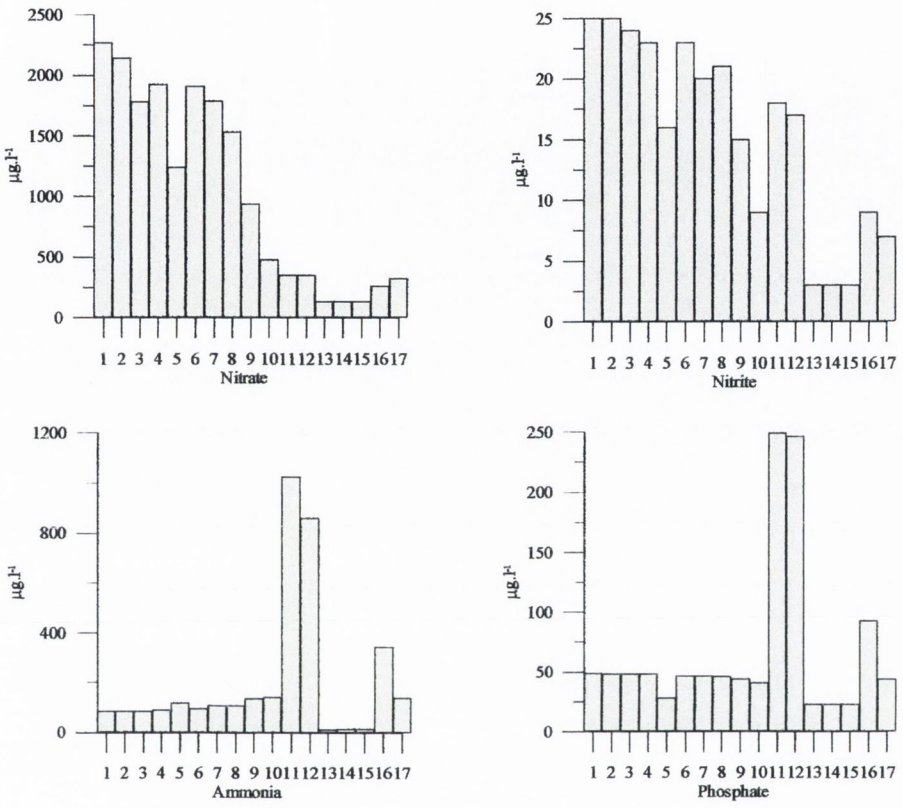


Figure 3.2: Typical winter distribution of nutrients in the walled part of the estuary prior to the upgrading of the Ringsend sewage treatment plant (data from 30th of November 2000). The numbers on the x-axis are station numbers.

Table 3.1: Mean, standard deviation (s.d.), number of measurements (n) and coefficient of variance (C.V.) for NO_3, NO_2, NH_4 and PO_4 at each station all concentrations are expressed in $\mu g.l^{-1}$.

	Nitrate				Nitrite				Ammonia				Orthophosphate			
Stn.	Mean	s.d.	n	C.V.	Mean	s.d.	n	C.V.	Mean	s.d.	n	C.V.	Mean	s.d.	n	C.V.
1	1301	551	10	42	24	20	12	82	82	35	12	42	57	16	11	29
2	1122	620	11	55	18	8	13	45	79	36	12	46	57	19	12	33
3	1402	681	37	49	21	8	42	39	69	28	41	40	60	23	43	39
4	1372	720	39	52	19	8	42	42	58	29	42	51	65	23	43	35
5	1047	633	40	60	15	6	42	37	53	82	43	155	53	17	43	31
6	1211	712	40	59	18	6	42	36	54	48	42	88	62	17	44	27
7	837	543	43	65	14	5	43	40	65	39	44	59	54	15	45	29
8	741	514	43	69	12	5	42	42	74	36	44	48	49	14	45	29
9	467	406	41	87	12	17	42	143	69	1249	43	1798	47	184	44	390
10	423	326	41	77	11	9	42	74	93	582	43	625	54	72	45	134
11	448	400	40	89	18	18	43	98	327	555	42	170	232	184	45	79
12	369	267	42	72	18	18	43	97	432	423	41	98	196	87	44	45
13	348	261	40	75	12	10	40	83	279	252	41	90	120	56	42	47
14	239	236	40	99	10	8	38	80	216	257	39	119	97	52	40	53
15	294	261	40	89	10	9	40	91	171	164	41	95	89	52	42	59
16	307	221	40	72	11	8	38	71	151	157	43	104	89	45	42	51
17	329	253	39	77	9	5	40	56	81	196	42	242	65	36	42	55
18	126	139	40	110	5	4	40	78	55	49	10	90	23	13	41	58
19	121	136	33	112	5	3	34	74	44	48	11	110	23	14	35	60
20	92	97	36	105	4	4	36	83	34	37	3	109	19	13	37	69
21	98	102	35	105	5	4	32	82	28	29	3	105	19	10	36	54
22	92	100	33	109	4	4	34	91	25	24	3	94	18	10	34	55
23	108	104	39	96	5	4	40	81	36	31	3	87	21	11	40	55
24	105	103	40	98	5	4	40	85	37	37	3	101	21	13	41	60
25	97	96	40	99	5	4	40	84	33	32	3	96	19	12	41	61
26	97	96	40	99	4	4	40	84	31	24	3	77	20	11	41	58
27	91	92	40	100	4	4	40	98	28	22	15	79	19	10	41	54
28	89	88	39	99	4	4	40	90	29	26	4	90	18	11	41	60
29	83	85	40	103	4	3	40	87	19	14	3	76	17	10	41	61
30	83	87	39	105	4	4	39	94	30	26	8	86	18	11	40	60
31	91	87	39	96	4	3	39	81	35	41	13	116	21	14	40	66
32	88	86	39	98	4	3	39	85	34	39	3	115	21	14	40	66
33	82	86	39	104	4	4	38	88	22	23	3	105	17	11	40	65
34	84	87	40	103	4	3	39	84	21	20	3	92	17	10	40	61
35	84	76	38	91	4	3	38	78	25	28	3	114	19	12	39	65
36	80	76	36	96	4	3	36	86	14	13	3	93	16	10	37	63
37	82	81	36	98	4	3	36	79	17	17	3	102	17	11	36	67
38	83	84	36	102	4	3	36	91	17	20	3	122	17	11	37	67
39	86	80	35	93	4	3	35	77	21	26	37	124	19	12	33	63
40	83	82	37	98	4	3	37	83	31	34	3	111	20	13	37	68
41	101	91	18	90	4	3	17	65	17	22	3	129	17	11	18	63

3.1.2 Mixing curves

In order to investigate the variability in nutrient concentrations and identify any sources and sinks of nutrients, linear mixing curves of all nutrients with salinity were carried out on the data from all monthly sampling cruises. Table 3.2 summarises the data from these mixing curves (full data for the mixing curves can be found in Appendix II). Additional mixing curves of the ratio DIN:P with salinity were also carried out for sampling cruises in the walled part of the estuary in order to predict the salinity at which the molar ratio of N:P reached the Redfield (1963) ratio.

In the walled part of the estuary all linear mixing curves of TON with salinity were significant, 43 were significant at $p<0.01$ and two were significant at $p<0.05$. Mixing curves of PO_4 with salinity did not show statistical significance at $p<0.05$ if the entire estuary was taken as a whole. As a result the PO_4 mixing curves were limited to those stations 1 to 8, representing waters from the Liffey and upstream of other major sources of PO_4. Of the 45 mixing curves 35 showed statistical significance at $p<0.05$ while 10 showed no statistical significance at this level. As with PO_4, mixing curves of NH_4 alone with salinity were not statistically significant at $p=0.05$ if the entire estuary was taken as a whole, nor did mixing curves from the stations of the upper estuary (stations 1 to 8) show a consistent pattern.

Table 3.2: Predicted freshwater concentrations of nutrients from statistically significant regressions with salinity in the walled part of the estuary (stn. 1-17) and in the bay (stn 18-41). PO_4 regressions are from the upper estuary only.

	Estuary			Bay		
	Mean	Max	Min	Mean	Max	Min
TON	986	3304	489	1922	3760	42
PO4	41	296	17	583	2851	123
NH4	-	-	-	2266	7452	384

Typical examples of mixing curves form the estuary are shown in Figure 3.3a. The variability in the predicted freshwater concentrations of TON and PO_4 is shown in Figure 3.3b the molar ratio of these inputs is shown in Figure 3.4

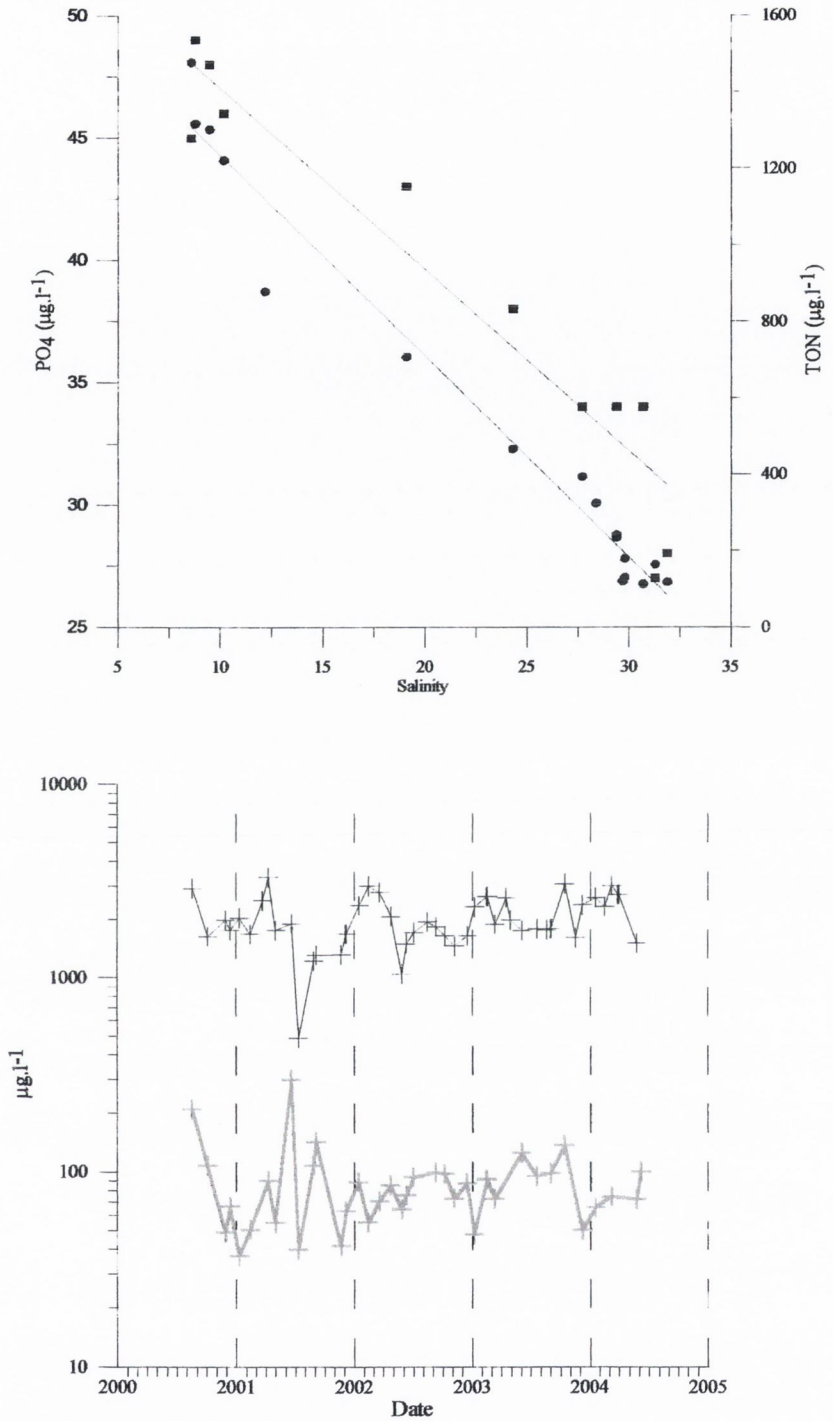


Figure 3.3: a) typical mixing curves (2/5/2001) for TON (circles) and PO_4 (squares) in the Liffey estuary relavent statistics are given in aooendix II. b) Freshwater TON (black) and PO_4 (grey) concentrations calculated from monthly linear mixing curves in the Liffey estuary, plotted against time, note the log scale.

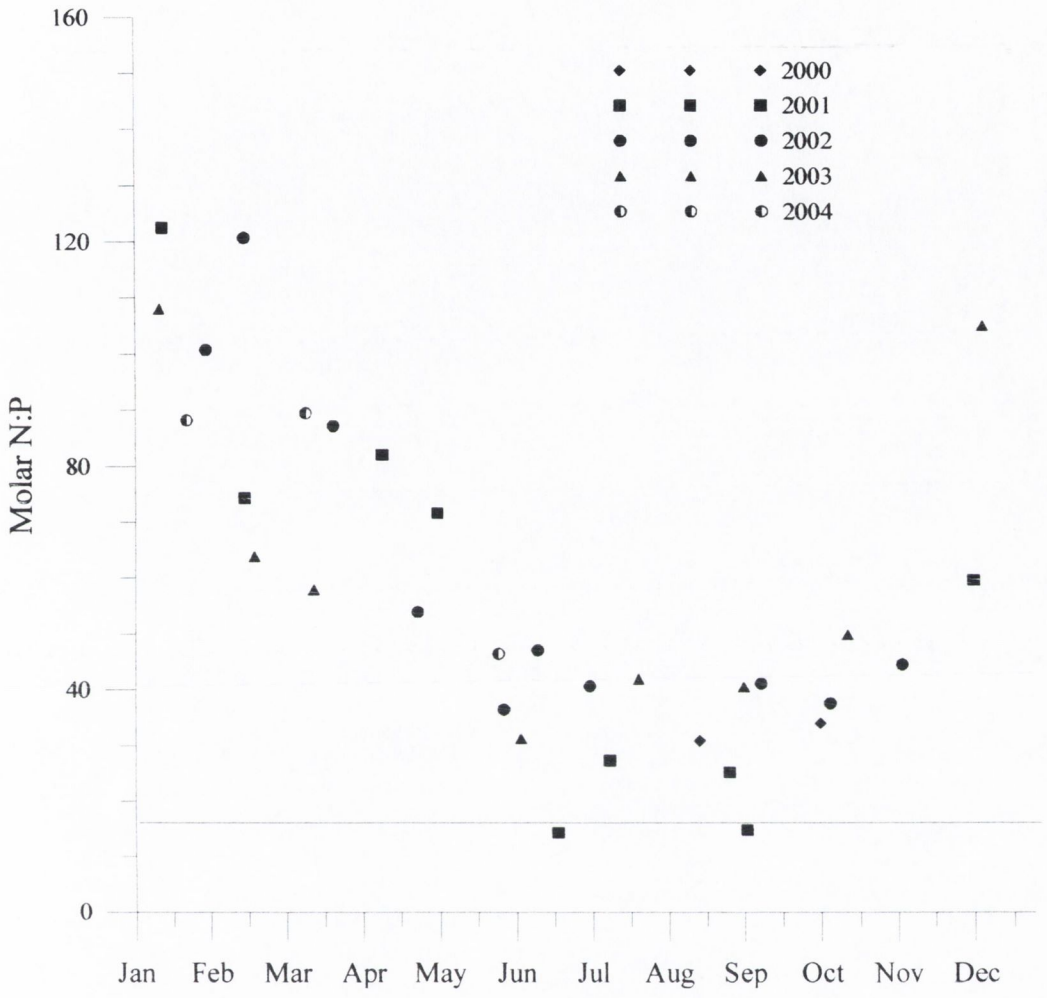
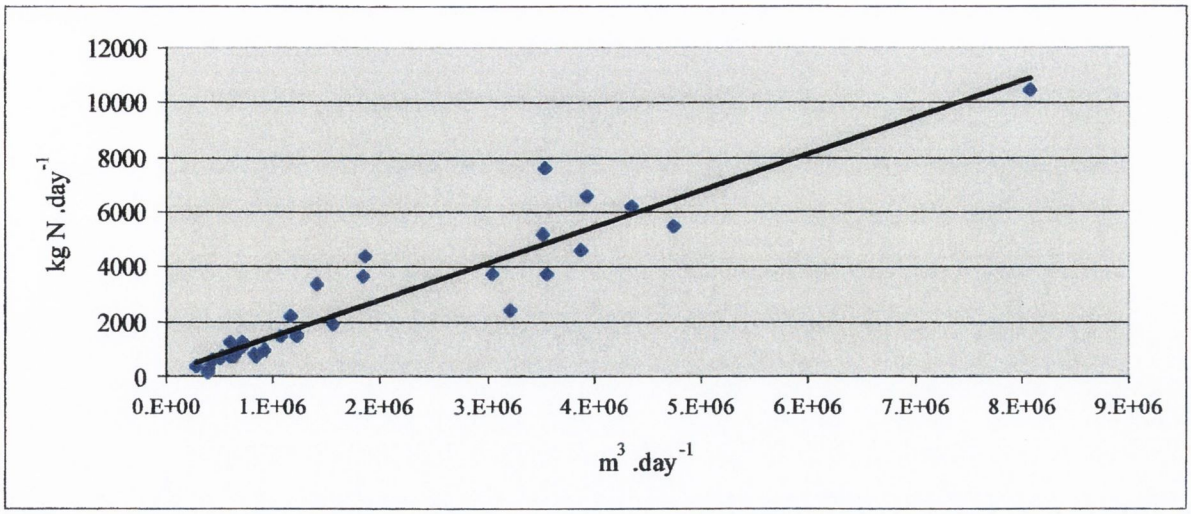


Figure 3.4: The molar ratio of nitrogen (as TON) and phosphorus (as PO_4) in the freshwaters of the Liffey (as predicted by linear regressions) plotted against Julian day for the entire study period. The black line marks the Redfied ratio.

For statistically significant nutrient mixing curves the freshwater endmembers were combined with freshwater flows on the sampling dates to estimate fluxes of the nutrients. Since mixing curves of ammonia were not significant in the walled part of the estuary, fluxes for ammonia were calculated by multiplication of observed values at stations 1, 2, and 3 with flows for these dates. The fluxes estimated from significant mixing curves produced apparent linear relationships between riverine nutrient fluxes and freshwater flow (Figures 3.5). The low slope values in these linear relationships (1.3×10^{-3} for TON and 4×10^{-5} for PO_4) indicate that higher flows have a dilution effect on nutrient concentrations. A weaker relationship existed between river flow and the molar ratio of TON:PO_4 (Figure 3.6)

There was some evidence for a seasonal draw down of N in the freshwaters of the Liffey, though this varied annually in timing and magnitude (Figure 3.3). However the persistent presence of high concentrations of both N and P throughout the year suggested that delivery was always in excess of demand. There was a clear seasonal cycle in the molar ratio of riverine TON:P (as estimated by linear regression) (Figure 3.4). Molar ratios were highest in winter (max=123) but between the months of June to August these ratios approached the Redfield ratio of N:16:P:1.

Of 44 mixing curves of DON:P with salinity, 36 showed significance at $p<0.01$ and six showed significance at $p<0.05$ while two were not significant at $p=0.05$. The mean salinity at which the predicted N:P ratio reached 16 was 31.9 (±s.d. =4.4) suggesting that the over supply of N in relation to P was widespread in the upper estuary but diminished with increasing salinity. Figure 3.7 shows typical mixing curves of DIN:P with salinity and the DIN:P ratio at each station. A seasonal signal was not apparent in the DIN:PO_4 mixing curves due to the continual supply of NH_4 and PO_4 from the sewage effluent. Despite the oversupply of DIN, concentrations of PO_4 never fell below detection limits in the estuary suggesting that it was always available for uptake and that Leibigian nutrient limitation never came into play i.e. that the estuary was hypernutrified with respect to N and P.



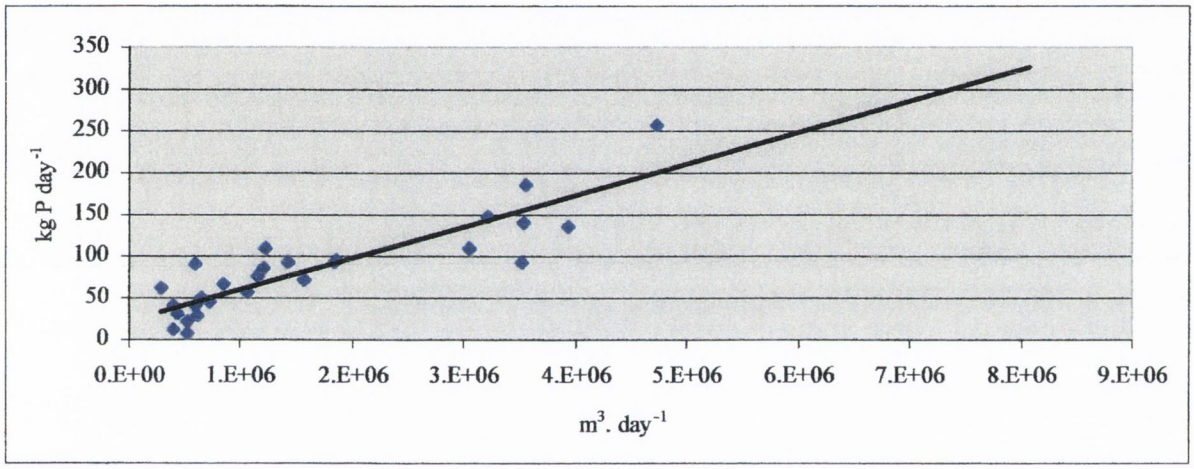


Figure 3.5: a) Relationship between River flow (m^3 day^{-1}) and N flux (as TON) ($kg.day^{-1}$)
$y = 0.0013x + 152.59$ $r^2 = 0.8789$ n=34 $p<0.001$

b)Relationship between River flow (m^3 day^{-1}) and P flux (as PO_4) ($kg.day^{-1}$)
$y = 4E\text{-}05x + 22.704$ $r^2 = 0.7776$ n=28 $p<0.001$

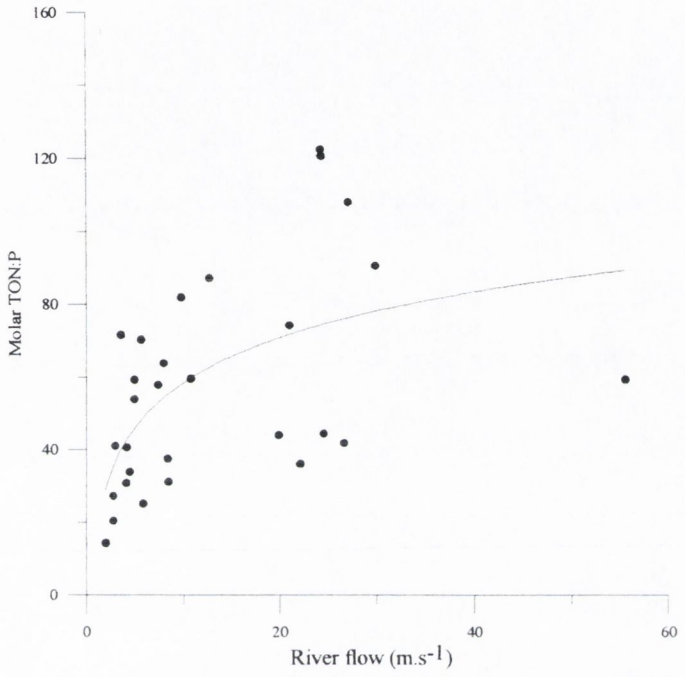


Figure 3.6: Plot showing the relationship between river flow and TON:PO_4 ratio as predicted by linear regressions.

TON:PO_4= 18.142 x Ln(flow)+16.612 (r^2=0.32, p=0.005).

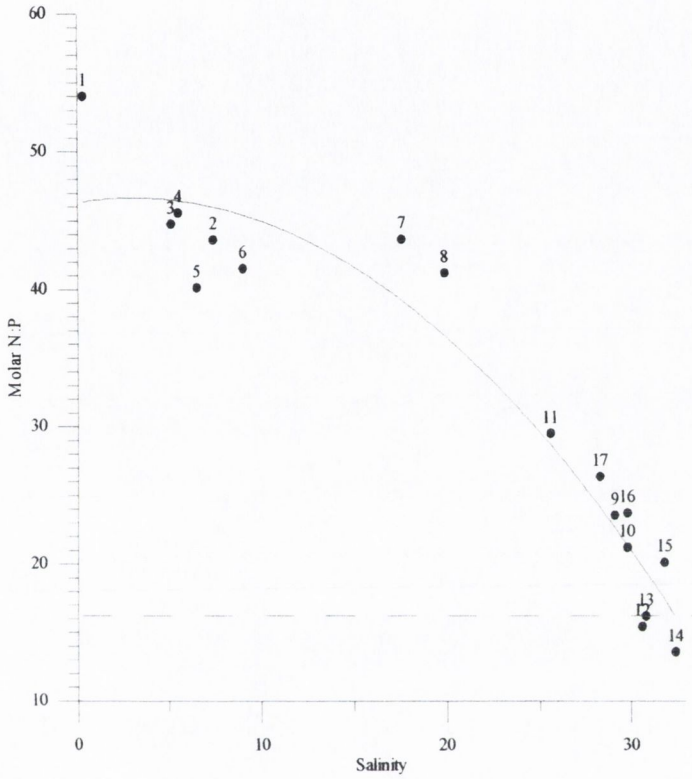


Figure 3.7: Typical regression of N:P with salinity in the walled part of the Liffey estuary. The numbers represent the station. The dashed line marks the Redfield ratio.

The mean annual riverine fluxes of TON from the River Liffey was 769.9 t $N.y^{-1}$ while the mean annual riverine flux of PO_4 28.8 $t.P.y^{-1}$. The three-year mean catchment area normalised TON and PO_4 concentrations give values of 647 kg $N.km^{-2}.y^{-1}$ and 22 kg $P.km^{-2}.y^{-1}$ respectively. The mean annual flux of ammonia was 37.6 t $N.y^{-1}$. The average molar ratio of these inputs was **N**:62:**P**:1 and is lower than the average molar ratio predicted by DIN: PO4 mixing curves (**N** 80: **P**:1) which takes into account the inputs from the sewage treatment plant.

In the outer bay, 37 linear mixing curves of TON with salinity were carried out, of which 33 showed significance at $p<0.01$ and one showed significance at $p<0.05$. The predicted freshwater endmembers of these mixing curves were higher but not significantly different ($p=0.05$) from those predicted in estuarine mixing curves (Table 3.2). This indicated that that while the Ringsend sewage effluent raised the TON load, concentrations in the effluent were similar to those in the Liffey waters. Of the 28 linear regression of PO_4 carried out in the bay 18 showed statistical significance at $p<0.01$ and 3 at $p<0.05$. The predicted freshwater concentrations of PO_4 from the significant mixing curves in the bay were significantly higher on average by five times ($p<0.01$) than those predicted by mixing curves in Group I, illustrating the high concentrations of PO_4 in the Ringsend sewage effluent and the importance of the treatment plant as a source of PO_4 to the bay. Of the 33 mixing curves of NH_4 with salinity carried out in the bay, 26 showed statistical significance at $p<0.01$ while two showed significance at $p<0.05$ and five were not significant at $p=0.05$. The mean predicted freshwater endmember of these mixing curves (2089 $\mu g.l^{-1}$) was far in excess (by two orders of magnitude) of any of the measured values of NH_4 in the upper estuary stations 1-6 beyond the immediate influence of the Ringsend sewage treatment plant.

3.1.3 Sewage effluent inputs

The other main input of nutrients to the Liffey estuary and Dublin Bay is that of the Ringsend sewage treatment plant. Accurate flow data from the sewage treatment plant were available only from 2003 and 2004; flow remained relatively constant over the two year period, with mean flow 4.27 $m^3.s^{-1}$. However mean nutrient concentrations

of the sewage effluent varied greatly over the upgrade of the sewage treatment plant (Figure 3.8). The principal differences in the composition in sewage effluent were an almost tenfold increase in the concentrations of TON and a concurrent decrease in NH_4 concentrations. PO_4 concentrations remained similar and suspended solid concentrations were reduced by half over the study period. Table 3.3 illustrates how sewage effluent inputs have changed over the last decade.

Table 3.3: Comparison of annual inputs of nutrients and suspended solids to the Liffey estuary from the Ringsend sewage treatment plant ($t.y^{-1}$). (Data for 1992-1993 from Brennan *et al.*, 1994).

	TON	NH_4	PO_4	DIN	SS
1993	33	1863	396	1896	12870
2001	38	2147	424	2185	28463
2002	149	2088	268	2237	19384
2003	720	873	325	1594	5990
2004	1298	450	352	1747	4895

The mean four year sewage DIN flux was 1941 $t.y^{-1}$ with ammonia accounting for 98% in 2001 but only 26% by 2004. The mean PO_4 flux was 342 $t.y^{-1}$. Fluxes of PO_4 remained relatively constant over the study period. The molar ratio of these inputs was N:13:P:1.

3.1.4 Spatial distribution

In some months the Liffey plume of low salinity water was detectable stretching from the mouth of the Liffey, northwards and eastwards towards Howth Head (Figure 3.9a). The plume was discernible to the furthest northeast extent of the study area. By this point the freshwaters had undergone near complete mixing (0.6% freshwater) with Irish Sea water to give a north/south partitioning either side of the 33.8 isohaline. The Liffey waters brought higher nutrient concentrations to the north of the bay while the south remained relatively unaffected (Figure 3.9 b, c). TON was the principle component of the DIN in the bay, and was approximately five times as abundant as NH_4.

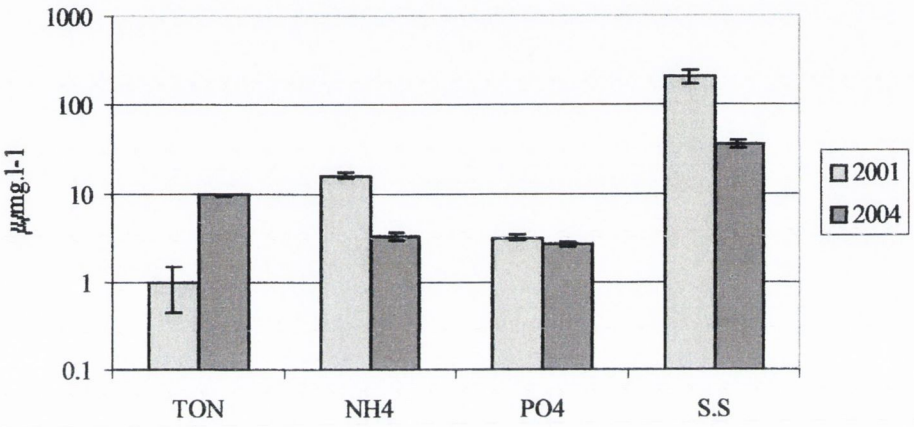
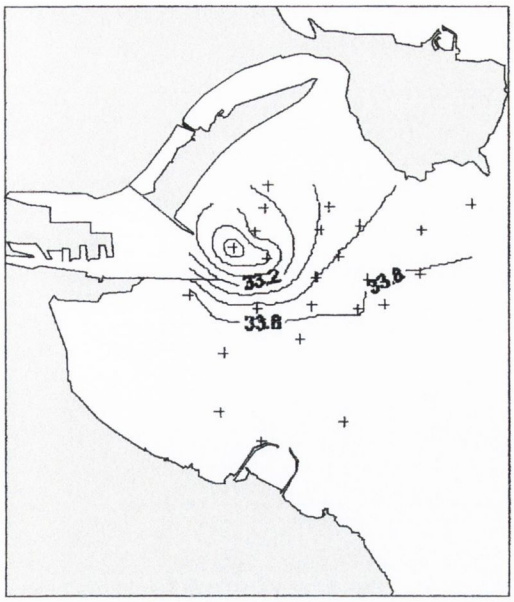
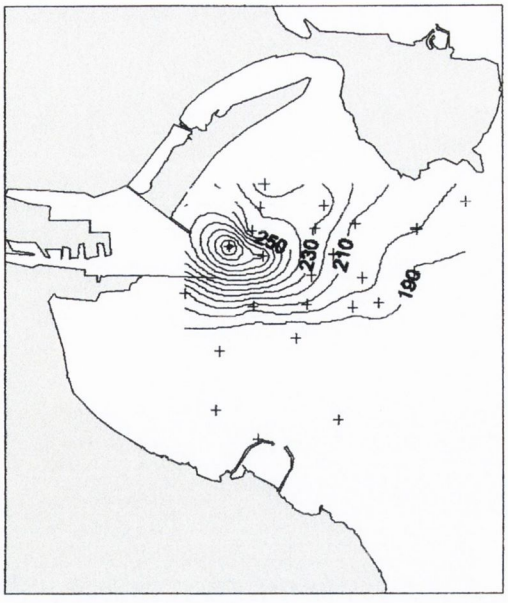


Figure 3.8: Mean nutrient and suspended solid concentrations in Ringsend sewage effluent before and after the upgrading of the sewage treatment plant. Error bars are 95% confidence intervals.



a



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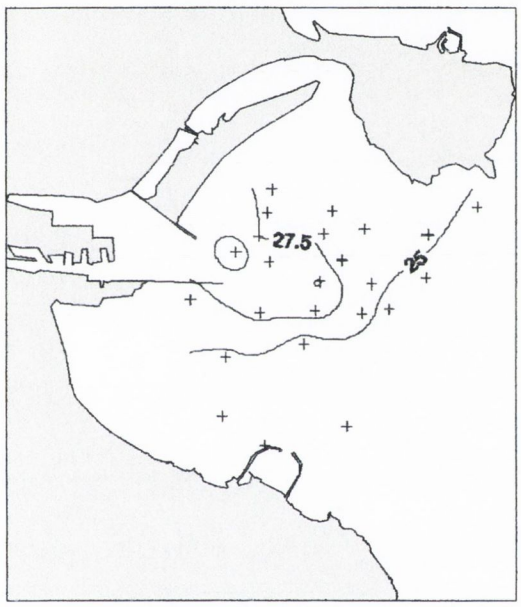

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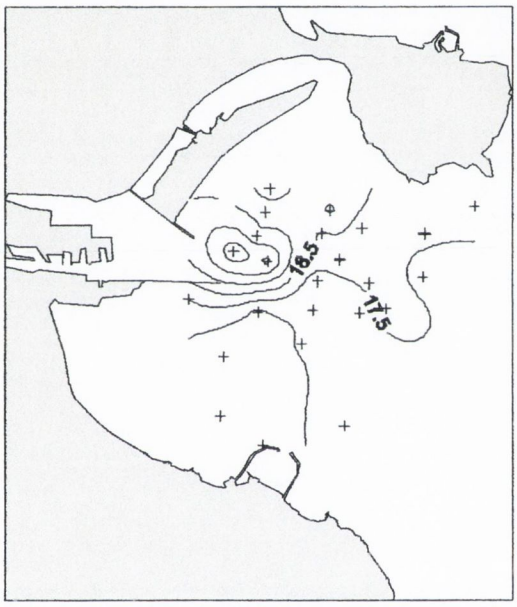

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Figure 3.9:

a) Average distribution of salinity (contours spaced at intervals of 0.2 p.s.u.)

b) Winter distribution of DIN (contours spaced at intervals of 10μg.l^{-1}).

c) Winter distribution of PO_4 (contours spaced at intervals of 2.5μg.l^{-1}).

d) Winter distribution of DIN: PO_4 (contours spaced at intervals of 1).

The average winter ratio of DIN:P was slightly elevated throughout the bay but highest ratios were at the mouth of the Liffey and the north of the bay (Figure 3.9d). A regression of winter N:P ratios against DIN ($p<0.01$, $r^2=0.832$) showed that most of the variability in N:P was due to the supply of nitrogen rather than phosphorus.

In winter, average DIN concentrations were 210 $\mu g.l^{-1}$ and average PO_4 concentrations were 26 $\mu g.l^{-1}$. Figure 3.10 shows the annual cycle in nutrient concentrations and ratios in the open bay for 2000-2003. Maximum concentrations in Bay waters were 910 $\mu g.l^{-1}$ and 53 $\mu g.l^{-1}$ for DIN and PO_4 respectively and these were associated with the Liffey plume of slightly brackish water. N:P ratios were elevated above the Redfield ratio in winter. After the spring bloom concentrations of all nutrients fell below detection limits (TON<10 $\mu g.l^{-1}$, PO_4<5 $\mu g.l^{-1}$) outside the Liffey plume and remained below these limits throughout the summer. Figure 3.11 shows the distribution of molar N:P in the Bay during the spring bloom of 2001. At this time, nutrients were still present in concentrations above detection limits yet the molar N:P ratio was below 16 in the south bay suggesting that nitrogen would shortly be limiting.

3.1.5 Dilution Model

Given the consistently linear behaviour of TON in the estuary it was possible to predict its concentrations at different salinities using known riverine and sewage fluxes and a simple dilution model. Table 3.4 lists the various inputs and outputs of the model along with their data sources and units. Mean freshwater TON flux (F_{IN}) and the mean freshwater TON concentration (N_{IN}) were calculated as

$$F_{IN}=(V_L x N_L)+(V_E x N_E)$$

$$N_{IN} = F_{IN}/(V_L+V_E)$$

where inflowing volumes of water V_L (Liffey volume) and V_E (Effluent volume) were the known water volumes for Liffey and Ringsend flows respectively and N_L and N_E are TON concentrations in the Liffey and the sewage effluent (taken from

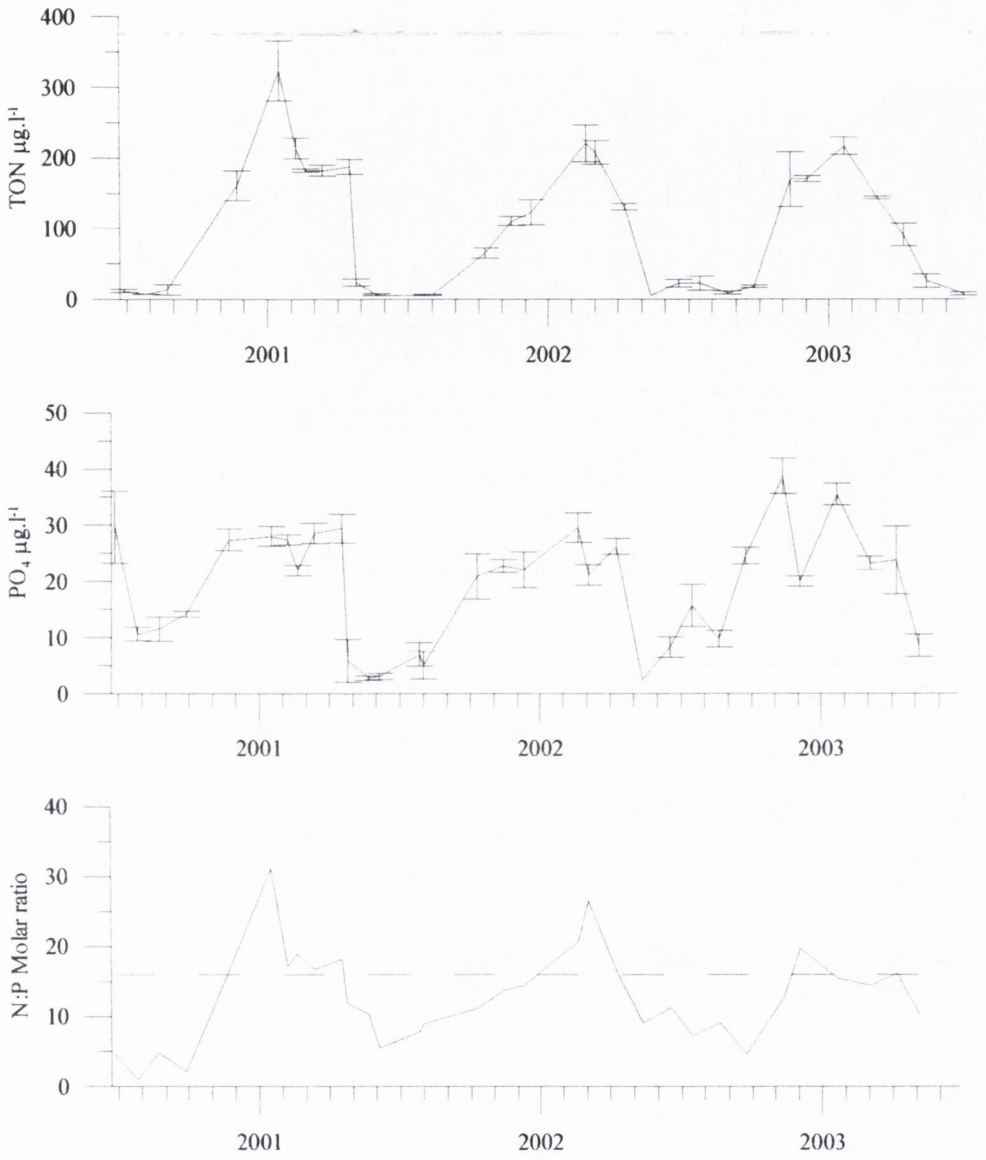


Figure 3.10:

a) Temporal pattern in TON concentration for the three full year periods studied, error bars are 95% confidence intervals.

b) Temporal pattern in PO_4 concentration for the three full year periods studied, error bars are 95% confidence intervals.

c) Temporal pattern in N:P molar concentration for the three full year periods studied.

Figure 3.11: Distribution of DIN:PO_4 ratio in April 2001 immediately prior to the reduction of nutrients below detection limits. The ratio lies above 16:1 in the Liffey plume and below this value in the south bay.

regression values for the Liffey and measured for Ringsend). The TON concentration N_{local} at a given salinity S_{local} was calculated as

$$N_{local} = [(N_{IN} \times (1-(Sea_{\%}/100)+(N_{SEA} \times (Sea_{\%}/100)]$$

Where $Sea_{\%}$ is the percentage of seawater at the salinity S_{local} calculated as 2.9586 x S_{local} (Figure 3.12). The salinity of seawater is taken to be 33.8 which is the mean salinity of waters in Dublin Bay not affected by the Liffey plume and represents the salinity boundary of the model.

Table 3.4: Parameters, type of data, units and source of data for simple dilution model.

Parameter		Description	Unit	Source
V_L	input	Liffey inflow	$m^3.day^{-1}$	EPA-data
V_E	input	Ringsend effluent	$m^3.day^{-1}$	Ringsend flow data
N_L	input	Liffey TON conc.	$mg.l^{-1}$	Mixing curves
N_E	input	Effluent TON conc.	$mg.l^{-1}$	Ringsend data
F_{IN}	output	Freshwater TON flux	$kg.day^{-1}$	$(V_L x N_L)+(V_E x N_E)$
N_{IN}	output	Mean freshwater TON conc.	$mg.l^{-1}$	$F_{IN}/(V_L+V_E)$
S_{SEA}	input	Salinity of sea (boundary)	-	From data (33.8)
N_{SEA}	input	Marine TON conc.	$mg.l^{-1}$	Mixing curves
S_{local}	input	Salinity at a given station	-	from data
$Sea_{\%}$	output	% seawater at S_{local}	%	(2.9586 x S_{local})
N_{local}	output	Mean TON at required salinity value	$mg.l^{-1}$	$[(N_{IN} \times (1-(Sea_{\%}/100)+(N_{SEA} \times (Sea_{\%}/100)]$

Validation of the model was used by comparing modelled values N_{local} to measured values of TON at different salinities. Only three dates were available when the full set of measured inputs for the model, i.e. Ringsend flow and effluent data and TON concentrations were available for the validation. Figure 3.13 illustrates the models predictive capabilities. The model predicted the nutrient concentrations accurately on the 13/3/03 and 16/4//03. On 4/9/03 modelled TON concentrations diverged form measured TON concentrations (Figure 3.14). The discrepancy between modelled and measured concentrations on 4/9/03 is due to the fact that sampling took place prior to the discharge of sewage effluent on that day which is timed to occur on ebbing tides.

The modelled TON concentrations represent daily average values. The measured values also diverged from modelled values at stations 5 and 6 due to the freshwater input of the river Dodder which has lower TON concentrations than the Liffey (Brennan *et al.*, 1994).

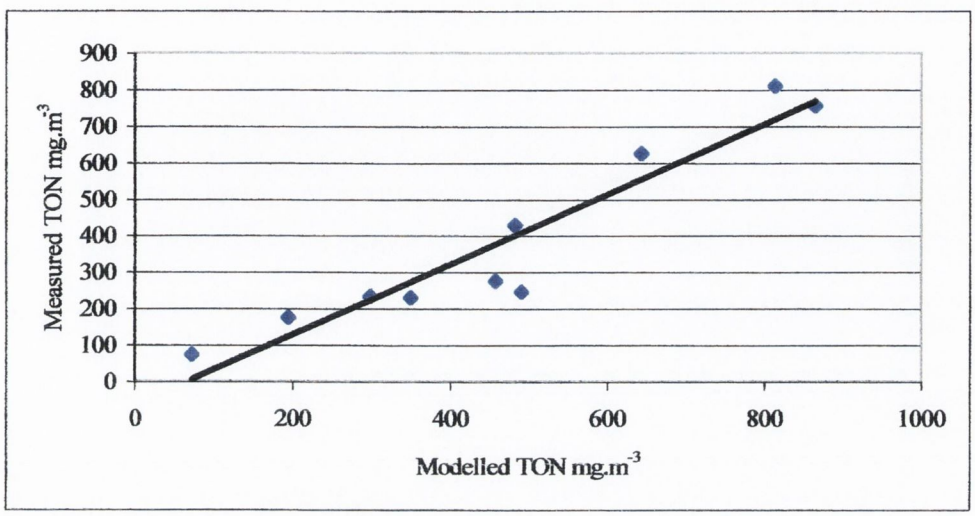


Figure 3.12: Measured and modelled concentrations of TON in the lower estuary. y = 0.9622x - 63.452 $r^2 = 0.899$ $p<0.001$. Data are from 13/3/03; 16/4/03 and 4/9/03.

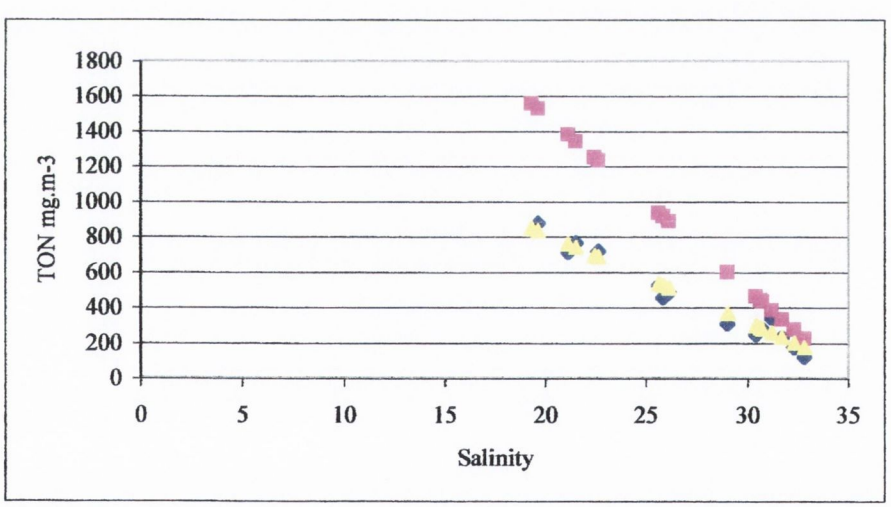


Figure 3.13: Measured TON concentrations 4/9/04 (blue); modelled TON concentrations (Pink) and TON concentrations modelled ignoring the Ringsend input for the day (Yellow) plotted against salinity.

On dates when the TON measurements were not available from the river Liffey the relationship between flux and flow (Figure 3.5a) was used to estimate the TON flux from the Liffey

$$V_L x N_L = 0.0013 \times V_L + 152.59$$

Since the N was apparently the limiting nutrient in the open bay, the parameter critical to the assessment of the impact of the TON increase was mean summer concentration of TON. The area chosen for the model investigations was that within the 33.2 isohaline, this is the area which has historically shown the most symptoms of eutrophication. The model was used to investigate the effects of

1) The observed and planned changing TON load due to the Ringsend sewage treatment plant upgrade.
2) The effect of variable river flow on TON concentrations

1) Mean summer concentration of TON at the 33.2 isohaline was estimated using fixed annual mean river and effluent flows and annual mean riverine nutrient concentrations and by varying the annual mean measured nutrient concentrations of the sewage effluent. Marine N concentrations were set to 0. Figure 3.15 shows the mean summer concentration of TON in waters of 33.2 salinity for the period 2001-2004 as well as the projected concentration in the north bay based on the planned volume increase in effluent discharge of 20%.

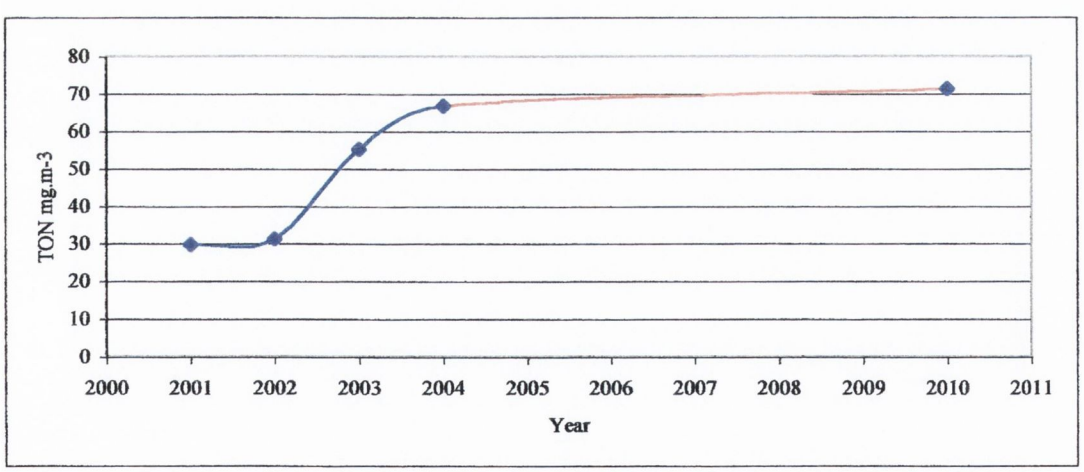


Figure 3.14: Modelled changes in summer TON concentrations at the 33.2 isohaline over the period of upgrade of the treatment plant, the red line is the projected increase associated with a 20% increase in discharge.

2) Figure 3.16 shows the modelled TON concentrations at the 33.2 isohaline from May to August 2004 (when measured nutrient concentrations in the open bay fell below detection limits).

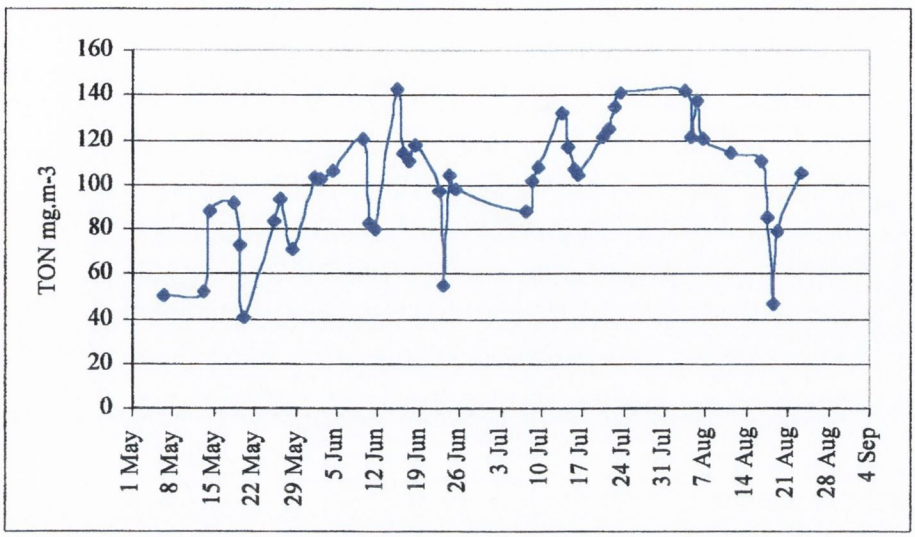


Figure 3.15: Modelled summer TON concentrations ($\mu g.l^{-1}$) at the 33.2 isohaline.

Figure 3.17 shows the relationship between river flow and modelled nutrient concentration for the period plotted above. The negative slope indicates the dilution effect as riverine inputs increase, most of the variation in nutrient concentrations is attributable to river flow.

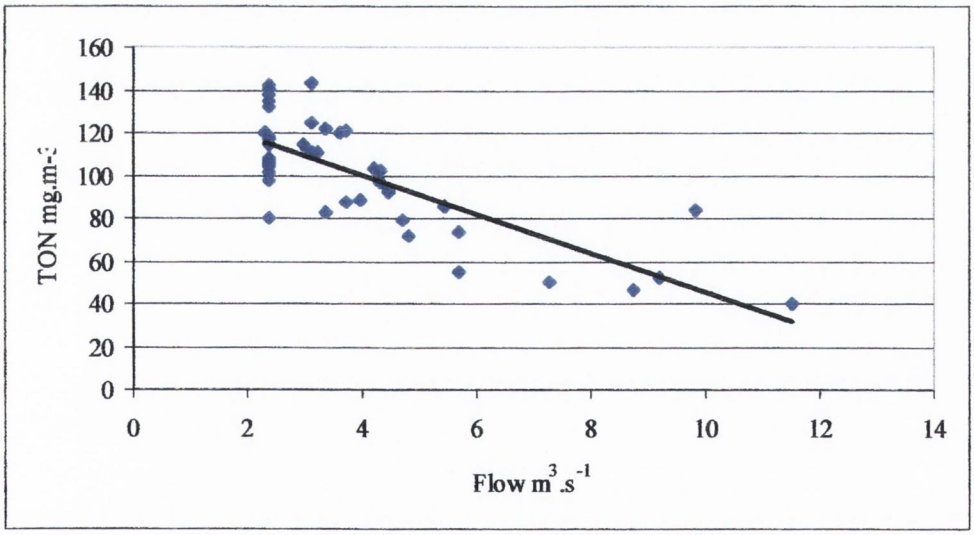


Figure 3.16: Negative linear relationship between river flow and TON concentration ($\mu g.l^{-1}$). TON = -9.1214*Flow+ 136.62, $r^2 = 0.5967$, $p<0.001$.

3.2.0 Discussion

The concentrations of nutrients in the Liffey estuary are at the high end of the moderately eutrophic category of Bricker *et al.* (1999). The mean DIN concentration was 891 μg $N.l^{-1}$ and values exceeding 1000 μg $N.l^{-1}$ are considered highly eutrophic. Similarly PO4 concentrations are at the upper end of the moderately eutrophic category with a mean of 73 μg $P.l^{-1}$ where 100 μg $P.l^{-1}$ is considered highly eutrophic. The concentration of nutrients is determined principally by mixing of Liffey water, sewage effluent and Irish Sea water.

The N:P ratios were consistently above the Redfield ratio in the estuary and indicate that P was the more likely to be potentially limiting to phytoplankton growth though excess nutrients were always available for uptake. Since within the walled part of the estuary nutrients (particularly N) are always in oversupply it appears that the estuary is hypernutrified. The fluxes of N and P from the river Liffey are highly variable being controlled largely by stochastic processes and having linear relationships with flow, but the ratio of these riverine inputs undergoes a seasonal pattern which is correlated to river flow. The equation constant in the relationship between river flow and TON: PO_4 indicates that a baseline TON:PO_4 ratio of 16:1 exists in the River Liffey and the ratio is elevated with increasing fresh water flow.
Further evidence for hypernutrification includes the consistently significant linear mixing curves between TON and PO_4 with salinity, these indicate that the nutrients act largely in a conservative fashion in the walled part of the Liffey estuary. This suggests that uptake through primary production is not a major factor altering nutrients in the estuary and that factors other than TON and PO_4 concentration (which were constantly superabundant) may control the proliferation of phytoplankton growth within the walled part of the estuary.

By contrast the Bay shows a marked seasonal cycle with slightly elevated winter N:P ratios, being driven chiefly by oversupply of nitrogen followed by spring nutrient depletion typically associated with a phytoplankton bloom. Although both DON and PO_4 concentrations fell below detection limits in the summer, N:P ratios prior to depletion were below the Redfield ratio. Taken together these suggest that N is the

limiting nutrient in the south of the bay as is contended for the Irish Sea as a whole (Evans *et al.*, 2003). The clockwise circulation of waters in the bay was reflected in the horizontal salinity distribution and suggests that any stimulation effects caused by nutrients exiting the river mouth is likely to occur on the north side of the bay, which is in agreement with previous studies of eutrophication phenomena in Dublin Bay (Brennan *et al.*, 1994). When mixing processes were strong due to strong tides or turbulence caused by bad weather the Liffey plume zone was not detectable and even when the plume was detectable off Howth Head it was practically indistinguishable from surrounding waters.

The calculated riverine fluxes of TON were two orders of magnitude lower than the major riverine contributors to TON in the Irish Sea, such as the Severn Mersey and Clyde but higher than most of the rivers in West Wales (Nedwell *et al.*, 2002). Mean catchment normalised nutrient fluxes of 647 kg $N.km^2.y^{-1}$ (as TON) and 22 kg P $km^2.y^{-1}$ compared favourably with their U.K. equivalents entering the Irish Sea, with average annual TON flux in the Liffey being only 46% of the U.K average and orthophosphate being only 16%. This level of nitrogen represents a moderate human influence on the river Liffey according to the system of Hessen (2000). The annual TON and orthophosphate inputs from the Liffey (averaged over 2001 and 2003) represent 0.9% and 0.02% respectively of the total annual nitrogen and phosphorus fluxes to the Irish Sea (Simpson & Rippeth, 1998). However the N flux above does not account for NH_4, which did not show consistent linear behaviour, nor do the calculated fluxes include the point source input of the P and N from Ringsend sewage treatment plant or the inputs from the river Tolka. These sources combined caused a five-fold elevation (up to 363 $\mu gP.l^{-1}$) in P levels in the bay when compared to PO_4 mixing curves from data in the Liffey estuary. Statistically significant mixing curves of NH_4 with salinity in the estuary, upstream of the Ringsend sewage treatment plant generally showed an increase of NH_4 with increasing salinity, while mixing curves in the open bay (downstream of the sewage treatment plant) showed a decrease of NH_4 with decreasing salinity; this suggests that the Ringsend sewage treatment plant was a principal source of NH_4 to the system. The high coefficient of variations for NH_4 and PO_4 may be due more to the timing of the discharge of sewage (licensed for ebb tide

discharge) than variation in amounts river flow or tidal flushing. The higher freshwater TON concentrations from mixing curves in the open bay when compared to the walled estuary also indicate the Ringsend sewage treatment plant as an important source of TON.

The volume of fluxes from the sewage treatment plant remains relatively constant but the upgrading of the plant which took place during this study has caused dramatic changes in the composition of the effluent. The most striking feature of the changing nutrient loading to the estuary is the increase in TON flux from the Ringsend Sewage treatment plant. The annual TON effluent load in 2004 was more than 2.5 times the loading from effluent in 1993. TON effluent loads in 2004 were 68% higher than the mean riverine TON inputs. However the corresponding reduction in Ammonia concentrations means that the overall flux of DIN from the treatment plant is only 92% of its value in 1993. The loads of suspended solids from the Ringsend sewage treatment plant have also been dramatically reduced to 38% of the load in 1993. The four year mean combined Liffey and sewage DIN was 2748 t $N.y^{-1}$. This constitutes 3.4 times the mean flux of DIN for the Liffey alone while the combined PO_4 flux is 8.7 times the PO_4 flux of the Liffey alone. The total DIN flux from the Liffey and the sewage treatment plant accounts for 2.9% of the freshwater DIN flux to the Irish Sea and the total PO_4 flux accounts for 3.6% of the total freshwater flux to the Irish Sea (OSPAR, 2003). These combined fluxes yield catchment normalised fluxes of 2309 kg $N.km^{-2}.y^{-1}$ and 311 kg.$P.km^{-2}.y^{-1}$ these compare less favourably with their U.K. equivalents than the riverine fluxes alone. The catchment normalised Liffey and effluent DIN flux is 61% greater than the U.K average and exceeds the upper bound of the "moderately influenced" category (2000 kg $N.km^{-2}.y^{-1}$) (Hessen, 1999). Similarly the catchment area normalised PO_4 flux is just over twice the U.K. average of 152 kg $P.km^{-2}.y^{-1}$ (Nedwell *et al.*, 2002). The combined DIN and PO_4 fluxes have a molar ratio of N16.1:P1 and account for 2% and 1.3% respectively of the total annual Irish Sea N and P fluxes (Simpson & Rippeth, 1998). These fluxes however are still orders of magnitude lower than other major contributors to the Irish Sea.

Modelling of nutrient concentrations illustrates that mean summer supply of TON at the 33.2 isohaline doubled from the years 2002 to 2004 due to the change in effluent composition at the sewage treatment plant. The planned increase in the size of the

sewage treatment plant is liable to have less of an impact since it is the volume of effluent rather than composition that will change. Nutrient concentration in this area is also under strong control of riverine flux with drier periods resulting in higher TON concentrations which may stimulate phytoplankton production. Climate change projections for the Dublin area suggest that summer precipitation will be ~15% lower (Sweeney & Feale, 2002). Applied to the 2004 data this reduction in flow would lead to a 7% increase in TON concentrations at the 33.2 isohaline, while this may have implications for eutrophication in the area the impact of the change is likely to be slight compared to that of the change which has occurred between 2002 and 2004.

The shift in the composition of the Ringsend sewage effluent is likely to have a profound effect on the observed patterns of eutrophication in the bay. Previous eutrophication problems have been associated with particulate inputs with high N content, as a source of nutrition for the tubiculous polychaete *Lanice concheliga* which provide a site for the attachment of the opportunistic alga *Ectocarpus siliculosis* (Jeffery *et al.*, 1993) or as a direct source of nutrients to the green algal mats in the Bull Lagoons (Brennan *et al.*, 1994). These particulate inputs have been reduced six fold (from 28.4 $x10^3$ $t.y^{-1}$ to 4.8 x 10^3 $t.y^{-1}$) over a matter of four years and the reduction in suspended particulates is likely to have an effect on the abundance of the *Lanice concheliga* worms. TON fluxes from the treatment plant have shown the opposite trend and their tenfold increase may favour diatom growth since diatoms are adapted to exploit nitrate rich conditions. The model indicates that the concentrations of TON in the north of the Bay (where eutrophication effects have previously been observed) have doubled in the last five years as effluent composition has changed.

The nutrient flux figures clearly illustrate the large impact that the city's wastewater has on the Liffey estuary. The riverine fluxes of TON alone now account for only 32% of the total TON discharge with the sewage effluent making up 68%. This is in marked contrast to the situation in 1994 when sewage effluent accounted for only 42.5% of TON. The combined inputs from Ringsend and the river Liffey have resulted in an estuary which is bordering on the heavily impacted category in terms of nutrient concentrations in two classification systems. However the conservative behaviour suggests that there is no major nutrient sink in the estuary which suggests that the symptoms of eutrophication at least within the walled part of the estuary may

be limited. By contrast the seasonal nutrient depletion in the bay indicates that eutrophication may have a more profound effect in this location.

3.3.0 Conclusions

The walled part of the Liffey estuary is hypernutrified due to the loads of nutrients from the Liffey and the Ringsend Sewage Treatment Plant- suggesting that the estuary is moderately to highly eutrophied. The conservative behaviour of TON and PO_4 in the walled part of the estuary indicate that there are no major sinks of nutrients within this area which suggests that phytoplankton growth in the area may be limited by other factors.The fluxes of nutrients from the system to the Irish Sea are not large compared to other contributors, of the two sources the sewage treatment plant is now the larger contributor. The waters of Dublin Bay undergo seasonal N limitation. TON inputs from the Liffey estuary are likely to stimulate enhanced productivity during summer. Increasing river flows result in dilution of the TON concentrations entering the bay, highest modelled concentrations in the plume of the estuary occur during conditions of low flow.

CHAPTER 4: THE PHYSICAL ENVIRONMENT

4.0.1: Physical constraints on phytoplankton growth

Physical processes in both the horizontal and vertical directions exert controls over phytoplankton biomass accumulation. Phytoplankton biomass production is controlled by a balance between algal photosynthesis and respiration which are often strongly influenced by the relationship between the vertical processes of mixing and light attenuation in the water column. In turn distribution of the biomass is often determined by horizontal processes such as tidal currents or riverine flow. In these ways, the physical processes, water column structure and dynamics, control observed patterns in phytoplankton biomass (Lucas *et al.*, 1999a, b). Since an estuary marks a gradient from fresh to saline waters the physical structure of an estuary changes along its length. Light and nutrients (the essential requirements for phytoplankton development), and the physical processes determining the availability of these parameters differ between the fresh and saline ends of an estuary. At the saline end marine processes in general contribute most to the observed physical patterns while at the freshwater end riverine inputs may be more important.

4.0.2 Vertical Processes

The classic oceanographic example of physical processes resulting in biological effects is the critical depth model (Sverdrup, 1953) critical depth model. Phytoplankton biomass increase occurs when photosynthesis is greater than respiration (i.e. net photosynthesis). In the water column, respiration is a depth independent process while photosynthesis, being dependent on light, decreases exponentially with depth. Sverdrup (1953) defined a critical depth above which the integrated sum of photosynthesis was greater than the integrated sum of respiration (and net photosynthesis could occur) and below which respiration was greater than photosynthesis preventing phytoplankton biomass accumulation. Typically in temperate shelf seas the effects of turbulent mixing during winter months result in phytoplankton being mixed below the critical depth. Thermal stratification occurs when in spring solar irradiation heats the surface waters and a density discontinuity develops resulting in a warmer upper mixed layer and a cooler lower mixed layer. If

the surface mixed layer is shallower than the critical depth net photosynthesis occurs and a phytoplankton spring bloom may develop. After a rapid period of growth (the spring bloom) nutrients become depleted and the stratification which promoted the bloom now acts as a barrier to vertical nutrient transport preventing further bloom development. The above scenario is well known and widely applicable in coastal shelf environments (eg. Holligan & Harbour, 1977; Sharples, 1999; Kelly-Gerreyn *et al.*, 2004).

Tidal and wind driven mixing processes act in opposition to buoyancy inputs (thermal or saline) and may prevent stratification and promote vertical homogeneity in the water column. Simpson and Hunter (1974) reasoned that the occurrence of stratification was a balance between vertical mixing energy (tending towards unstratified conditions) and potential energy (tending towards stratification) and where these two quantities were equal tidal fronts would occur, they developed a stratification parameter

$$\mathbf{h/U^3}$$

where h is the depth of the water column and U is the surface stream amplitude in $m.s^{-1}$. This parameter was successfully used in order to predict the location of the occurrence of tidal fronts in the Irish Sea, these lie along critical contours of h/U^3 (Simpson & Pingree, 1978). This method predicts two important fronts in the Irish Sea, the Celtic Sea front and the Western Irish Sea front which runs from the Isle of Man southwards and eastwards towards Ireland. The Western Irish Sea front is of more relevance to the current study lying ~30 km north west of Dublin Bay and the Liffey Estuary. To the north of this front the waters are stratified due to weak tidal flows and a deeper water column while shallow depths to the south of the front result in a vertically well mixed water column (Simpson & Hunter, 1974). North of the front a seasonal gyre begins development in spring due to density gradients caused by freshwater inputs (salinity stratification) this is strengthened in summer as thermal stratification develops (Horsburgh *et al.*, 2000). Variations in h/U^3 occur over time as well as over space. Simpson and Pingree (1978) used the English Channel to illustrate how the position of tidal fronts may change as tidal currents vary over the spring-neap cycle.

As in the marine environment the development of phytoplankton biomass in an estuary is dependent on the interplay between mixing and stratification. However the physical dynamics of the estuarine environment differ from those of shelf seas and the open ocean in that the buoyancy of freshwater sources is often of particular importance. Such freshwater inputs may result in salinity rather than thermal stratification. In some estuaries, increases in freshwater flow promote salinity stratification leading to a surface layer of fresh water. The reduced vertical mixing may result in more favourable light conditions which can promote phytoplankton blooms (Walker *et al.*, 1996; Pickney *et al.*, 1998). Cloern (1991a) demonstrated that a reduction in vertical mixing during neap tides promoted regular occurrence of phytoplankton bloom formation over a ten year period in San Francisco Bay while freshwater influx and vertical stratification could also produce blooms in the same area (Cloern 1991b). Bottom topography, tidal conditions and the shape of the estuary all effect the mixing and stratification as a result all estuaries have differing physical conditions.

Another difference between estuaries and the marine environment is that estuaries often carry larger loads of Suspended Particulate Matter (SPM). Concentrations of SPM and values of the diffuse attenuation coefficient of light (Kd) are often directly correlated in estuaries and it is common practice to estimate light attenuation from SPM concentration (eg. Irigoien & Castel, 1997, Wilson & Parkes, 1998). High SPM concentrations result in high turbidity and the reduction in light penetration can reduce the productivity of an estuary (Cloern, 1987; Cole *et al.*, 1992; Walker & Demaster, 1996; Shiah *et al.*, 1996; Irigoien & Castel, 1997). Since light availability to phytoplankton is dependent both on attenuation of light and vertical mixing in the water column, estimates of the potential for an estuary to be productive are often based on considerations of water column mixing depth and the depth of the euphotic zone (i.e. the area in which light penetration is greater than 1%, or 4.61/Kd). There are several similar approaches towards estimating the potential for productivity as a function of light and mixing. For San Francisco Bay net photosynthesis was found to occur only where the ratio of mixing depth (Z_m) to photic depth (Z_p) was <6, respiratory carbon loss was found to exceed photosynthetic fixation at Z_m/Z_p ratios in excess of this value (Cole & Cloern, 1984). Wofsy (1983) estimated that under non nutrient limiting conditions phytoplankton populations cannot be self sustaining when $Z_m.Kd > 5$. It is often found that much of the temporal and spatial variability in

phytoplankton biomass in the estuarine environment can be explained by the ratio of mixing depth to euphotic zone depth (Z_m/Z_p) (Cloern, 1987).

4.0.3: Horizontal transport

Flushing time of the water in an estuary is also an important factor in determining whether phytoplankton biomass increases may occur. Since (by definition) the scales of motility of phytoplankton are lower than the scales of motion of water flow, water transport out of an estuary on a timescale shorter than the timescale of phytoplankton growth prevents bloom formation (e.g. Muylaert & Raine, 1999; Muylaert *et al.*, 2000; Jassby *et al.*, 2002). In estuaries the flow of water comes from two directions, both from the marine end and from the freshwater end. Tidal inputs of saline water occur on a diurnal basis and also vary over the spring neap cycle on a regularly predictable basis. Le Pape & Menesguen (1997) demonstrated that large tidal water fluxes effectively prevented the occurrence of eutrophication in the Bay of Brest. Freshwater flows are generally less predictable; in the absence of human interference (i.e. dams etc.) they are most often under the influence of the stochastic processes controlling weather.

As illustrated by the examples above estuarine dynamics are extremely complex varying on many different timescales. Mathematical modelling of physical dynamics in the estuarine environment varies from the simple estimates of flushing time (e.g. Abdelrhman, 2005) to complex three-dimensional coupled physical and biological models (e.g. Koseff *et al.*, 1993; Le Pape & Menesguen, 1997; Hagy *et al.*, 2005). As an initial investigation into the estuarine dynamics of the river Liffey it is prudent to take the simple approach. By comparison of simple flushing times with the timescales for phytoplankton growth it may be determined whether or not the propensity for bloom formation to occur exists. If the simplistic approach is sufficient to explain the observed patterns in phytoplankton biomass, further, more complex modelling may not be required. Flushing time may be defined as "the ratio of mass of a scalar in a reservoir to the rate of renewal of the scalar" and may be calculated as the volume of water in a defined system divided by the volumetric flow rate through the system (Monsen *et al.*, 2002). In simpler terms flushing time is a first order approximation of the amount of time taken to flush all the existing water from a system. Many

variations for the calculation of flushing time are used in order to assess the possible impacts of anthropogenic nutrients to an estuary (e.g. Schallenberg & Peake, 2003; Webster & Harris, 2004). Each method carries its own particular assumptions and it is essential to consider these assumptions and their relevance to the system in question in order to avoid erroneous conclusions (Monsen *et al.*, 2002). For our purposes the timescales of relevance are those of phytoplankton growth, which range from 0.4 day^{-1} to 3.3 day^{-1} (Sarthou *et al.*, 2005). Considering these timescales a minimum doubling time for slow growing plankton is 2.5 days and for rapidly growing plankton 0.3 days.

4.0.4: Hydrography of the study area

The river Liffey is approximately 80 km long from its source in the Dublin Mountains to its estuary which discharges into Dublin Bay. The Liffey estuary extends 11.2 km from the weir at Isalndbridge (which provides a discrete landward boundary) to the Poolbeg lighthouse (station 14) where it enters Dublin Bay. The morphology of the estuary is almost entirely man made being bounded by walls for most of its length and with several commercial basins and piers in its lower reaches. This port area of the estuary undergoes constant dredging and there has been recent land reclamation which has unknown effects on the complex physical dynamics of the estuary. The estuary is macrotidal (sensu Dyer, 1973) with a tidal range of ~4 m. Tidal fluctuations occur on a semidiurnal basis (~12.45 hr) and over the spring neap cycle (~14 day period). Some studies of the hydrography and physical dynamics of the study area exist (Crisp 1974, Jones & Jordan, 1979; Wilson *et al.*, 1986, ERU; 1992). From this literature the area may be divided into four distinct zones on the basis of water column structure.

From the Weir at Islandbridge to Butt Bridge the estuary is narrow (~40 m wide) and is dominated by freshwater. At low tides the waters are entirely fresh, with saline waters only intruding as the tide advances. In this part of the estuary water depth at low tide is generally less than 1m rising to approximately 5 m at high tide. This section of the estuary exhibits strong salinity stratification when the tide is high.

Because this zone lies in the upper tidal reaches of the estuary sampling access was severely limited by tidal conditions.

Immediately east of Butt Bridge (Station 1) is a transitional zone, stretching as far as the Toll Bridge (Station 6). The width of the estuary in this zone broadens from ~60 m at station 1 to ~130 m at station 6. Water depths are variable in this area. Stations 1-6 are not dredged and have depths about 5 m. In this zone strong salinity stratification is always evident though weakening during ebbing tides. Maximum vertical gradients in salinity occur in this section particularly around the area of the Customs House (Station 2). Here the deeper salt water is trapped below the freshwater in a classic salt wedge. Currents in the deeper more saline waters are weak and stagnation and anoxia occur (Crisp, 1972, Wilson *et al.*, 1986). Here seawater occupies the bottom 4-5 m of the water column with a thin layer surface layer of freshwater 1-2 m in depth.

From Alexandra Basin (Station 7) to the Poolbeg lighthouse (Station 14) the channel is deep, dredged to a depth of 7.8 m and the width is highly variable with a number of man made shipping basins and piers. From Tanker Pier (Station 10), a wide flat area of mud and sand extend northward to the Bull Wall. This area is bounded on either side with the Bull Wall to the North and the Great South Wall to the south. This was built in the 18th century in order to increase scouring of the sea bed and maintain adequate water depths in the busy shipping port (Jeffrey, 1977). At high tides this area is largely well mixed particularly at stations 13 and 14 seaward with salinities of ~33.7 homogenously from top to bottom.

From its mouth at Poolbeg (Station 14) the brackish waters of the Liffey estuary enter Dublin Bay. Dublin Bay is a horseshoe shaped bay bounded to the south, west and north by the conurbation of Dublin. Maximum water depths (14 m) in the Bay occur at its eastern side, though most of the bay is shallower being 10 m or less in depth throughout with about half being <5 m in depth. The tidal currents within the bay vary on a semidiurnal basis with maxima of 0.5 $m.s^{-1}$ (ERU 1992) these currents are sufficient to maintain a well-mixed water column (Crisp 1972). Waters in Dublin Bay are principally Irish Sea waters advected from offshore by tidal currents (Wilson & Parkes 1998; Wilson, 2005).

As a zone of transition from freshwater to marine the physical structure of estuaries changes from the landward to the seaward end resulting in varying physical controls on the potential for phytoplankton to develop. The spatial variations in physical structure also exhibit temporal variations on timescales from months (seasonal changes) to weeks (spring neap cycles) and days (rainfall and freshwater inputs). The aim of this chapter is to characterise the physical variability within the Liffey estuary and Dublin Bay both in terms of spatial distributions and temporal changes and to examine the possible physical limitations on phytoplankton growth within the study area.

4.1.0: RESULTS

4.1.1: Spatial distribution of salinity

Over the study period salinity ranged from freshwater (s=0) at the surface in the upper estuary to entirely marine water offshore (s=34.8) in the south east of the study area. In the upper estuary strong salinity stratification was evident. This salinity stratification is illustrated by the vertical profiles (Figure 4.1). The difference between mean surface salinity and mean salinity at depth at stations 1-7 was greater than 10. Ranges in salinity were highest in the surface waters of the upper estuary frequently spanning several groups of the Venice classification (Table 4.1). The depth of the surface mixed layer (of fresh water) in the stations of the upper estuary varied with tidal stage but was generally about 2 m (Figure 4.1) confirming the work of previous authors (Crisp, 1974; Wilson *et al.*, 1986). Moving seaward from east to west, salinity stratification became less pronounced as did the variability in surface salinity. At the mouth of the estuary (Station 14) the water column was almost completely vertically mixed and salinities were close to those of the Irish Sea, here the difference between mean surface and depth salinities was only 1.8. (Table 4.1).
Surface salinity at stations 1, 2 and 3 in the upper estuary was found to decrease logarithmically with increasing daily average Liffey flow (Figure 4.2) indicating that rainfall was the principal factor controlling salinity in this area. This relationship allowed calculation of Liffey flows from the continuous salinity data produced by the YSI sonde. Tidal inputs had a greater effect downstream and no relationship between freshwater flow and salinity was observed; rather tidal stage (ebb or flow) was more important at the seaward stations.

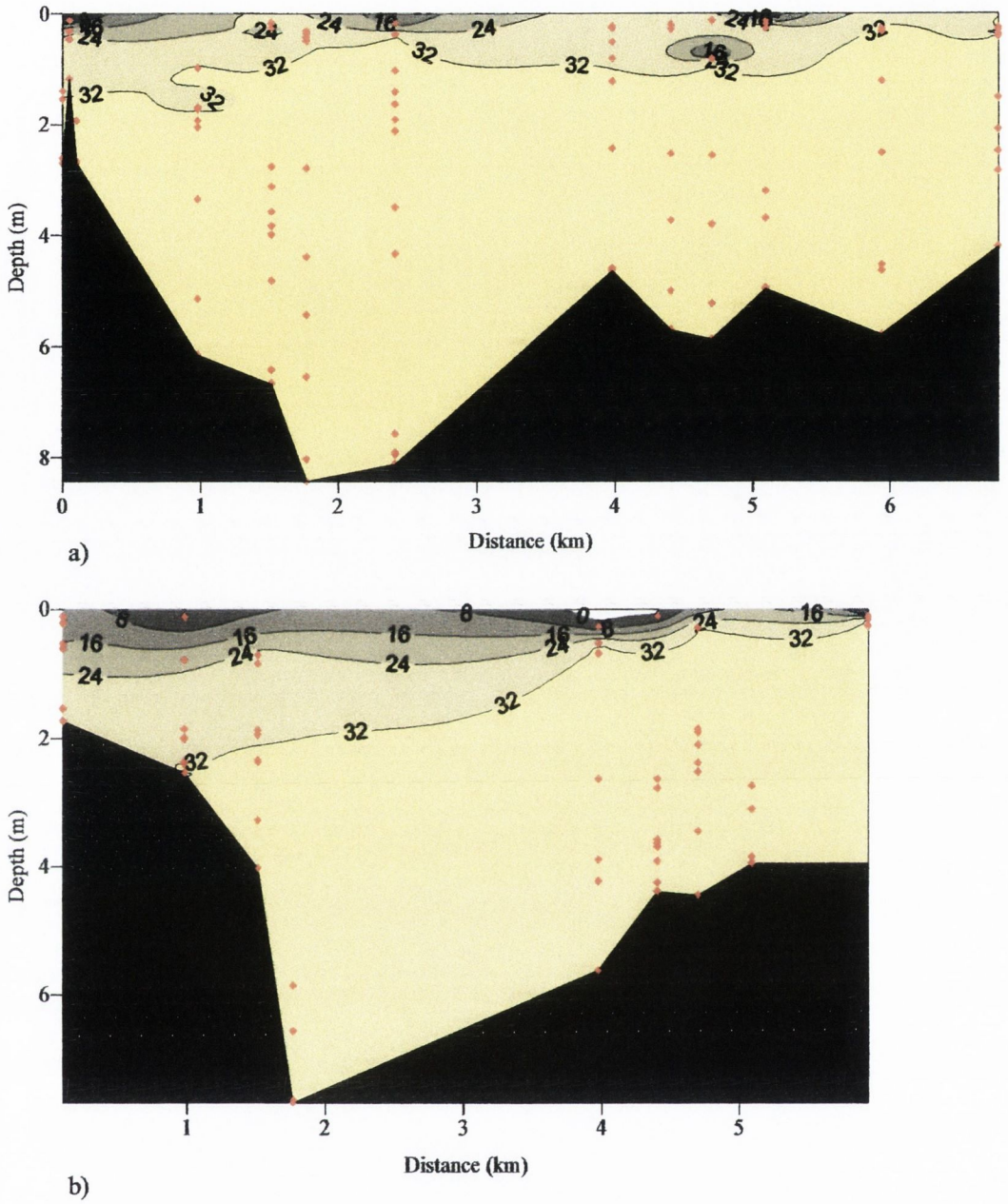


Figure 4.1: Salinity profiles (0km is Butt Bridge, station 1) of the Liffey estuary, isohalines spaced at 8 (p.s.u.)(a) Salinity stucture 2.5 hours after high tide (9/3/03) note the intruding tongue of saline water and the increased stratification in the upper estuary.(b) Salinity stucture 45 minutes before low tide (16/3/03). Note the recession of the tongue of saline water. Profiles taken at low river flow and neap tides.

Table 4.1: Summary of the salinity data collected during the four years of sampling cruises. s.d. standard deviaton, maximum, minimum and n, the number of data points. Note the high variability in surface salinties in the upper stations.

	Surface					Depth				
Station	Mean	s.d	max	min	n	Mean	stdev	max	min	n
1	11.4	9.1	25.8	0.1	14	29.8	6.1	33.4	8.4	15
2	12.8	9.8	30.6	0	16	31	2.1	33.5	26.6	16
3	11.5	9.1	30.9	0.6	46	30.8	3.3	33.7	19.3	46
4	13.3	9.1	31.2	0.5	46	32.7	0.8	34.5	30.7	46
5	12.7	9.1	31.8	0.3	46	32.1	2.2	33.7	20.4	46
6	14.7	8.3	31.9	0.8	49	32.3	3.5	34	9	49
7	21.5	8	33.2	6.3	48	33	1	34.1	29.8	47
8	23.4	7.6	33.2	3.8	48	33	1.7	34.1	22.2	48
9	26.9	6.6	33.2	17.3	48	32.8	1.3	34.4	26	48
10	27.9	5.5	33.3	20.9	48	33.3	0.8	34.2	30.8	48
11	28.3	3.6	33.4	11.2	48	32.5	1.9	34.2	21.6	47
12	29.5	2.9	33.5	6.8	47	33	1.2	34.2	26.6	46
13	31	2.6	34	22	45	33.2	1.1	34.4	28	45
14	31.8	2.5	34	19.6	46	33.6	0.6	34.4	31.9	46
15	30.9	3.4	34.1	18.5	46	33	1	34.5	30.3	46
16	30.6	3.1	34.3	24.8	47	33.1	1	34.4	30.2	46
17	30.2	3.6	34.4	19.4	46	32.5	2.4	34.5	22.9	45
18	33.2	1.1	34.4	29	43					
19	33.2	1.2	34.2	28.3	37					
20	33.5	0.7	34.3	31.7	40					
21	33.6	0.7	34.3	30.5	38					
22	33.6	0.6	34.3	30.9	37					
23	33.6	0.7	34.5	30.7	43					
24	33.6	0.7	34.4	30.7	43					
25	33.7	0.6	34.4	31.9	42					
26	33.6	0.5	34.4	32.2	43					
27	33.7	0.5	34.3	32.1	43					
28	33.8	0.4	34.3	32.8	43					
29	33.8	0.4	34.4	32.9	43					
30	33.8	0.5	34.5	32.6	42					
31	33.7	0.6	34.5	31.9	42					
32	33.7	0.5	34.5	32.4	42					
33	33.8	0.5	34.5	32.4	42					
34	33.8	0.4	34.4	32.9	41					
35	33.8	0.4	34.8	32.8	42					
36	34.0	0.4	34.5	32	39					
37	33.9	0.4	34.5	32.8	38					
38	33.9	0.4	34.5	32.7	39					
39	33.9	0.4	34.4	32.8	37					
40	33.8	0.5	34.4	31.9	40					
41	33.9	0.4	34.4	32.9	22					

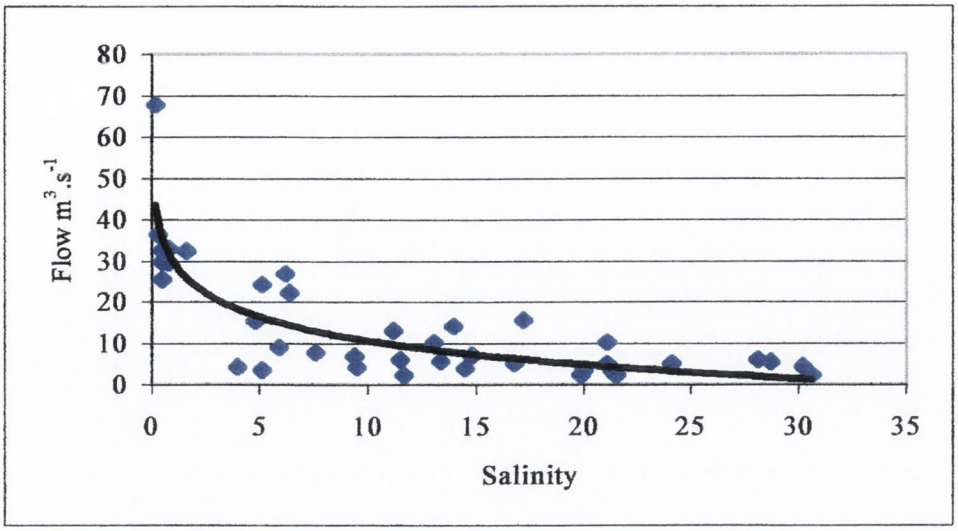


Figure 4.2: The relationship between daily mean river flow and salinity at station 3. $r^2 = 0.7443$ $p<0.001$ $n= 39$.

$$flow = -8.4099Ln(salinity) + 30.014$$

4.1.2: Annual spatial and temporal patterns of temperature

Table 4.2 summarises the temperature data over the study period. Temperature throughout the study area displayed a distinct annual cycle with maximum temperatures occurring in August of each year and minimum temperatures occurring in January. In general the more saline waters in the open bay showed less extreme temperature values i.e. lower maxima and higher minima than the less saline waters of the estuary (Figure 4.3). At station 1-6 in the upper estuary the fresher surface waters were cooler than more saline waters at depth which indicates that salinity alone was causing the stratification here. Downstream at stations 7-17 in the estuary surface waters were warmer than waters at depth. This phenomenon is attributed to inputs of cooling water effluent from the local thermal power stations. Stations 11 and 12 (lying immediately adjacent to the thermal output) showed highest mean temperature throughout the study period. The maximum recorded temperature for the study area was 23.8 °C occurring at station 11 (closest to the thermal output at Poolbeg) in August 2002. Warmest water temperatures in the open bay occurred in the shallow waters of the north west of the bay (stations 18-22) and may be partly attributable to the thermal plume. Though there was some evidence for a north south divide in temperature (as observed in salinity) this division was less pronounced (Figure 4.4).

4.1.3: High frequency temperature data (Spring 2004)

High frequency temperature data collected using the YSI 6600 sonde at station 16 in the estuary in late spring 2004 showed regular daily cycles in temperature associated with the ebbing and flowing of warmer fresher water and cooler more saline water. Mean daily temperature at station 16 for the month of April was negatively correlated with daily tidal range (r^2=0.7331 $p<0.001$) (Figure 4.5). From the 19th of April to the 26th of April there was an increase in daily average temperature of 0.2 °C (Figure 4.6). Minimum tidal ranges occurred on the 28th of April and water temperatures remained consistently at or above 10.8°C following this date. At this time the relationship with tidal velocity became weaker and less significant (r^2=0.4936 $p<0.05$) (Figure 4.5). Maximum daily averaged temperature of 11.7 °C (s.d. 0.8) occurred on the 2nd of May.

Table 4.2: Mean temperature (°C) at all stations from monthly sampling cruises 2000-2004. Note the elevated temperatures at stations 11 and 12.

	Surface					Depth				
Station	Mean	Max	Min	stdev	count	mean	max	min	stdev	count
1	12.6	17.5	4.3	4.5	14	13.1	16.7	5.4	3.8	15
2	12.9	17.2	4.2	4.3	16	13.1	16.7	6.4	3.5	16
3	11.1	17.6	3.6	4.3	46	11.4	17.8	6.3	3.5	45
4	11.1	17.5	3.8	4.2	46	11.4	17.5	6.3	3.4	46
5	11	17.5	4.2	4.2	47	11.3	17.1	6.1	3.4	46
6	10.8	17.4	3.8	4.2	48	11.2	17.4	6.1	3.4	49
7	11.2	17.8	3.8	4	48	11.3	17.5	5.9	3.4	48
8	12.0	20.5	4.5	4.3	48	11.3	17.9	6	3.5	48
9	11.6	18.3	5.2	3.7	48	11.2	17.3	5.9	3.5	48
10	11.5	18.2	5.4	3.6	48	11.1	17.2	6	3.4	48
11	14.1	23.8	6.1	4.3	48	11.6	17.6	6.1	3.4	47
12	14.1	20.6	5.7	3.7	47	11.3	17.4	5.4	3.4	46
13	12.5	19	5.6	3.5	46	11.3	17.5	5.8	3.3	45
14	11.9	18.4	5.7	3.6	46	11.3	17.5	6.1	3.3	46
15	11.9	19	6.1	3.6	46	11.6	17.4	5.9	3.5	47
16	12.0	18.8	5.6	3.5	47	11.4	18.2	5.7	3.5	47
17	11.5	19.6	5.6	3.6	45	10.9	17.5	5.9	3.3	45
18	11.3	17.1	5.8	3.5	43					
19	11.7	18.1	5.3	3.5	37					
20	11.7	17.9	5.7	3.4	40					
21	11.6	17.9	5.7	3.4	38					
22	12.0	18	5.5	3.5	37					
23	11.3	16.8	5.8	3.4	43					
24	11.3	16.8	5.9	3.4	43					
25	11.3	16.8	6	3.4	42					
26	11.3	16.7	6.1	3.4	43					
27	11.2	16.4	6	3.3	43					
28	11.3	16.4	6.1	3.2	43					
29	11.3	16.4	6.1	3.2	43					
30	11.5	17	6.1	3.2	42					
31	11.5	17.5	6.1	3.3	42					
32	11.6	17.5	6.1	3.4	42					
33	11.4	16.8	6.1	3.2	42					
34	11.2	16.6	6.1	3.3	40					
35	11.5	17.5	6.2	3.3	43					
36	11.2	17.2	6.3	3.2	39					
37	11.2	17.8	6.1	3.3	38					
38	11.3	17.6	6	3.3	39					
39	11.0	17.4	6.1	3.1	37					
40	11.6	17.6	6.1	3.4	40					
41	10.8	17.6	5	3.6	22					

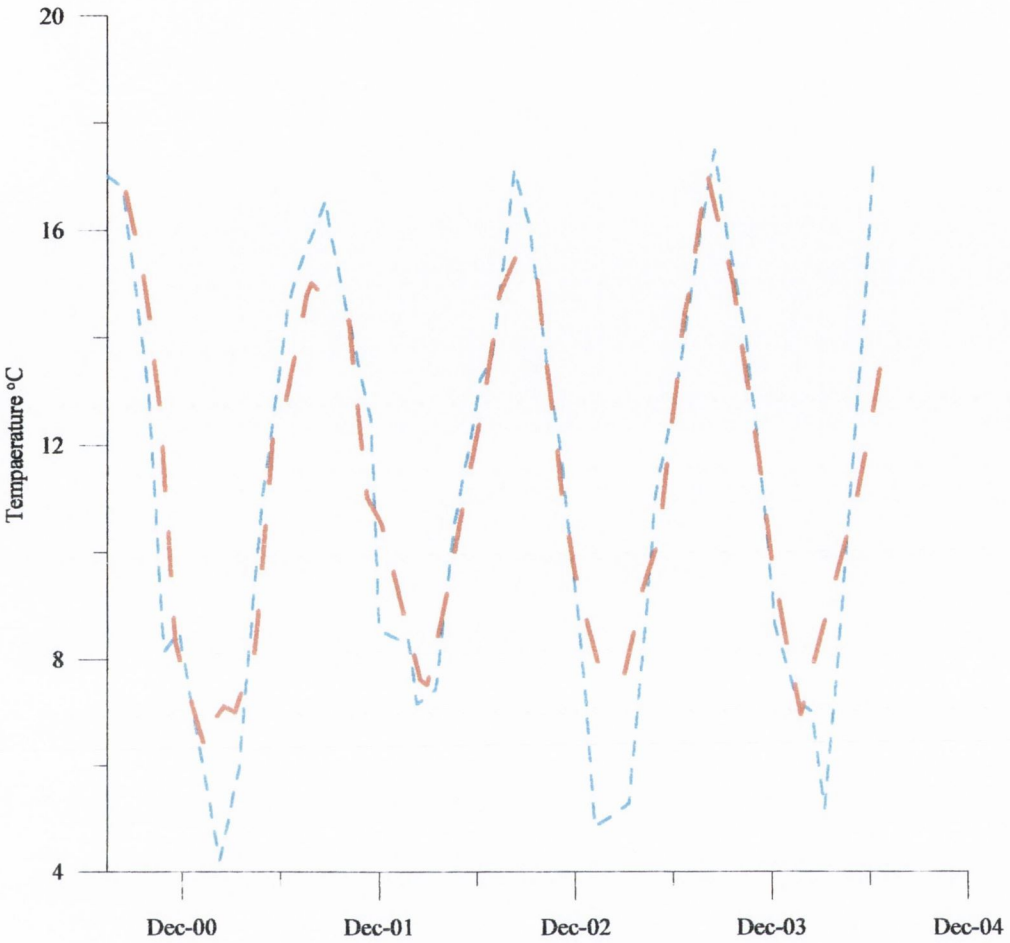


Figure 4.3: Water temperature in Dublin Bay (red) and the Liffey estuary (blue) for the period 2000-2003.

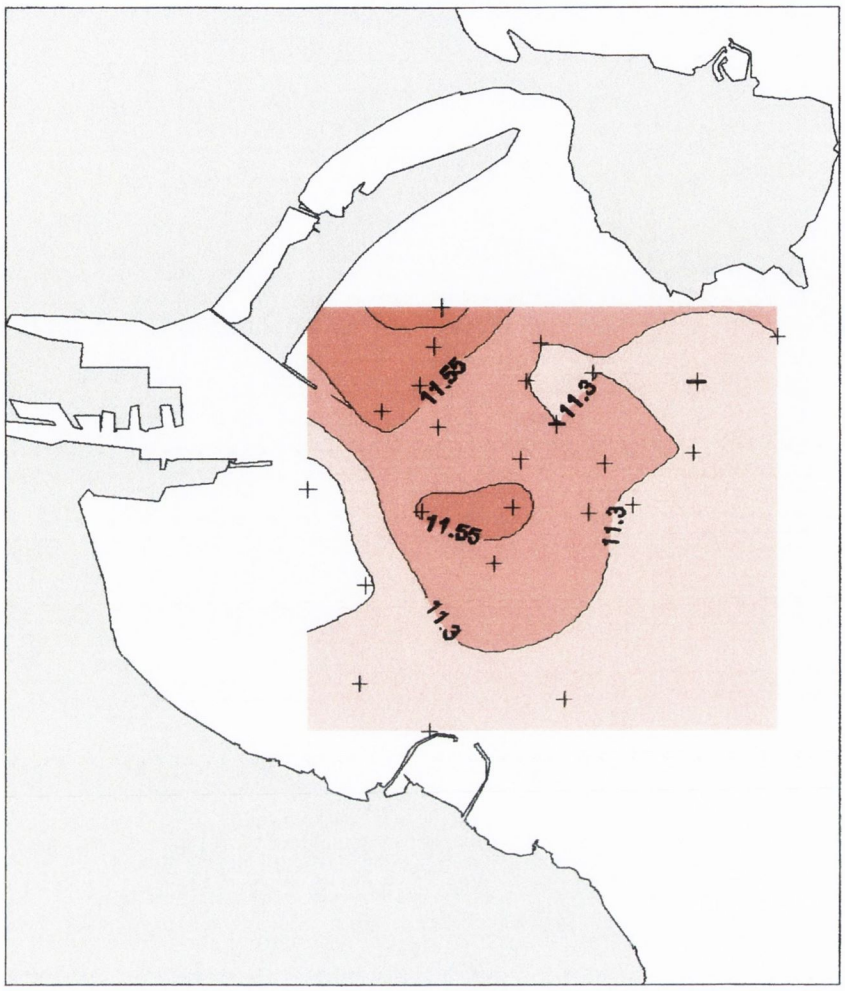


Figure 4.4: Mean surface water temperature (°C) in Dublin Bay from monthly sampling 2000-2004.

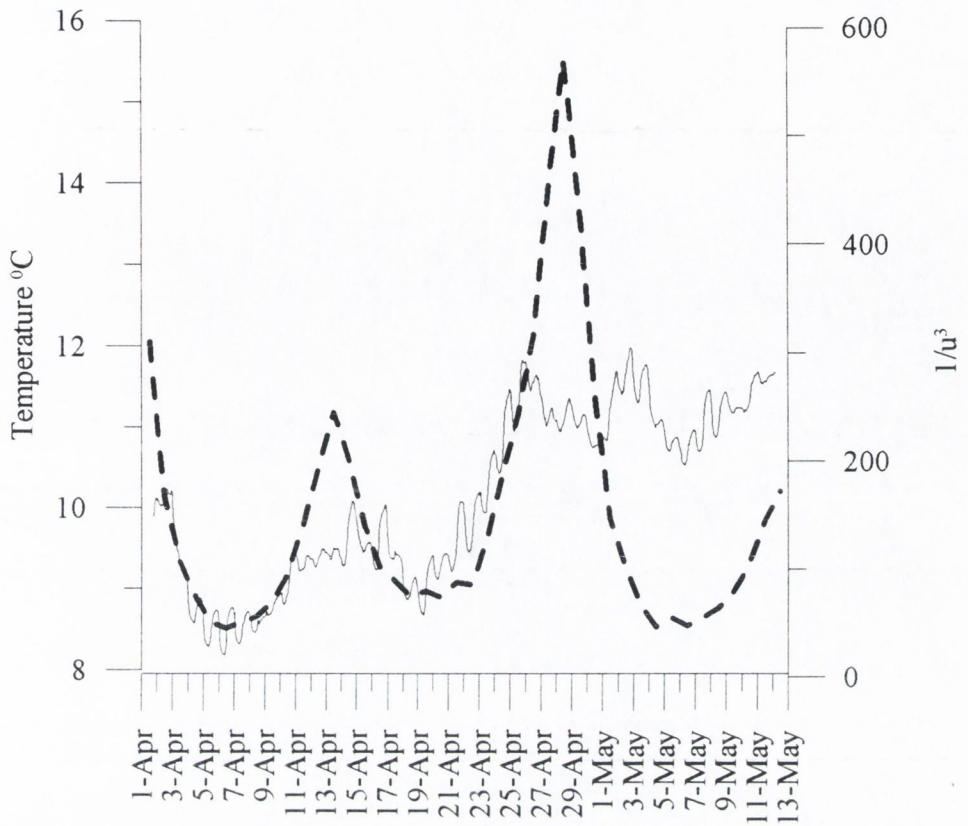


Figure 4.5: Plot of measured daily mean temperature at the north bank lighthouse April-May 2004 (solid) and modelled $1/u^3$ predicted from published (ERU 1992) tidal and current data, dashed.

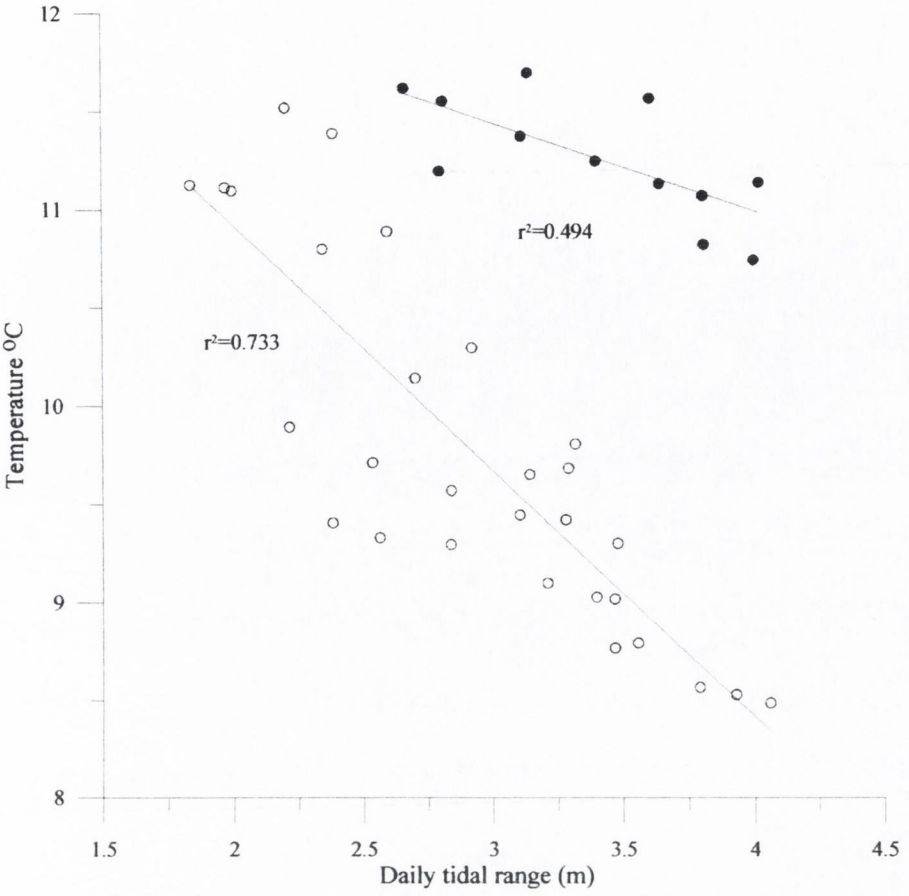


Figure 4.6: Relationship between daily tidal range and mean daily temperature at the north bank lighthouse April –May 2004. Open circles are data from April, filled circles show data from May.

4.1.4: Light Conditions in the study area

Table 4.3 summarises the Secchi depth measurements and associated vertical attenuation coefficients taken throughout the course of the study period. Mean Secchi depths throughout the walled part of the estuary (Stn 1-17) were lower than those in the open bay and showed less variability. Lowest Secchi depths for the study area were found adjacent to the combined outflow of the power station at Poolbeg and sewage treatment plant (stations 10 and 11). These are attributed to the high suspended solids loads from the treatment plant, particularly prior to its upgrading. There was no apparent seasonal cycle in Secchi depth in the walled part of the estuary.

In the offshore waters there was a distinct seasonal cycle in Secchi depth, and k(PAR) (Figure 4.7a) which resulted in a seasonal variability in $Z_m.k_d$ values (Figure 4.7b).

Z_p/Z_m, the ratio of mixing depth to mean euphotic zone depth (calculated as the 1% light level) varied throughout the study area, mixing depth over a tidal cycle was assumed to be the depth of the water column in stations not exhibiting strong salinity stratification i.e. stations 7-41. (Figure 4.8). Highest values >2 were found in the upper estuary stations 1-6 due to the salinity stratification. Lowest values <0.5 were found in the vicinity of the sewage treatment plant. This was attributed to the relatively unstratified conditions and reduced Secchi depths. There was a weak but significant positive correlation between the natural log transformed data for mean chlorophyll concentration and mean Z_p/Z_m, at each site (r^2=0.5833 n=41 $p<0.001$) (Figure 4.9).

Table 4.3: Mean secchi depths (m) for each station from monthly sampling cruises 2000-2004 and mean K(PAR) (m^{-1}) calculated as 1.41/Secchi depth (Bowers et al. 2002)

	Secchi depth					$K_{(PAR)}$		
	mean	max	min	stdev	count	kd	max	min
1	1.5	2.3	0.5	0.5	13	0.9	0.6	2.8
2	1.4	2.5	0.8	0.5	15	1.0	0.6	1.8
3	1.3	2.5	0.5	0.6	44	1.1	0.6	2.8
4	1.5	2.8	0.5	0.6	44	0.9	0.5	2.8
5	1.3	3	0.5	0.6	45	1.1	0.5	2.8
6	1.3	3.3	0.3	0.6	44	1.1	0.4	4.7
7	1.5	2.5	0.5	0.5	45	0.9	0.6	2.8
8	1.4	2.5	0.5	0.6	45	1.0	0.6	2.8
9	1.2	3	0.5	0.6	45	1.2	0.5	2.8
10	1.3	3	0.5	0.6	45	1.1	0.5	2.8
11	1	2.5	0.3	0.5	45	1.4	0.6	4.7
12	1.1	3	0.5	0.6	44	1.3	0.5	2.8
13	1.3	3	0.5	0.6	43	1.1	0.5	2.8
14	1.6	4.5	0.5	0.8	42	0.9	0.3	2.8
15	1.5	2.5	0.5	0.6	42	0.9	0.6	2.8
16	1.3	2.5	0.5	0.6	42	1.1	0.6	2.8
17	1.3	2.5	0.5	0.6	42	1.1	0.6	2.8
18	2.2	5	0.8	1.2	41	0.6	0.3	1.8
19	2.4	5	0.8	1.1	33	0.6	0.3	1.8
20	2.4	5.5	0.8	1.1	36	0.6	0.3	1.8
21	2.3	5	0.8	1	34	0.6	0.3	1.8
22	2.3	4.5	0.8	1	33	0.6	0.3	1.8
23	2.4	4.5	1	1	41	0.6	0.3	1.4
24	2.5	4.5	1	1	41	0.6	0.3	1.4
25	2.5	6	1	1.3	40	0.6	0.2	1.4
26	2.5	4.5	1.3	1	41	0.6	0.3	1.1
27	2.6	5.5	1	1.1	41	0.5	0.3	1.4
28	2.5	5.5	1	1.2	41	0.6	0.3	1.4
29	2.5	5.5	1	1.1	41	0.6	0.3	1.4
30	2.5	4.5	1	1	40	0.6	0.3	1.4
31	2.5	5.5	1	1.2	39	0.6	0.3	1.4
32	2.4	6.5	1	1.3	39	0.6	0.2	1.4
33	2.8	6	1	1.4	39	0.5	0.2	1.4
34	2.6	5	1	1.2	39	0.5	0.3	1.4
35	2.6	5.5	1	1.1	39	0.5	0.3	1.4
36	2.7	6	0.8	1.4	35	0.5	0.2	1.8
37	2.6	5.8	0.5	1.2	34	0.5	0.2	2.8
38	2.7	5.5	0.8	1.3	35	0.5	0.3	1.8
39	2.5	7	0.8	1.2	32	0.6	0.2	1.8
40	2.5	4.5	1	1.1	36	0.6	0.3	1.4
41	2.1	4.5	1	0.9	18	0.7	0.3	1.4

Figure 4.7: (a) Annual pattern in secchi depth in the open bay for the years 2000-2002 error bars are 95% confidence intervals. (b) Plot of annual cycle in mean $K_m.Z_d$. for a water depth of 10m (heavy) and 5m (dashed heavy) , the straight line marks the limiting value of 5 (Wofsy, 1983)

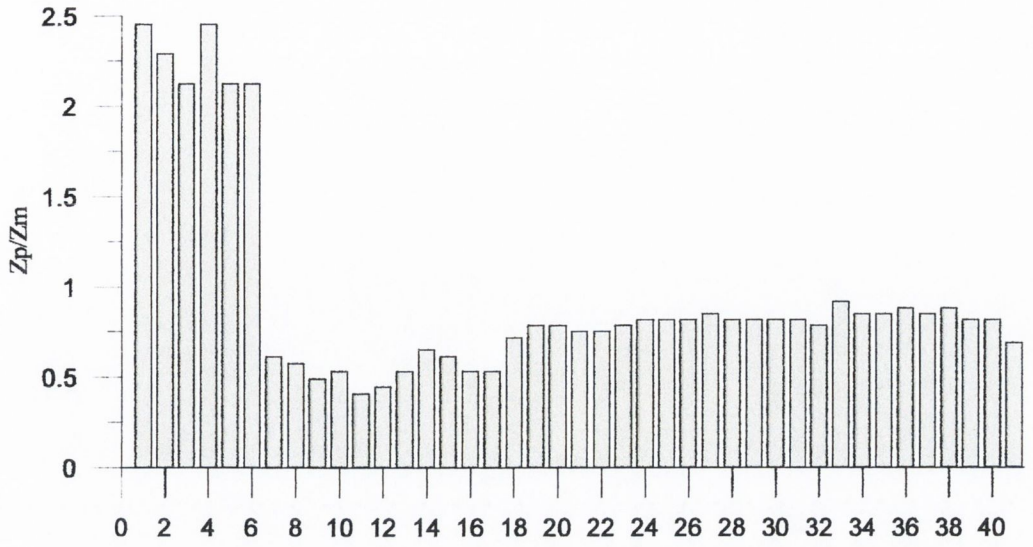


Figure 4.8: Z_p/Z_m at each station (numbered on x axis) in the study area indicating the potential for primary production.

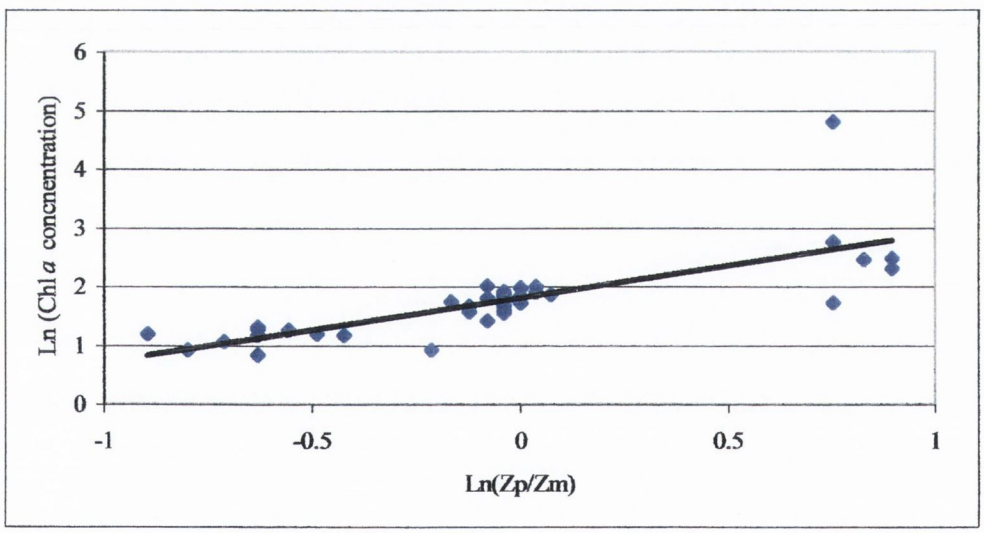


Figure 4.9: Relationship between natural log transformed data for photic zone depth to mixing depth against mean chlorophyll *a* concentration ($mg.m^{-3}$). (r^2=0.5833 n=41 p<0.001).

4.1.5: Flushing time

Flushing times were calculated separately for different sections of the estuary. Since the tidal prism method is designed to estimate flushing time in a well mixed estuary (Dyer, 1973) this method was applied only to the mixed part of the estuary. In the highly stratified part of the estuary, flushing time in the surface layer of water only was modelled (bottom currents in this area are known to be extremely weak (Crisp, 1972) and dilution by freshwater flow was assumed to be the removal mechanism. Figure 4.10 shows the response of modelled flushing time to increased river flow for each section of the system over the range of flow values experienced during the study period. From Figure 4.10 it is apparent that flushing times caused by flow lie around the critical timescale of phytoplankton growth in the upper estuary. Flushing times greater than one day occur only at flow rates <4 $m^3.s^{-1}$. Table 4.4 summarises the flushing time characteristics calculated for each part of the estuary. Flushing times were less than one day in the upper estuary for 69% of the study period due to river flows. By contrast in the lower estuary river flow had little effect on flushing time (except at times of extreme flow ~70 m^3s^{-1}) and tidal flushing dominated. River flow never affected flushing time in the bay significantly on the timescales of phytoplankton growth. The relatively small area of water between stations 1-6 and the shallow mixing depth result in a surface layer in which flushing time is highly sensitive to freshwater flow. Downstream higher water volumes due to deeper water depths result in a tidal flushing much greater than that caused by riverine influx. In the open part of the bay the calculated flushing timescales indicate that riverine input plays virtually no role in flushing (mean flushing time due to riverine input is almost 1.5 years) but tidal exchanges flush the bay completely in less than three days, even at neap tides.

Calculations of tidal flushing rate for the lower estuary and the bay indicate that the regular tidal fluxes of water in and out of the estuary have a much greater influence on flushing time than river flow in these areas. In the lower estuary flushing timescales due to tidal flushing are consistently lower than the timescales necessary for phytoplankton growth, while in the bay flushing times remain sufficiently long to support phytoplankton development throughout the spring neap cycle.

Table 4.4: Dimensions of each section where flushing time was modelled. Mean, maximum and minimum modelled flushing times for each location. %>1day is the percentage occurrence of modelled flushing times greater than 1day.

		Upper estuary	Lower Estuary	Bay
		Stn 1-7	Stn 8-17	Stn 18-41
Area	m^2	210,820	825,693	120,300,000
Mixing depth	m^2	2	8	8.5
Riverine Flushing time				
Mean	days	1.7	28.7	522.8
Max	days	4.7	79.2	1442.2
Min	days	0.3	5.8	105.5
%>1day		31	100	100
Tidal Flushing Time				
Mean	days	*	0.6	2.1
Max	days	*	0.7	2.9
Min	days	*	0.5	1.3
%>1day		*	0	100

The mean daily river flows for the Liffey are presented in Figure 4.11. On an annual timescale a pattern in river flow was apparent with maximum flows occurring in winter and minimum flows occurring in summer. However there was great interannual variability in the timing and magnitude of flows, these being under the influence of the stochastic processes controlling weather. Mean river flow for the four year period was 13.2 $m^3.s^{-1}$.

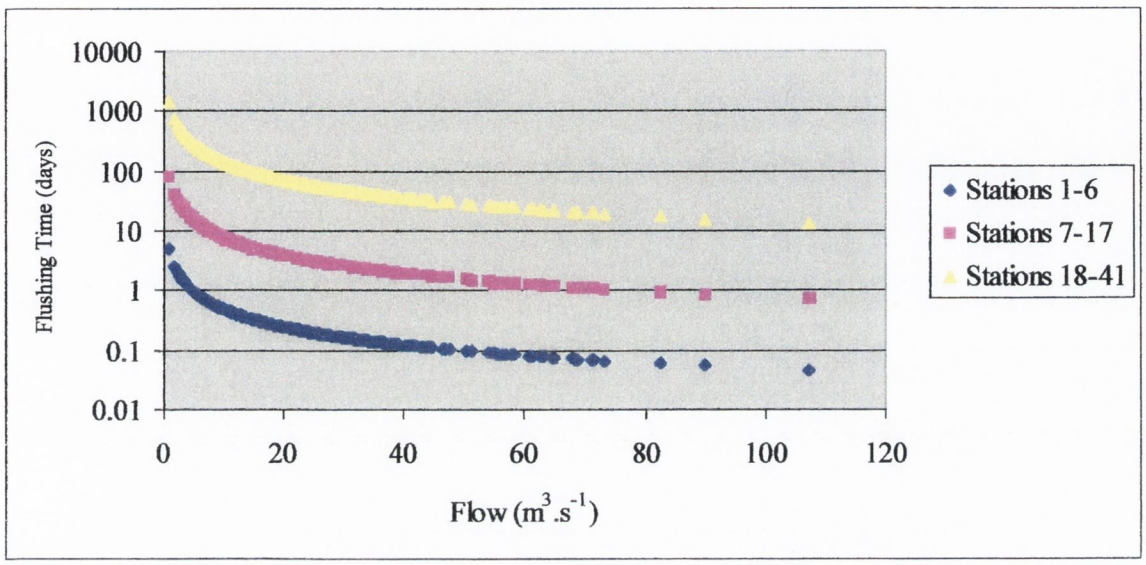


Figure 4.10: Flushing times estimated for the different sections of the estuary over the range of observed river flows.

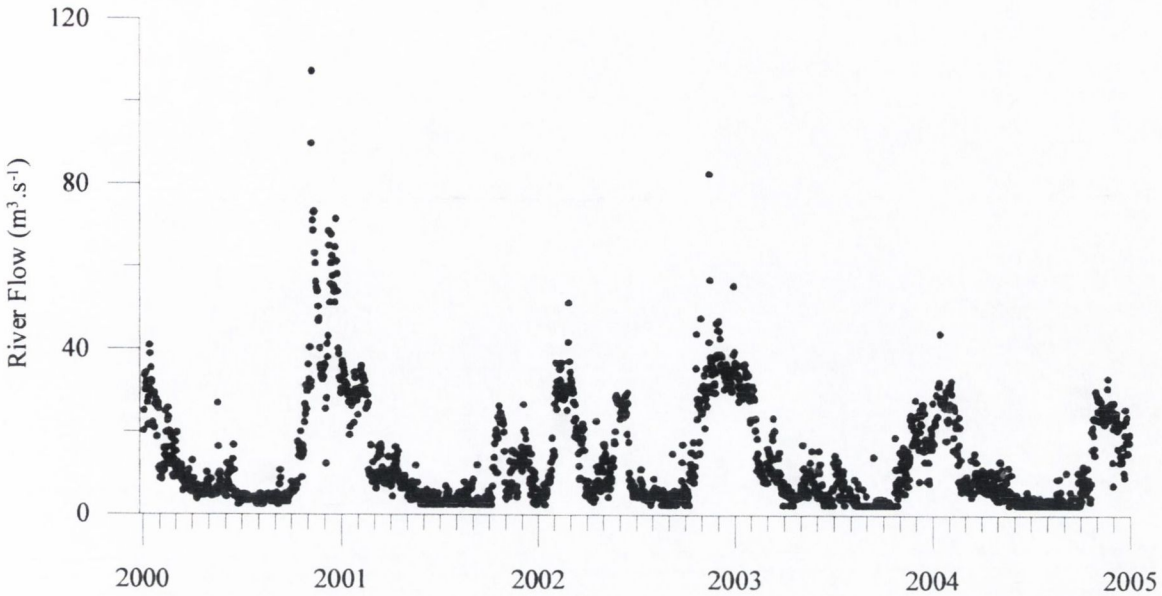


Figure 4.11: Mean daily flow in the Liffey estuary for the period 2000-2004.

4.2.0: Discussion

The study area experiences highly diverse physical conditions which vary from the freshwater end to the open bay; these result in varying controls on the potential for phytoplankton production.

In the upper estuary the freshwater inputs account for 70% of the variability in surface salinity. Strong salinity stratification is always evident and vertical mixing occurs to a depth not more than 2 m. The fresher waters of this area are turbid and there is no apparent seasonal signal in light penetration, this is attributed to the variability in river flow. High flows are likely to result in high concentrations of terrigenous SPM resulting in the observed variable Secchi depths. Euphotic depths are comparable to many other estuaries considered turbid such as North San Francisco Bay, the Tamar and the Columbia River (Cloern, 1987). Despite the high turbidity in the upper estuary, the pronounced stratification and resultant shallow mixing depth (Z_m) lead to a $K_d.Z_m$ of 2, lower than the critical limiting value for production of five suggested by Wofsy (1983). Thus the upper estuary has the potential for net phytoplankton production. However, while the influence of freshwater promotes stratification, the reduced vertical mixing also results in a zone where river flows result in low flushing times. Calculated flushing times greater than one day only occurred 31% of the time suggesting that flsuhing time is generally too low for phytoplankton blooms to occur. Periods when flushing times are longest generally occur during the dry summer months. Since river flow is under the control of stochastic processes the occurrence of the low flows necessary for phytoplankton growth to occur is unpredictable. Since both flushing time and salinity decrease in the upper estuary with increasing river flows, the high flushing times necessary for phytoplankton blooms to occur should coincide with times of high salinity.

Further downstream as the estuary broadens and the water column deepens to 8m. Salinity stratification gives way to more vertically mixed water such that at station 7 mean vertical gradient in salinity over a the four year period was ~10 and at high tide vertical density gradient in salinity <6 (Jones & Jordan, 1979). This zone receives

large inputs of suspended solids which are particularly concentrated at stations 11 and 12; these are associated with anthropogenic inputs from the Ringsend sewage outfall (Brennan *et al.*, 1994). The high SPM load reduces light penetration and combined with the deep mixing depths this leads to Kd.Zm values throughout the zone which are less than the critical limiting value of five (Cloern, 1987) where net production is negative. The lack of a seasonal cycle in vertical attenuation in the walled part of the estuary is attributed to variability in terrigenous suspended particulate matter loading from the rivers Liffey, Dodder and Tolka and the sewage treatment plant.
In addition to poor light-mixing conditions, flushing time estimates indicate that throughout the spring neap cycle phytoplankton are likely to be removed more rapidly than they can grow. In this zone tidal flushing and light conditions combine to prevent aggregation of phytoplankton.

Tidal flushing calculations in the bay indicate the importance of the diurnal advection of water in to the area; this has previously been noted as an important source of diffuse nutrient input (Wilson, 2005). The importance of this diurnal advection is supported by the high frequency temperature data from April and May 2004. Tidal velocities in the bay vary over the spring neap cycle (ERU, 1992) and vertical mixing energy varies as a cube of tidal velocity. The inverse relationship between tidal range and water temperature in April 2004 indicates that vertical mixing of cool bottom waters into surface layers of water increased as tidal range increased. The change in this relationship and its coincidence with neap tides indicates the onset of thermal stratification (Figure 4.1.3a,b). However the shallow water depths and strong tidal currents in Dublin Bay are known to result in top to bottom mixing of the water column (Crisp 1972) and the observed pattern in temperature, consistent with the occurrence of thermal stratification, indicates that the temperature of the waters in the bay is also a result of the advection of offshore waters. Most of the waters immediately offshore of Dublin Bay are too shallow to support stratification (Simpson & Pingree, 1978). However the closest known stratified waters in this area are those to the north of the Western Irish Sea Front lying about 30km to the north east of Dublin Bay. Modelled residual currents in this area run in a southerly direction with speeds of up to 8 $cm.s^{-1}$ (Horsburgh *et al.*, 2000). Given this speed and distance waters from north of the front would require five days to arrive in Dublin Bay.

Waters north of the Irish Sea Front have low turbidity compared to inshore waters at Dublin Bay (Bowers *et al.*, 2005). Mean Secchi depth for Dublin Bay stations (2.4 m) are just over half the mean Irish Sea Secchi depths from a range of offshore and inshore stations (Bowers *et al.*, 2002). The light conditions experienced by plankton vary greatly over a daily timescale to due high turbidity, vertical mixing and variable water depths. The resultant light conditions are unlikely to be favourable to phytoplankton which are not photoacclimated. The timescale required for photoacclimation by adjustment of cell chlorophyll concentration (often the primary determinant of light limited photosynthesis) is in the order of a week (MacIntyre *et al.*, 2000), i.e. longer than the time it takes to arrive from the stratified waters to Dublin Bay. This means that phytoplankton assemblages occurring in the bay are likely to be unacclimated and consequently in situ production may be low.

4.3.0: Conclusions

The physical processes limiting the proliferation of phytoplankton differ throughout the study system. Freshwater flow resulting in rapid flushing times is the main limiting physical phenomenon to phytoplankton bloom development in the upper estuary where light and mixing conditions are well suited to phytoplankton growth.

In the lower estuary a combination of the rapid tidally driven flushing, and poor light mixing conditions resulting from weaker stratification combined with high turbidity mean that it is unlikely that phytoplankton production can occur in this area.

In the open bay advection of large volumes of water from a seasonally stratifying offshore source is the principal control on the physical conditions. Though flushing times may be long enough for phytoplankton growth to occur, the waters of Dublin Bay are highly turbid compared to other parts of the Irish Sea and light conditions are likely to be unfavourable to phytoplankton which are have not undergone photoacclimation.

Overall the good agreement between light-mixing conditions throughout the study area and mean chlorophyll concentration indicates that the physical structure of the water column greatly effects the spatial distribution of phytoplankton biomass. Flushing timescales are also critical in determining the times when phytoplankton blooms may occur. In the upper estuary flushing considerations indicate that despite

suitable light conditions the frequency of bloom occurrence will be limited to times when low riverine flows occur.

CHAPTER 5 PATTERNS IN PHYTOPLANKTON BIOMASS

5.0.1 Introduction

Under the E.U. Water Framework Directive (WFD) (EU, 2000) phytoplankton are the primary biological quality element that determine the ecological status of transitional waters (i.e. waters in the vicinity of a river mouth which are partly saline in character). High status is afforded the water body if phytoplankton are consistent with undisturbed conditions, slight changes in biomass from undisturbed conditions lead to good quality status, and where phytoplankton cause an "undesirable disturbance" moderate quality is assigned. After extensive study the U.K Undesirable Disturbance Study team defined an undesirable disturbance as follows.

"*Undesirable disturbance is a perturbation of a marine ecosystem that appreciably degrades the health or threatens the sustainable use of that ecosystem*" (Anon, 2004)

While this definition is to be applied throughout the U.K. for application of the W.F.D, it is very broad in nature and in itself requires further interpretation.

First the boundaries of the marine ecosystem must be defined. To this end, Tett (2004) suggests an approach whereby ecohydrodynamically similar waters are classed together as an ecosystem. For the Irish Sea, five ecosystems have already been defined on this basis (Gowen *et al.*, 1995; Anon, 2004) corresponding to different mixing, stratification regimes and different phytoplankton growth seasons.

A. Embayments and regions of freshwater influence with salinity <30;
B. Coastal frontal zones in the proximity of transition from mixed to more persistently stratified waters with salinity 30-33
C. Offshore mixed waters with salinity >34
D. Offshore waters of transitional stability with salinity >33
E. Offshore seasonally stratified waters with salinity >34.

Each of the above typologies has a different pattern of succession in phytoplankton biomass and abundance. While Dublin Bay is considered to be of type B, (Gowen *et al.*, 1995; Anon, 2004) its salinity characteristics have similarities to more offshore waters and the temperature signature (Chapter 4) suggests strong influence from waters which show at least some stability (i.e. type D or E) which may complicate the assessment of baseline conditions. The typical seasonal pattern in phytoplankton composition and abundance in type B waters includes a long production season with a diatom dominated spring bloom beginning in shallow inshore waters spreading eastwards as deeper waters begin to thermally stratify (Gowen *et al.*, 1995). Typically there is a shift to slower growing dinoflagellates which make use of recycled nutrients and the new nitrogen diffused through the thermocline. Such successional patterns appear to be limited in the western Irish Sea with the in summer dinoflagellates making up only 50% of phytoplankton carbon in the western Irish Sea in summer (Gowen *et al.*, 2000). On a practical level, some authors point to the lack of interannual records of chlorophyll concentrations in the western Irish Sea as a baseline (Gowen & Stewart, 2005) against which perturbations in such large systems may be measured. The practical difficulties in detecting long-term trends over such large areas as the Irish Sea are illustrated by the continuing debate over the cause of the observed nutrient increases, despite a detailed long-term data set (Gibson *et al.*, 1997; Allen *et al.*, 1998).

In the case of this study ecosystem boundaries are taken to be the geographical boundaries of Dublin Bay. This does not constitute an ecohydrographical typology but a geographical division corresponding to the urban area of Dublin. The small size of this area (relative to the much larger ecohydrodynamical typologies) means that small-scale events and trends in the relevant parameters are more easily detectable, and quantifiable.

Second, the term ecosystem health, which is analogous to human health and may be measured in terms of vigour, organization and resilience (Boesch & Paul, 2001) requires rigorous definition. The properties of vigour, organization and resilience are not easily measured with standard methods and definitive metrics for these characteristics are not yet in place. By contrast the "symptoms" of eutrophication are already well defined throughout the literature and as such provide a more solid basis for the assessment of eutrophication.

The main symptoms relative to phytoplankton biology are:

1. Increased algal biomass: for instance in the Wadden Sea a shift from P to N limitation resulted in doubling of spring bloom chlorophyll concentrations in the 1970s and 1980s (Ducrotoy, 1999). In the U.K. a figure of 10 $mg.m^{-3}$ is often taken to represent bloom concentrations (Iriate & Purdie, 2004).
2. Hypoxia: the extent of hypoxia may be localized such as that found in the sediments of the Liffey estuary (Wilson *et al.*, 1986) or on a large geographical scale such as in the Gulf of Mexico (Turner & Rabalais, 2003) but marine hypoxia has not been observed in the Irish Sea.
3. Change in the balance of organisms for instance in the ratio of diatoms to dinoflagellates which may occur as subtle ratio shifts or may result in the formation of nuisance or harmful algal blooms (Anon, 2004). Blooms of the haptophyte alga *Phaeocystis globosa* and the heterotrophic dinoflagellate *Noctiluca scintillans* are a relatively common occurrence in the Irish Sea (Claustre *et al.*, 1990; Anon., 2004). However it is unclear whether these are natural occurrences or whether they are enhanced by human activities.

These symptoms are not entirely separate from one-another, for instance large monospecific algal blooms resulting from eutrophication may involve larger summer blooms as well as a shift in the ratio of diatoms to dinoflagellates. Here the above symptoms are taken as a measure of eutrophication.

Third the "sustainable use" of the ecosystem must be defined. Dublin Bay has many uses as defined in the Dublin Bay Water Quality Management Plan (ERU, 1992): its role as a vessel for waste discharge; its function as a busy industrial port and its many recreational uses, swimming, boating fishing, kite surfing as well as some small scale shellfish harvesting. While wastewater dumping or use as a commercial port may have profound effects on ecosystem function, the functioning of the ecosystem has little effect on the sustainability of these activities. Recreational usage by contrast is fundamentally affected by ecosystem function and as such this is a suitable criterion on which to base an interpretation of undesirable disturbance.

Tett (2004) proposes that small scale "pulse disturbances" are of little concern and the principle "undesirable disturbances" examined should be those categorized as extensive "press disturbances" i.e. large scale continuous disturbance to the ecosystem (Tett, 2004). Since an ecosystem (however it is defined) is composed of many interacting elements, undesirable disturbances on small scales have impacts on the system as a whole. In a small geographically well defined ecosystem where recreational usage is of primary concern small-scale disturbances be they pulse or press are of definite significance.

A further requirement of the Water Framework Directive is that the frequency of operational sampling be sufficient to produce an "acceptable level of confidence and precision" in monitoring of transitional waters. Since phytoplankton growth and chlorophyll concentrations are dependent on seasonal conditions, and the processes promoting or preventing phytoplankton growth may vary on much shorter timescales which are dependent on the individual location, determining the frequency of operational sampling adequate to the stated purpose of the water frame work directive is not a trivial process. For instance a recent study (Gowen & Stewart, 2005) illustrates how chlorophyll values during the spring bloom vary widely with measured chlorophyll concentrations ranging from 0.33 mg $Chla.m^{-3}$ to 43.9 mg $Chla.m^{-3}$. The low values presented are barely above background concentrations suggesting that these measurements perhaps missed the peak of the spring bloom. The same authors point to the paucity of data for comparison. As a result the temporal frequency of sampling is critical to avoid aliasing of the phenomena being studied.

In this chapter the spatial and temporal patterns in phytoplankton abundance and composition are explored in the context of eutrophication.

5.1.0 Results

5.1.1 Spatial Variation

Table 5.1 summarizes the chlorophyll *a* and phaeopigment data collected during the monthly sampling cruises over the study period. Chlorophyll *a* concentrations spanned four orders of magnitude over the study area ranging from values of less than detection limits to 121.6 $mg.m^{-3}$. Within the walled part of the estuary mean chlorophyll *a* concentrations varied greatly from the freshwater to the saline end. At stations 1-6 highest mean chlorophyll a concentrations ≥ 3 $mg.m^{-3}$ were observed, at these stations there was also great variability in chlorophyll concentrations. In the lower estuary stations 7-17 the lowest mean concentrations of the entire study area were found and variability was also low. In the open Bay stations 18-41 mean chlorophyll concentrations showed less variability though considerable variation was found within the bay on any given sampling date. Highest summer average chlorophyll *a* concentrations were found at stations 26-30 in the Liffey plume area off Howth Head.

While chlorophyll concentrations in the estuary did display a seasonal pattern (Figure 5.1.2a) with highest concentrations occurring between the months of May and August, there was great spatial variation in concentrations on any given date as illustrated by the large 95% confidence intervals. Linear regressions of chlorophyll and total phaeopigments with salinity generally displayed significant negative relationships (Table 5.2), indicating that in general dilution of higher chlorophyll fresh waters with lower chlorophyll more saline waters was the principal control on chlorophyll distribution. On dates when significant regressions of chlorophyll with salinity occurred, phytoplankton was generally composed of a mixture of freshwater and marine diatoms. On occasions when neither chlorophyll concentrations or total phaeopigments showed linear relations with salinity maximum measured chlorophyll concentrations tended to be higher than $10mg.m^{-3}$ in some or all of the stations in the inner estuary (Figure 5.2a). These high chlorophyll concentrations were found to coincide with times when high salinity waters were in this location, i.e. when freshwater flow was low (Figure 5.2b). At times when high chlorophyll concentrations were present phytoplankton cell counts revealed high numbers of the flagellated phytoplankton *Cryptomonas* sp. (Plate 2).

Table 5.1: Mean, maximum, minimum standard deviation (stdev) ($mg.m^{-3}$) and number of data (n) for chlorophyll a and phaeopigments from monthly sampling cruises at each sampling station over the study period.

	Chlorophyll *a*					Phaeopigments				
Station no.	Mean	Max	Min	stdev	n	Mean	Max	Min	stdev	n
1	4.3	10.0	0.5	3.5	7	1.8	4.3	0.1	1.3	7
2	3.8	11.6	1.0	3.6	8	4.4	19.0	0.8	6.1	8
3	11.0	121.6	0.1	27.2	19	4.9	23.4	0.9	5.7	19
4	3.3	11.9	0.4	3.1	19	4.2	39.1	0.5	8.6	19
5	3.1	15.1	0.4	3.2	19	10.8	99.0	0.5	25.9	19
6	3.0	15.8	0.3	3.4	18	2.9	16.0	0.8	3.4	18
7	1.3	3.3	0.0	0.8	20	1.7	8.0	0.2	1.8	20
8	1.3	3.5	0.0	0.9	20	1.7	7.1	0.2	1.6	20
9	1.4	2.9	0.0	0.8	20	2.0	5.0	0.5	1.5	20
10	1.8	3.6	0.4	1.0	18	1.2	2.8	0.2	0.6	18
11	1.4	3.3	0.2	0.9	20	2.0	11.0	0.1	2.5	20
12	1.1	2.5	0.1	0.6	20	1.3	2.9	0.1	0.9	20
13	1.5	3.7	0.4	0.9	17	1.1	1.9	0.2	0.5	17
14	1.5	3.2	0.1	1.0	20	1.3	6.3	0.0	1.4	20
15	1.4	3.3	0.1	1.0	19	1.2	3.0	0.0	0.8	19
16	1.7	3.7	0.5	0.9	18	1.5	3.4	0.1	0.9	18
17	1.6	4.9	0.2	1.0	18	1.3	3.3	0.3	0.7	18
18	2.1	5.7	0.5	1.5	17	1.5	4.9	0.0	1.3	17
19	2.1	4.1	0.4	1.1	17	1.2	4.1	0.3	1.1	17
20	1.9	6.1	0.5	1.4	17	1.3	5.0	0.0	1.3	17
21	2.0	4.8	0.7	1.3	18	1.3	4.3	0.0	1.1	18
22	2.0	5.3	0.5	1.3	18	1.5	4.4	0.1	1.4	18
23	2.1	6.1	0.3	1.6	19	1.5	4.8	0.0	1.5	19
24	1.9	6.4	0.1	1.5	19	1.4	5.2	0.1	1.3	19
25	1.7	4.9	0.3	1.1	19	1.7	9.0	0.0	2.1	19
26	2.3	4.7	0.4	1.3	19	1.5	6.9	0.0	1.9	19
27	2.6	7.2	0.4	1.6	19	1.9	8.8	0.1	2.4	19
28	2.4	6.3	0.8	1.4	19	2.0	6.1	0.2	1.7	19
29	2.7	6.1	0.9	1.4	19	1.7	3.9	0.0	1.1	19
30	2.5	6.8	0.7	1.7	19	1.9	8.0	0.3	2.0	19
31	2.1	5.7	0.3	1.3	19	2.8	22.1	0.3	4.9	19
32	2.1	7.5	0.0	1.7	18	1.9	5.2	0.1	1.6	18
33	2.0	6.4	0.1	1.5	19	1.9	7.5	0.2	1.9	19
34	2.2	5.6	0.0	1.2	19	1.8	9.6	0.0	2.2	19
35	1.8	7.2	0.4	1.5	18	2.2	10.7	0.0	2.5	18
36	2.4	7.4	0.7	1.7	18	1.0	3.1	0.0	0.8	18
37	1.7	6.3	0.4	1.3	18	1.8	4.4	0.2	1.2	18
38	2.0	6.7	0.5	1.5	17	1.2	3.3	0.1	1.0	17
39	1.7	5.7	0.4	1.3	17	1.3	3.0	0.1	0.9	17
40	1.7	5.3	0.2	1.4	18	1.7	7.4	0.3	1.8	18
41	1.7	2.5	0.8	0.7	6	0.7	1.1	0.3	0.3	6

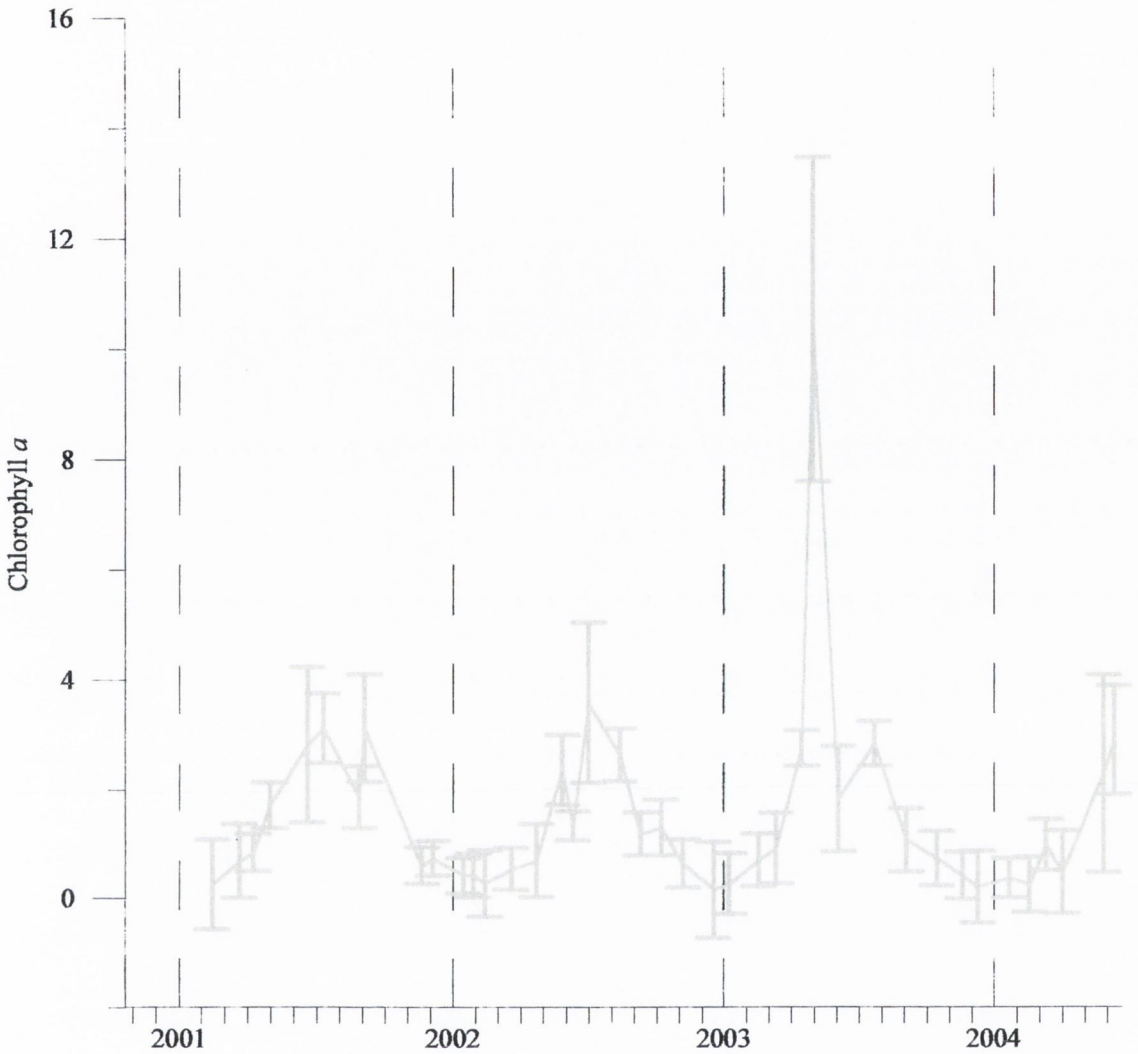


Figure 5.1: Mean chlorophyll concentrations in the walled part of the Liffey estuary from monthly sampling cruises 2001-2004: Error bars are standard error of the mean.

The highest recorded chlorophyll concentration 1st of May 2003 (121.3mg.m^{-3}) coincided with a monospecific bloom of *Cryptomonas* with cell concentrations of up to 43.8x10^{6} cells.l^{-1}. Oxygen saturation in the surface waters was observed to be at 108.2% at the same time as underlying waters were relatively hypoxic (69.5%).

Table 5.2: Mixing curves of chlorophyll *a* and total phaeopigments (i.e. chlorophyll *a* and phaeopigments combined) with salinity for the months April to September 2001, 2002, 2003 and April to June 2004 in the walled part of the estuary. *=p<0.05 **=p<0.01. N/S=not significant n = number of data points, Chl *a* and Tot Phae are the predicted values of chlorophyll and total phaeopigments at 0 salinity. r is negative in all cases.

	Chlorophyll a				Chlorophyll *a* and phaeopigments			
Date	n	r^2	Chl a	p	N	r^2	Tot Phae	p
10-Apr-01	12	0.395	2.11	*	12	0.711	7.80	**
02-May-01	17	0.259	2.60	*	17	0.589	5.20	**
20-Jun-01	15	0.074	-	N/S	15	0.010	-	N/S
11-Jul-01	17	0.278	8.96	*	17	0.409	20.08	**
29-Aug-01	15	0.578	6.61	**	15	0.369	8.80	*
05-Sep-01	17	0.001	-	N/S	17	0.001	-	N/S
24-Apr-02	15	0.197	-	N/S	15	0.697	3.58	*
29-May-02	15	0.090	-	N/S	15	0.255	11.06	*
12-Jun-02	17	0.031	-	N/S	17	0.007	3.12	*
03-Jul-02	15	0.347	23.47	*	15	0.388	29.40	*
14-Aug-02	17	0.388	4.67	**	17	0.692	8.59	**
11-Sep-02	15	0.283	1.76	*	15	0.087	-	N/S
16-Apr-03	15	0.324	4.36	*	15	0.566	8.18	*
01-May-03	15	0.000	-	N/S	15	0.000	-	N/S
05-Jun-03	15	0.062	-	N/S	15	0.196	-	N/S
23-Jul-03	15	0.293	4.40	*	15	0.395	3.12	*
4-Sep-03	17	0.373	1.04	**	17	0.102	-	N/S
1-Apr-04	15	0.336	-	N/S	15	0.398	1.53	*
27-May-04	16	0.129	-	N/S	14	0.069	-	N/S
10-Jun-04	11	0.255	-	N/S	11	0.035	-	N/S

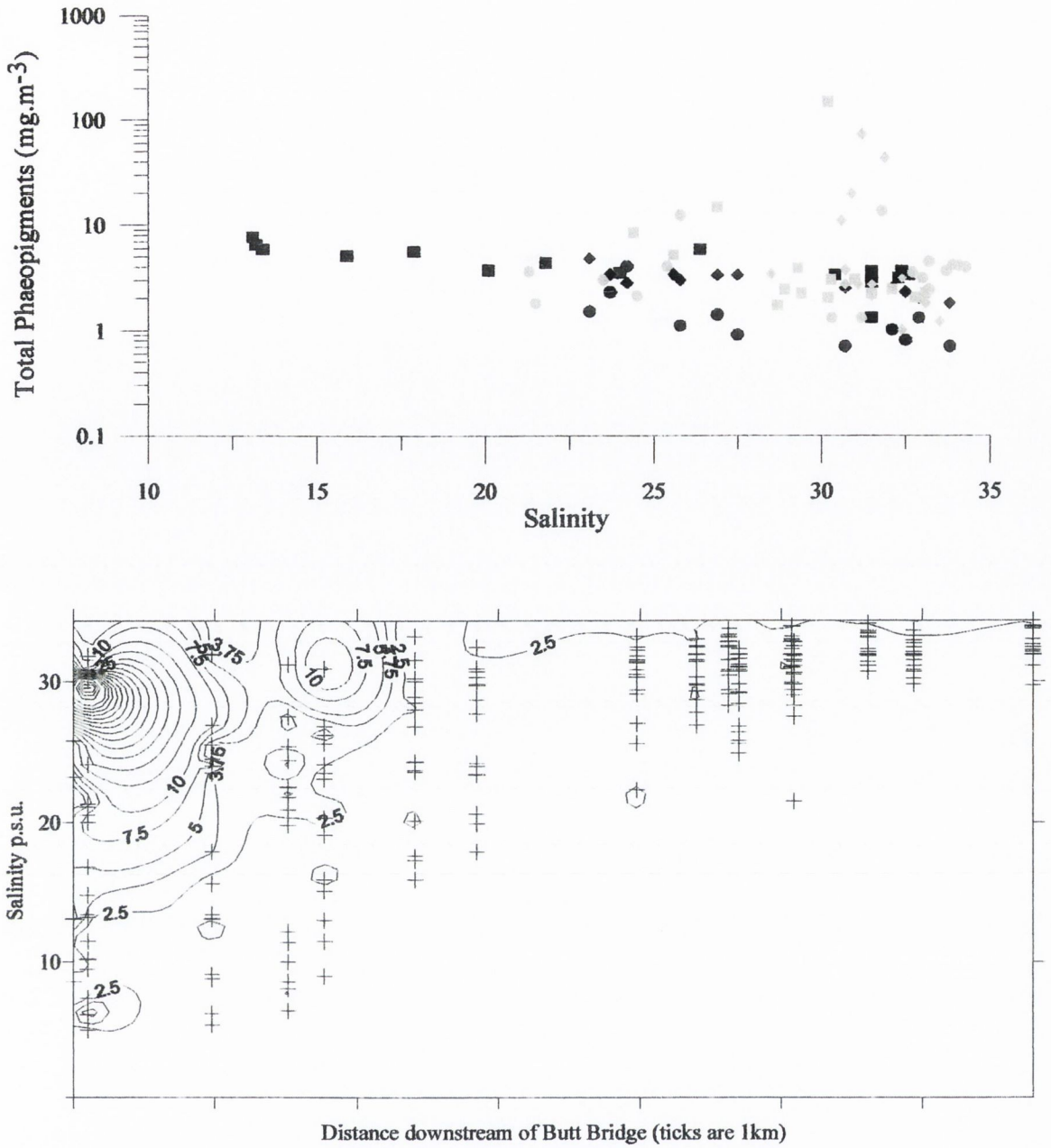
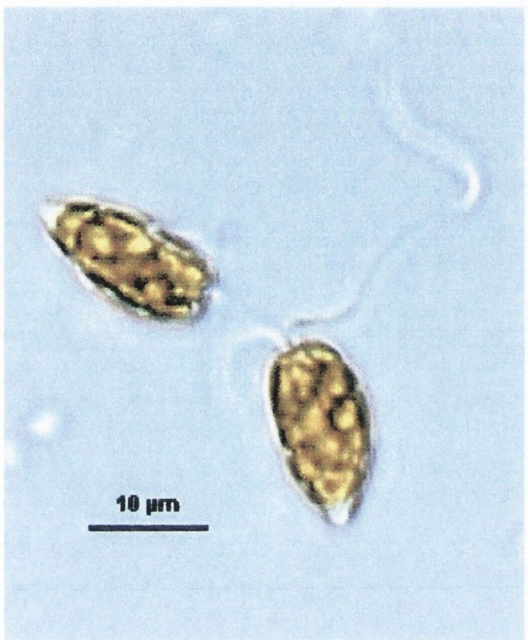


Figure 5.2: a) Plots of salinity versus total phaeopigments data from selected dates . Dates when mixing curves of salinity and total phaeopigments were statistically siginificant are shown in black: 10/4/01 (diamonds); 24/4/02 (circle), 14/8/02 (squares). Dates where mixing curves were not significant and total phaeopigment concentrations exceeded 10mg.m^{-3} are shown in grey: 20/6/01 (diamond); 5/9/01 (circle); 1/5/03 (square). b) Chlorophyll *a* concentrations (mg.m^{-3}) in the Liffey estuary April to September 2001-2003 plotted against distance downstream of Butt Bridge (x axis) and salinity (y axis). Crosses mark samples.

a



b

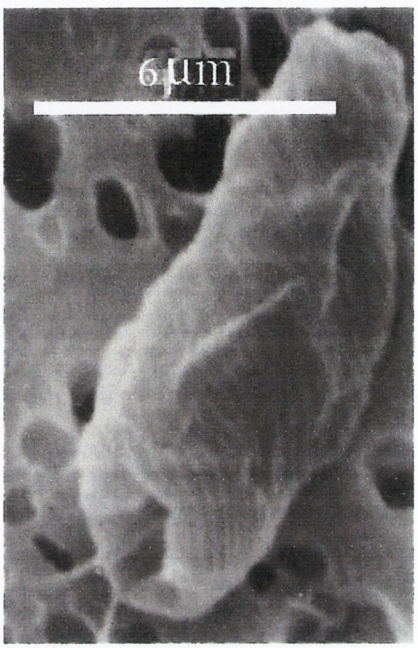


Plate 2: (a) Light micrograph of two of the *Cryptomonas* species showing two unequal flagella. (b) Scanning Electron micrograph showing furrow gullet complex. Note the striped pattern on the surface of the cell. Size complexity of the furrow gullet complex and the distictive stripes suggest the species may be *Cryptomonas stigmatica*, however Crytpomonad taxonomy is an ongoing process and newer classification schemes involve identification using biochemical, molecular and ultrastructural characteristics (Clay et al., 1999).

The statistically significant predicted freshwater chlorophyll *a* values were combined with average chlorophyll *a* values for the stations of the upper estuary (on dates when regressions were not significant) to calculate an annual carbon flux estimate. The resultant average annual phytoplankton carbon flux for the year 2001 was 15.9 $x10^3$ kg $C.y^{-1}$ and for 2002 was $31.1x10^3$ $kgC.y^{-1}$ Mass balance calculations based on the river flow estimate that around half of this phytoplankton flux from the river was retained in the estuary (Table 5.3).

Table 5.3: Annual riverine phytoplankton carbon output ($kg.C.x10^3.y^{-1}$); annual estuarine phytoplankton carbon output ($kg.C.x10^3.y^{-1}$); the difference between the two (i.e. that which is retained in the estuary) expressed as mass ($kg.C.x10^3.y^{-1}$) and also as a percentage of the total riverine output.

year	Riverine output	Estuarine output	Difference	
	kg C x $10^3 y^{-1}$	kg C x $10^3 y^{-1}$	kg C x $10^3 y^{-1}$	%
2001	16.0	6.7	9.3	58
2002	31.1	17.3	13.9	45
mean	22.1	10.6	11.5	52

5.1.2 Upper Estuary high frequency data.

Deployment of the YSI 6600 at Station 3 in the upper estuary during the summer of 2004 allowed detailed observation of the dynamics of the *Cryptomonas* bloom formation
At Station 3 low chlorophyll concentrations were prevalent throughout April. A bloom developed at Station 3 in early May and continued to develop until 27th of the month (Figure 5.3). A maximum net growth rate of 1 day^{-1} occurred during the development of the bloom on 15th of May. Maximum total phaeopigment concentrations measured by fluorescence reached 377 $mg.m^{-3}$ during this period and coincided with high modeled residence times <48 hrs. There was a decline in chlorophyll concentrations between the 28th of May and the 31st of May. The bloom decline coincided with a reduction in tidal cycle averaged

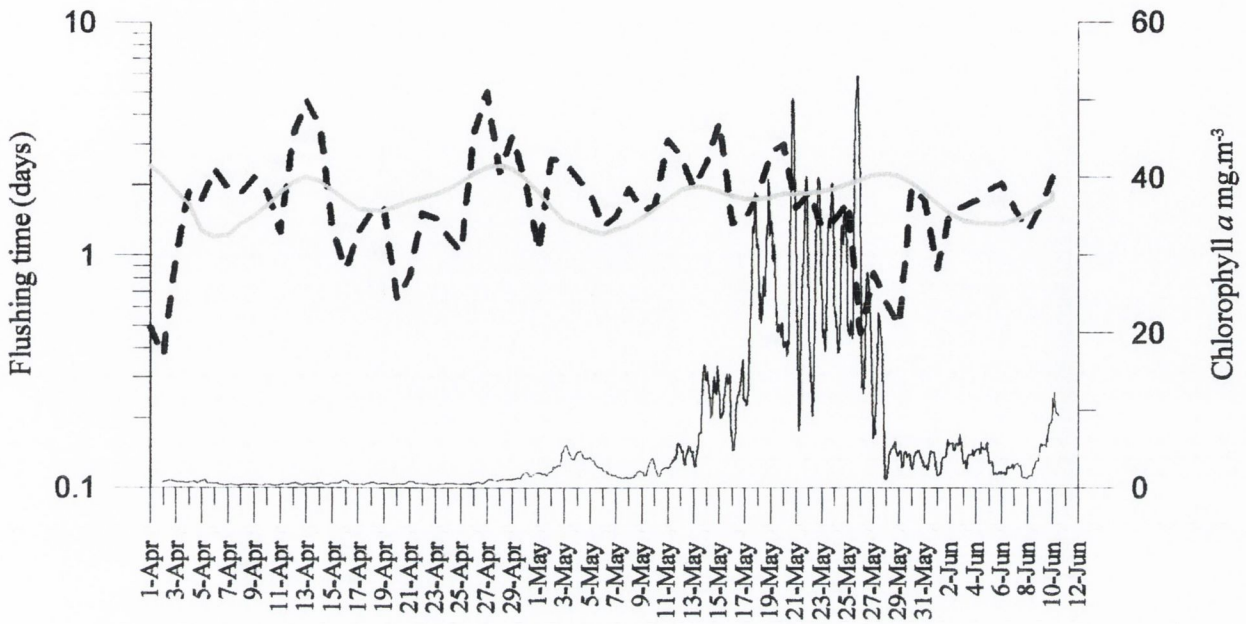


Figure 5.3: Running average chlorophyll *a* (black solid) concentration (estimated from fluorescence); modelled tidal estimated flushing time for whole estuary (grey) and flushing time for the upper estuary (dashed black) at station 3 April to June 2004.

salinity from values >20 during the bloom to values <10. At the beginning of June there was some evidence for a second bloom of plankton which again coincided with increased flushing time. The chlorophyll peaks during these blooms coincided with a monospecific bloom of *Cryptomonas sp.* The maximum number of cells counted was 9.8x 10^6 cell l^{-1} on the 27th of May, downstream of the sonde at station 5. The total phaeopigment concentration from this sample was 114.1 mg.m^{-3} with 15.1 mg.m^{-3} of chlorophyll *a* and the rest being phaeopigments suggesting a population in decline. The carbon content of each *Cryptomonas sp.*cell was estimated from biovolume calculations at 50 pg.$cell^{-1}$ yielding a carbon to chlorophyll *a* ratio of 32:1. The mean magnitude of the chlorophyll peak on the ebb tide was smaller than that on the flood. The mean difference between ebb and flood tide carbon flux was 45 kgC.tidal $cycle^{-1}$. Minimum oxygen saturation of 25.1% occurred on the 3rd of June after the decline of the bloom.

5.1.3 Temporal variability in the Bay

The timing and the magnitude of the spring bloom varied interannually and there was considerable variability in chlorophyll *a* concentrations on any given date (Table 5.4; Figure 5.4). The highest summer average chlorophyll *a* concentrations were found at stations 26-30 in the Liffey plume area around Howth Head and were 0.7mg.m^{-3} higher than averages for all other stations combined (Figure 5.5). Phytoplankton counts from summer 2003 (Appendix III) indicate that diatoms were dominant both in terms of biomass and numbers throughout the summer months making up a minimum of 89.6% of phytoplankton by numbers. *Leptocylindrus danicus* was generally the principal species. Dinoflagellates made up a maximum of 40.8% of the total phytoplankton carbon in June 2003. The late summer bloom in August 2003 (which had higher chlorophyll concentrations than those measured for the spring bloom of that year) was associated with a mixture of *Leptocylindrus danicus* and the potentially toxic diatom *Pseudo-nitzschia seriata* which has been linked to outbreaks of amnesic shellfish poisoning (Hallegraeff, 1993). A number of species known to cause harmful algal blooms in other locations were also noted (Table 5.5).

Table 5.4: Date of spring bloom in the bay, mean, maximum and minimum chlorophyll *a* concentrations ($mg.m^{-3}$) on that date standard deviations (s.d.) and number of data points (n).

Date	Mean	max	Min	s.d.	N
26/4/01	3.3	6.1	0.1	1.4	24
15/5/02	5.5	7.5	3	1.4	22
9/4/03	2.2	3.9	0	0.9	21
1/5/04	1.3	3.7	0	1.0	19

Table 5.5: List of the potentially nuisance and toxic phytoplankton species found in Dublin Bay.

Species
Karenia mikomotoii
Prorocentrum minmium
Pseudonitzschia sp.
Dinophysis acuta
Gymnodinium sp.
Protoperidinium sp.
Phaeocystis sp.

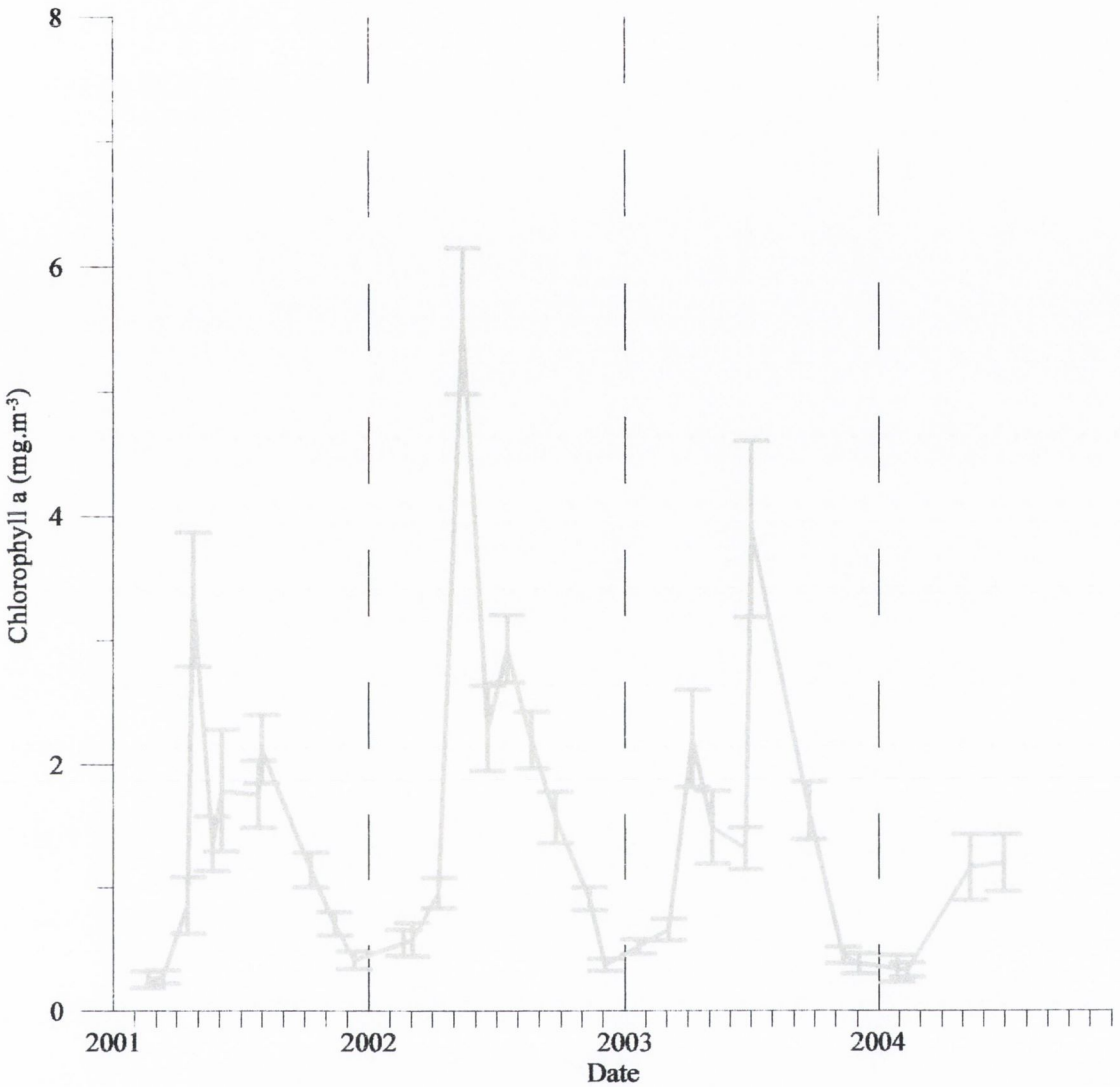


Figure 5.4: Mean monthly chlorophyll a concentrations ($mg.m^{-3}$) in the open bay collected during monthly sampling cruises. Error bars are 95% confidence intervals.

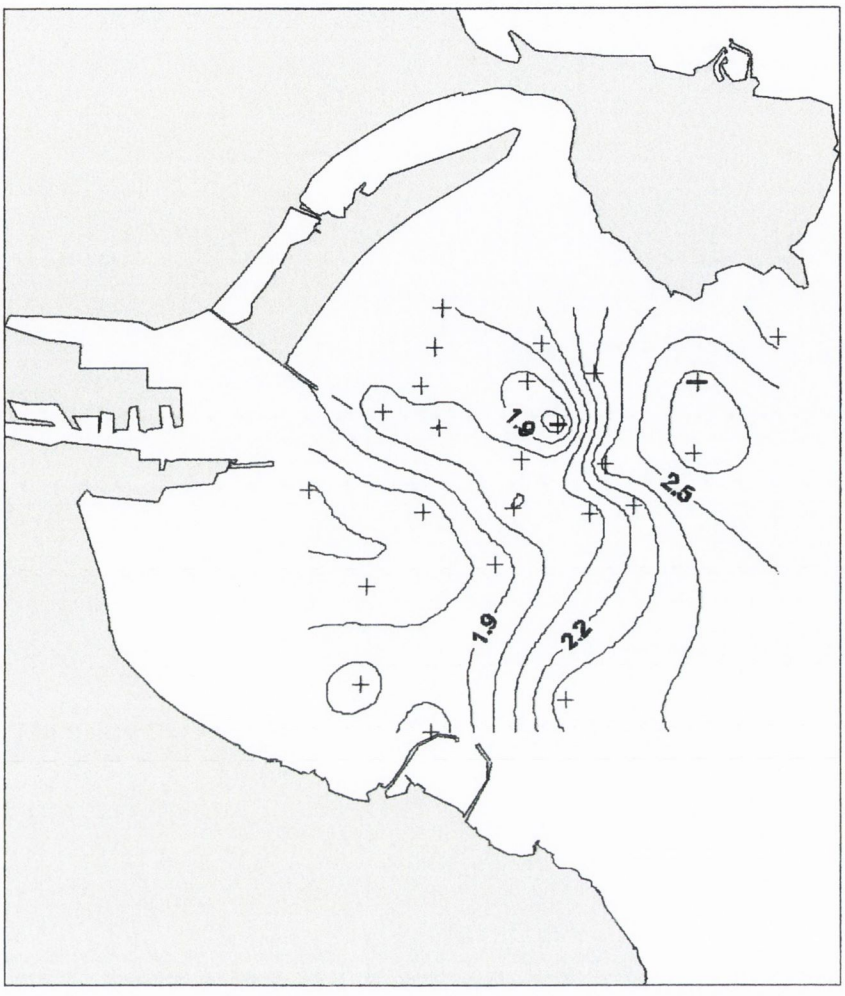


Figure 5.5: Distribution of mean chlorophyll concentrations ($mg.m^{-3}$) in Dublin Bay for the months April to September 2001-2003. Contours spaced at intervals of 0.1 $mg.m^{-3}$. Crosses mark sampling locations.

5.1.4 Lower estuary high frequency data

Data collected from the YSI sonde at site 16 (North Bank Lighthouse) were predominantly marine in character with a mean salinity 32.7. The fluorescence signal at this site gave a detailed picture of the spring bloom 2004. Following an initial (~3 mg. $a.m^{-3}$) peak in total phaeopigment concentration on the 3rd of April concentrations remained low until an increase began on the 25th of the month. Total phaeopigments rose continuously until the 3rd of May reaching a maximum 77.9 $mg.m^{-3}$ (Figure 5.6) the average net growth rate over this time was 0.3 day^{-1}. During this time maximum total phaeopigment concentrations were associated with the flood tide and maximum salinities. Oxygen concentrations reached 0.1% saturation in the early hours of the morning on the 2nd of May for a brief period (Figure 5.6). At this time there was a short-lived rise in temperature (4.5 °C) coupled with a drop in salinity, the two parameters being negatively correlated ($p<0.001$, $r^2=0.737$). The regressed freshwater temperature from this relationship was 31.6 °C indicating a non-natural source of heat input. A strongly significant correlation between the range in daily average total phaeopigment concentration and daily range in dissolved oxygen saturation was also observed at this time (Figure 5.7). The total phaeopigment concentrations (max = 21.1 $mg.m^{-3}$) measured at near peak levels (1st of May) had a mean composition of 20% chlorophyll *a* (Figure 5.8) suggesting that the bloom was in decline.

The phytoplankton assemblages in Dublin Bay on the first of May near the peak of the bloom were composed mainly of small diatoms (Table 5.6) with the principle species being *Leptocylindrus danicus* and *Thalassionema nitzchoides*. The estimated maximum phytoplankton carbon concentration was 906 mg $C.m^{-3}$.

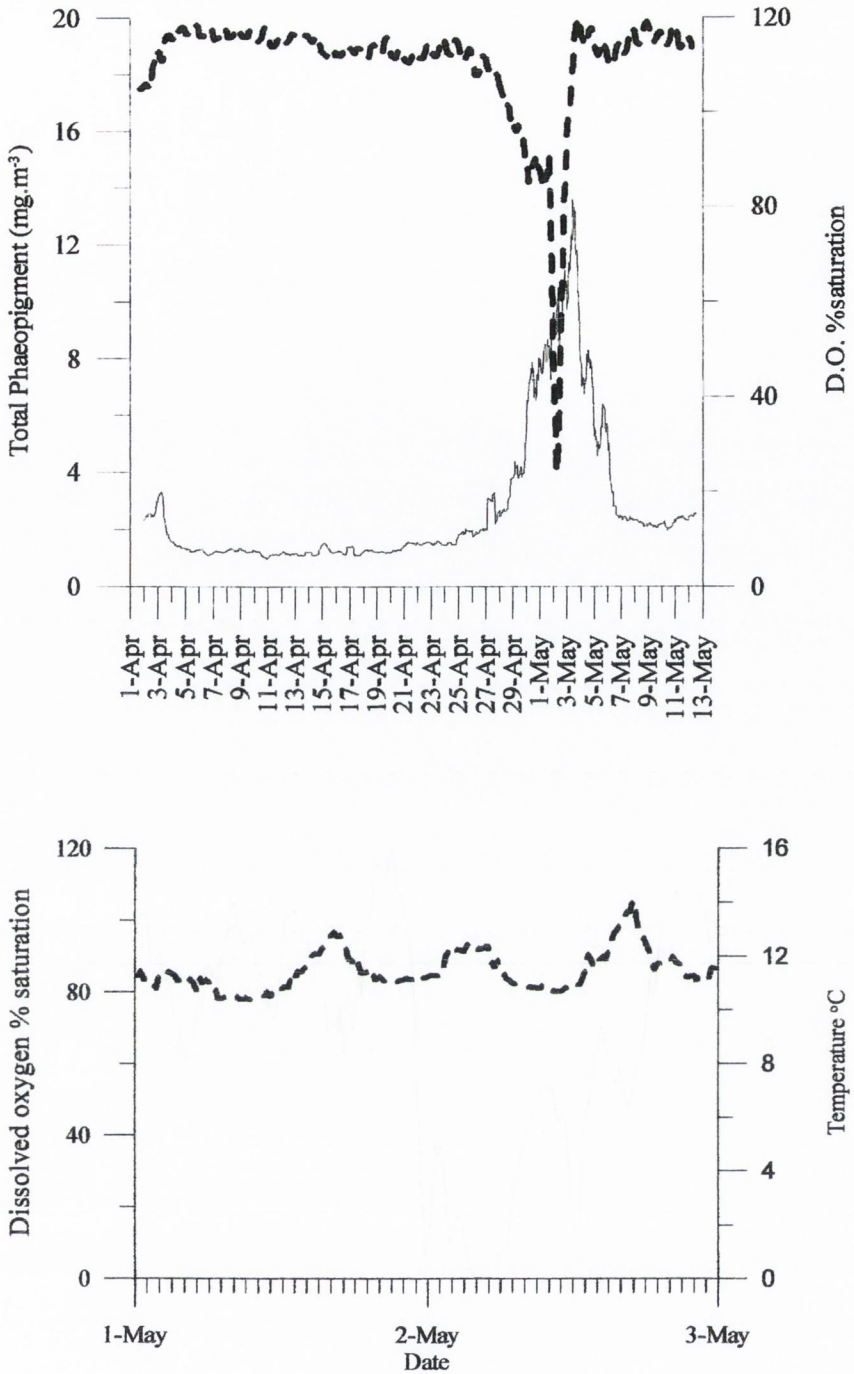


Figure 5.6: a) Running average total phaeopigment concentrations ($mg.m^{-3}$) at station 16 (estimated from fluorescence) during spring 2004 (solid) and running average dissolved oxygen concentration as percentage saturation (heavy dashed) at the time. b) Temperature (black dashed) and dissolved oxygen for the period 1st and 2nd of May 2004.

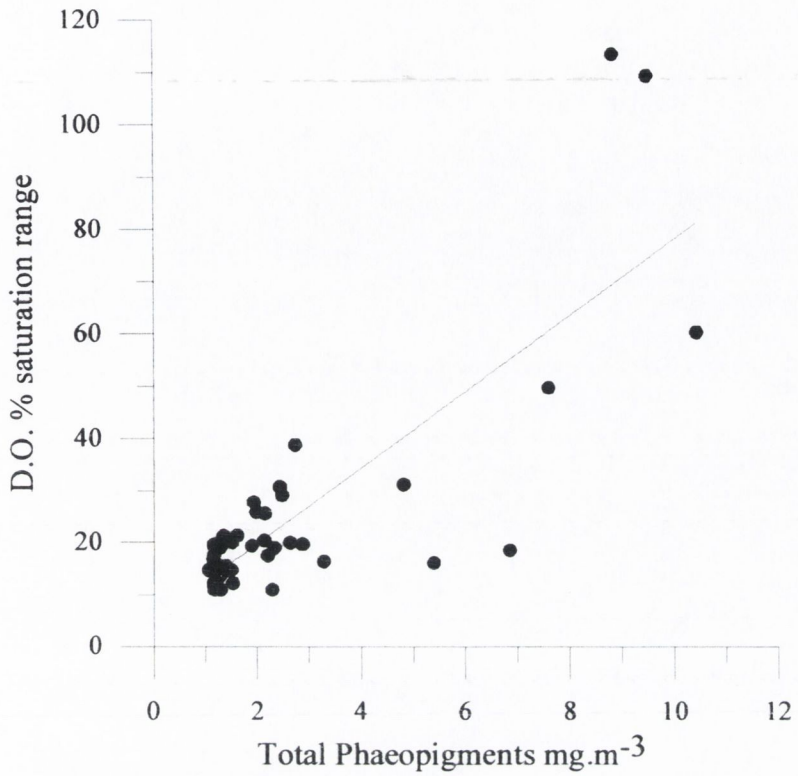


Figure 5.7: Relationship between daily range (maximum-minimum) in dissolved oxygen concentration and total phaeopigment concentrations at station 16 April to May 2004. $r^2=0.648$ $p<0.001$

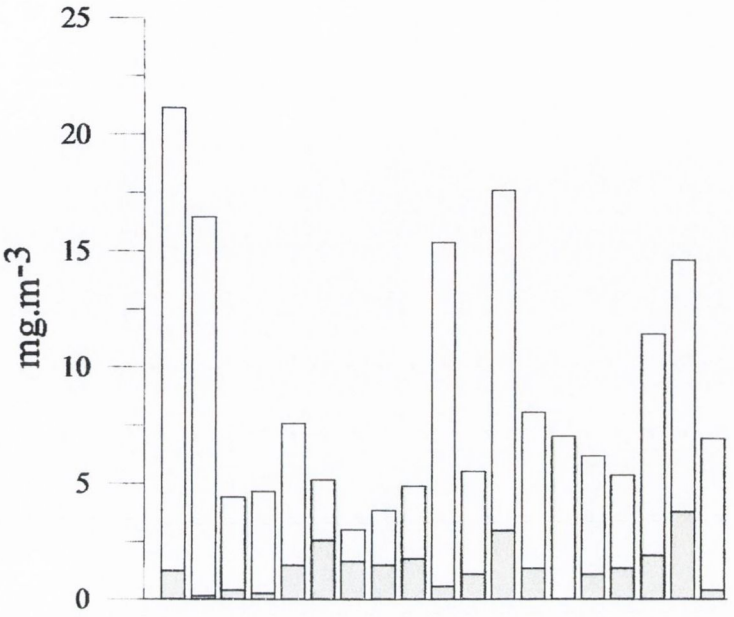


Figure 5.8: Total phaeopigments (white) and chlorophyll *a* concentrations (grey) at 19 stations in Dublin Bay on the 1st of May 2004 near the peak of the spring bloom.

Table 5.6: Phytoplankton composition in Dublin Bay (Station 36) 1st of May 2004 during the spring bloom, number of cells per litre and percentage of total phytoplankton carbon as estimated by biovolumes.

Diatoms	cells.l^{-1}	Carbon %
Leptocylindrus danicus	22920	95.6
Thalassionema nitzchoides	12680	2.0
Rhizosolenia habetata	240	1.5
Thalassiosira sp.	7840	0.4
Unidentified Centric	1280	0.1
Proboscia alata	200	0.1
Rhizosolenia stoltherfortii	200	-
Rhizosolenia fragilissima	520	-
Rhizosolenia setigera	80	-
Chaetoceros sociale (cells)	5560	-
Pseudo-nitzchia seriata	1000	-
Leptocylindrus minimus	360	-
Paralia sulcata	200	-
Odontella aurita	640	-
Pleurosigma sp.	40	-
Navicula sp.	360	-
Fragillaria sp.	200	-
Cylindrotheca closterium	360	-
Dinoflagellates		
Gyrodinium lachryma	240	-
Scripsiella	120	-
Gymnodimium sp.	40	-
Other		
Phaeocystis	1080	-

5.1.5 Bathing waters chlorophyll and phytoplankton

In February 2004 a pronounced brown discolouration of the bathing waters in the north of the Bay was noticed, Analysis of the sample indicated very high total phaeopigment concentrations 220.5 $mg.m^{-3}$ while no chlorophyll a was present, this accounts for the brown colour. This phenomenon prompted weekly monitoring of chlorophyll a, phaeopigment and phytoplankton compositions at 13 bathing water areas of Dublin Bay. Throughout the sampling period (May to August 2004) this discoloration was more or less apparent. Total phaeopigment concentrations in the intertidal waters of the bay showed a distinct north south divide (Figure 5.9). Mean total phaeopigments in the bathing waters of the south of the Liffey mouth was 2.8 $mg.m^{-3}$ compared to 26.2 $mg.m^{-3}$ for bathing waters to the north of the Liffey mouth. The ratio of chlorophyll to total phaeopigments varied over the study area making up on average 55% of total phaeopigments north of the Liffey mouth and 45% south of the Liffey mouth. To the north of the Liffey mouth, bathing water phytoplankton assemblages were found to be dominated almost entirely by the diatom species *Odontella aurita* (Plate 3). Maximum cell concentrations reached $7.2x10^{6}$ cells per litre and coincided with maximum total phaeopigment concentrations. There was a significant linear relationship in the north of the bay between cell number of *Odontella aurita* and total phaeopigment concentration (Figure 5.10)

Total Phaeopigment concentration ($mg.m^{-3}$) $= 2 \times 10^{-5}$ **Odontella* cells ($r^2=0.7057$)

Though the cells were variable in size there was no significant difference ($p=0.05$) in cell size between samples and the calculated mean carbon content was 600 $pg.cell^{-1}$. To the south of the Liffey mouth phytoplankton composition was also dominated by diatoms though in smaller numbers and with more variability.

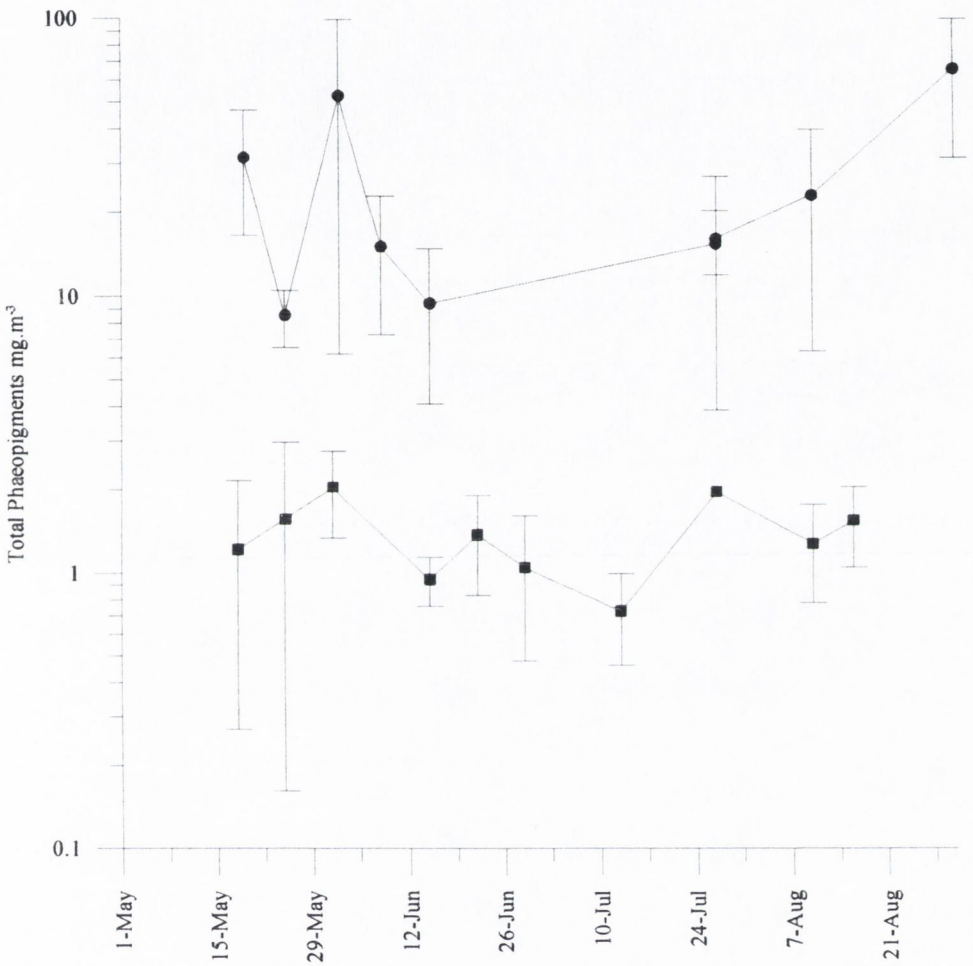


Figure 5.9: Mean total phaeopigment concentrations in bathing waters to the south of the Liffey mouth (square) and the north of the Liffey mouth (circles) for May to August 2004. Error bars are standard deviations.

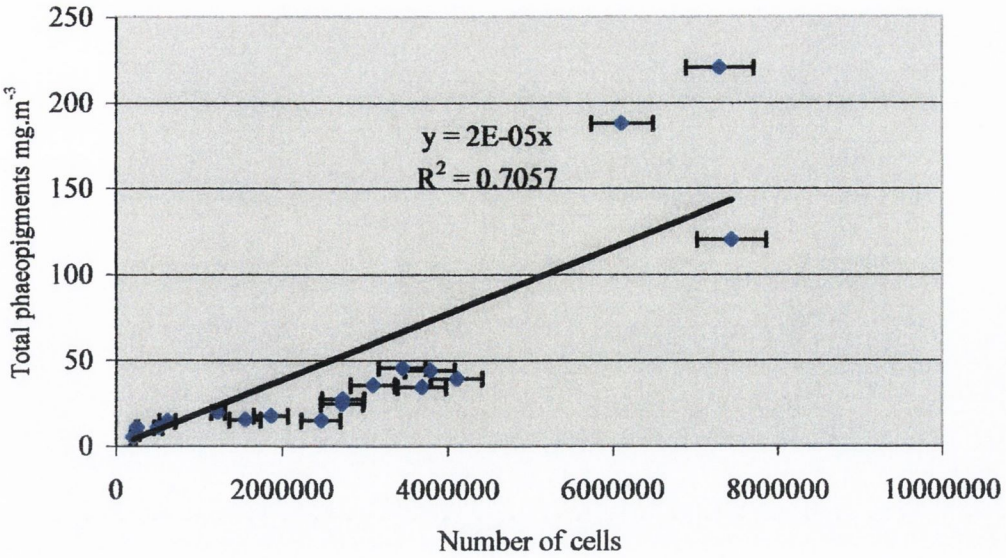


Figure 5.10: Total Phaeopigment concentrations ($mg.m^{-3}$) plotted against cell concentrations of *Odontella aurita* in the bathing waters of north Dublin Bay. n=19, p=<0.01

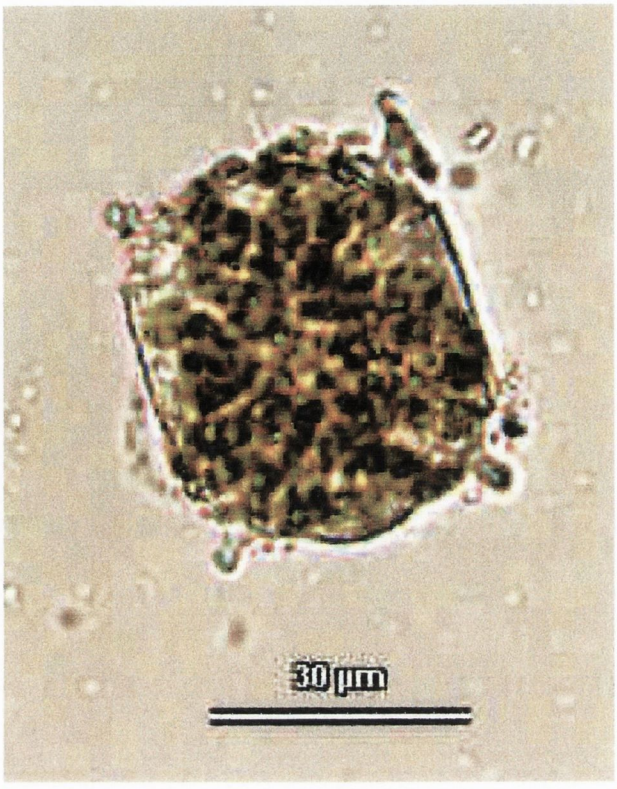


Plate 3: Light micrograph of *Odontella aurita* from bathing waters of north Dublin Bay

5.2.0 Discussion

The linear regressions of chlorophyll and total phaeopigments with salinity in the estuary demonstrate that at the times when chlorophyll *a* and phaeopigment concentrations were high (>10 $mg.m^{-3}$) mixing of freshwater with seawater alone could not explain their distribution. At these times higher than average salinity surface waters were present in the upper estuary which indicates reduced river flow and consequently reduced flushing. The data suggest strongly that populations of *Cryptomonas* existing in seasonally oligotrophic saline waters were provided with an opportunity for explosive population growth due to mixing with the hypernutrified Liffey waters. The motility of *Cryptomonas* species has previously been cited as a competitive advantage in stratified estuarine environments since less motile species (especially diatoms) may sink out into the deeper layers (Jones, 1988; Pickney *et al.*, 1998, 1999). The occurrence of phototaxis may also provide an additional advantage (Rhiel *et al.*, 1988). The highest concentrations of chlorophyll *a* encountered in 2003 (121.6 $mg.m^{-3}$) would require considerable time to develop given that *Cryptomonas* species have been shown to reach near optimal ~0.4 day^{-1} growth one day after transfer from oligotrophic to eutrophic conditions (Sciandra *et al.*, 2000). At this growth rate the high concentrations of chlorophyll *a* encountered on May 1st 2003 could develop from background levels (i.e. those of saline waters at the mouth of the estuary <2.5 $mg.m^{-3}$) in 15 days. Since salinity in the stratified upper estuary is negatively correlated with river flow, the high chlorophyll concentrations found sporadically throughout the study period in the upper estuary and their coincidence with times of high salinity suggests that river flow is an important factor controlling the accumulation of phytoplankton. In 2004 the *Cryptomonas* bloom lasted approximately 18 days with the abrupt decline in the fluorescence signal from the high frequency data occurring at a time of high freshwater flow suggesting that the high river flows flushed the plankton out of the estuary. The variability in chlorophyll concentrations of the upper estuary may thus be explained by the balance between suitable growth conditions caused by excessive nutrients and good light conditions but dependent on low flow which occur during dry periods.

The apparent loss of phytoplankton upstream of Station 3 during the *Cryptomonas* bloom of 2004 may have been caused by loss of buoyancy due to decreasing salinity upstream or through grazing. The magnitude of the carbon loss upstream during the bloom is large, 45 kg C for each of 30 tidal cycles yielding a full carbon flux to the upper estuary for the study period of $1.3x10^3$ kg. This figure is 7% of the monthly mean phytoplankton biomass in Dublin Bay (Wilson and Parkes, 1998) and 6% of the estimated annual phytoplankton carbon flux out of the Liffey calculated when the linear regressions of chlorophyll with salinity were significant i.e. when blooms were not occurring. Assuming that these blooms occur only when flushing times are greater than 48 hours and a six month growth season from April to September, in the absence of washout due to high rainfall, the blooms could exist for approximately 70 days a year with a maximum potential annual export upstream of $\sim 6x10^3$ kg.y^{-1} representing an annual phytoplankton carbon flux to the sediments of 15 gC.m^{-2}. This flux is close to the spring phytoplankton carbon flux to the benthos in Chesapeake Bay (25 gC.m^{-2}), which is known for its eutrophication and summer hypoxia (Boesch *et al.*, 2001; Bratton *et al.*, 2003; Hagy *et al.*, 2005)

The open waters of the bay generally showed a distinct spring bloom cycle with a distinct peak in chlorophyll occurring in late April or early May, and a second peak in late summer, generally of smaller magnitude, though in July 2003 a late summer peak exceeded the magnitude of the spring bloom. This is most likely an artifact due to the low sampling frequency at the peak in the spring bloom, since spring bloom chlorophyll a concentrations in 2003 were the lowest of the entire study period. The chlorophyll concentrations in Dublin Bay presented in this study are lower than those previously reported for the area (ERU 1992). Mean chlorophyll concentrations in June for the years 1986-1988 were 7.2 mg.m^{-3} while mean June concentrations measured in this study were only 3.2 mg.m^{-3}, this is attributed to differing methods rather than an actual reduction in chlorophyll concentrations, in previous studies chlorophyll a and phaeopigments were not differentiated (Toner *et al.*, 2005). The maximum total phaeopigment concentrations measured (21.1 mg.m^{-3}) are similar to chlorophyll a concentrations found in other coastal mixed sites in the western Irish Sea (26.5 mg^{-3}) (Gowen & Stewart, 2005) however the high percentage of phaeopigments measured here suggests an allochtonous source for the

phytoplankton biomass. Diatoms were greatly dominant in terms of abundance throughout the summer of 2003. In contrast to other studies (Gowen *et al.*, 2000) dinoflagellates were never observed to reach more than 40% of total phytoplankton carbon, this may be due to complete vertical mixing and continuous abundance of silicate for diatom frustules. The distribution of mean summer chlorophyll a concentrations indicates that the freshwater concentrations of N may be stimulating the production of excess phytoplankton biomass in the Liffey plume since chlorophyll concentrations are highest in summer in the plume zone. This may be enhanced by a degree of vertical stratification due to the salinity of the brackish waters and the extent of this phenomenon may reach beyond the bounds of the study area.

The timing of the peak in the fluorescence signal measured at station 16 fits the typical timing of the spring bloom in Dublin Bay. Such blooms generally occur in temperate shelf seas when thermal stratification occurs and phytoplankton present in the surface layer of the water column are no longer mixed below the "critical depth" (Sverdrup, 1953). The subsequent drop in fluorescence signal is generally attributed to nutrient limitation. While Dublin Bay itself is not thermally stratified (due to the shallow water column and strong tidal currents) such waters are widespread in the western Irish Sea (Horsburgh *et al.*, 2000) and advection of Irish Sea waters is known to be of great importance in Dublin Bay (Wilson, 2005). The change in the linear relationship between tidal range and surface water temperature indicates that the onset of neap tides may have been instrumental in promoting thermal stratification offshore. The waters closest to Dublin Bay known to undergo thermal stratification are those of the gyre in the western Irish Sea (Horsburgh *et al.*, 2000). Modelled residual current from these waters are of up to 8 $cm.s^{-1}$ (Horsburgh *et al.*, 2000) meaning that a bloom could travel the 34 km from the gyre to Dublin Bay in five days.

However the phytoplankton assemblages observed in Dublin Bay on the 1st of May 2004 were composed chiefly of smaller diatoms not the larger species typically associated with spring blooms and the net growth rate calculated from the fluorescence signal (0.3 day^{-1}) is lower than that of a typical spring bloom (Odata & Imai, 2003).

At site 16 the dramatic drop in oxygen concentrations observed on the 2nd of May (Figure 5.6b) and the relationship between dissolved oxygen and saturation and fluorescence (Figure 5.7) suggest that something other that an actively growing spring bloom was occurring. The lack of water samples from the immediate vicinity during the occurrence of the peak in fluorescence signal and the oxygen minimum precludes any definitive answer as to what was their cause. However the inputs of sewage effluent from the Ringsend plant and heat from the thermal power plant could exacerbate any tendency to anoxia caused by decaying phytoplankton populations in the area. It should be noted however that spikes in the temperature signal occurred throughout the study period but only this one (coincidental with the fluorescence peak) produced a dramatic decrease in oxygen concentrations. The hypoxia observed on the 2nd of May could have deleterious consequences for macrofauna in the Liffey estuary, particularly for sedentary species. Reduction in secondary producers such as filter feeding polychaetes or molluscs can decrease an estuary's capacity to absorb any increase in primary productivity due to eutrophication (Cloern, 2001). This anoxic event may be seen as a pulse disturbance and as such would not be considered an undesirable disturbance under the U.K. scheme to be adopted (Anon, 2004) however a reduction in benthic filter feeders could increase the supply of particulates from the estuary into the bay where excess particulates are already associated with the macroalgal eutrophication problem (Jeffrey *et al.*, 1994).

The phenomenon of discolored water due to high phytoplankton concentrations is new to the north of Dublin Bay. The appearance of the bloom is reminiscent of other diatomaceous blooms resembling the "Dutchman's baccy juice" referred to by Hardy (1956) and has been the subject of some concern to recreational users of the area (Kerrigan C., Pers. Comm.) and as such may be regarded as an undesirable disturbance. There is little evidence in literature for nuisance blooms of *Odontella aurita*, which is in fact cultivated as a health food for its Omega 3 fatty acids (Burtin, 2003) though it is listed as a HAB species in China (Yan *et al.*, 2002). The shift from macroalgal to microalgal productivity coincided with the changing composition of the Ringsend sewage effluent and may be seen as a response to the increased NO_3 loading, this is illustrated by the great difference in *Odontella* concentrations found between the north and south of the bay. Though the *Odontella* cells were collected in samples from the water column, it is

likely that they are associated with the sediments of the intertidal zone and become suspended on the tide; by this mechanism these diatoms may overcome the low calculated residence times in Dublin Bay i.e. true (drifting) phytoplankton would not remain in the Bay long enough to reach such high levels of biomass. The microscopic counts often revealed large aggregates of *Odontella* cells which could result in increased sinking rates since the sinking rate of an object is related to the square of its radius (Peperzak *et al.*, 2003) and increased residence times. The shallow water depths result in high light intensities compared to other parts of the bay and the continual nutrient supply from both the river Liffey and the Ringsend sewage treatment plant result in readily available supplies of macronutrients. Since diatom growth rates generally increase linearly to a maximum with temperature (Montagnes & Franklin, 2001) the shallow (rapidly warming) waters and the warm waters from the local power station may also play a role in the bloom development.

5.3.0: Conclusions

Overall the symptoms of eutrophication apparent in Dublin Bay and the Liffey estuary are quite varied. The *Cryptomonas* blooms in the upper estuary and the *Odontella* bloom in the bathing waters of the north of the bay exceed the limit of 60 $mg.m^{-3}$ set as the lower limit of highly eutrophied waters (Bricker *et al.*, 1999). The short-lived anoxic event is also a clear indicator of excess oxygen demand, most likely caused by organic loading, though a number of factors contributed to this event. In the water column of the open bay itself there is some evidence for increased phytoplankton biomass caused by the additional nutrients in the river Liffey plume. However the rapid flushing times of the estuary and the continual supply of waters from an allochtonous source limit the symptoms of eutrophication observed in the Bay. These findings support the ecohydrodynamical typology advocated by Tett (2004), though the importance of the local pulse disturbances and the definition of usage of the estuary must still be considered carefully.

CHAPTER 6: EUTROPHICATION STATUS

6.0.1 Variability and definition of metrics

Increased anthropogenic perturbations of the natural biogeochemical cycles of nitrogen and phosphorus, and the resultant increase in the phenomena of coastal and estuarine eutrophication have led to legislative obligations pertaining to monitoring and quantification of the effects of excess nutrient loading. In Europe, the WFD (EU, 2000) emphasises the ecosystem approach to coastal and estuarine measurement and management. Judgements of the ecological status of a water body are made on the basis of biological quality elements including, phytoplankton, macroalgae, benthic invertebrate fauna and fish. Physico-chemical elements include nutrient and dissolved oxygen concentrations, temperature and transparency. For the biological quality elements high status is afforded when the parameters are consistent with undisturbed conditions. Good status is afforded when slight changes are observed and moderate status is afforded when these parameters differ moderately from undisturbed conditions. The levels specified for the physico-chemical elements are those necessary to achieve the various biological standards i.e. good status is afforded if the physico-chemical elements are such as to allow the achievement of good biological status etc. The WFD stipulates that monitoring programs have sufficient sampling frequency to provide a reliable assessment of the relevant water quality elements and the directive also requires monitoring frequencies be chosen to achieve an acceptable level of confidence and precision. The minimum suggested frequency for monitoring of phytoplankton is six months while the physico-chemical variables require a minimum monitoring frequency of three months.

The approaches to measuring eutrophication taken by different groups and organisations vary in their detail but the main measurements are generally common to all systems. Principal amongst these are measurements of N and P concentrations, since these are the elements that drive eutrophication. However the concentrations of nutrients and chlorophyll deemed to indicate eutrophic status vary between jurisdictions and studies. For instance the U.S National Ocean Service (NOS) considers N concentrations above

1mg.l^{-1} anywhere in an estuary "high" (Bricker et al., 1999, 2003) while the Irish EPA considers 2.6 mg.l^{-1} in tidal freshwaters to be indicative of enrichment (Toner et al., 2005). Increased phytoplankton biomass is often the primary response to nutrient enrichment and chlorophyll *a* concentration is also a generally accepted metric of eutrophication. In terms of phytoplankton, a suite of indicator metrics is currently being developed for application in Ireland and the U.K. Principal amongst these metrics are the measurement of chlorophyll, and phytoplankton cell numbers are also to be used as an indicator, with values over 10^5 cells.l^{-1} of any given cell type considered to be indicative of eutrophication (Devlin & Best, 2005). The chlorophyll levels deemed to represent eutrophic conditions also vary between jurisdictions. While the Irish EPA considers a median value of <15mg.m^{-3} to be indicative of eutrophication in tidal freshwaters and waters of intermediate salinity, the NOS consider values >5 mg.m^{-3} to show a medium degree of eutrophication with chlorophyll concentrations >20 mg.m^{-3} being considered highly eutrophic for estuarine environments. In the U.K values >10mg.m^{-3} are generally considered to be indicative of eutrophication (Iriate & Purdie, 2004). Assessment of the appropriate chlorophyll value indicative of eutrophication is further complicated by the range of methods available for analysis of chlorophyll. Different methods may produce very different results. For instance methods where chlorophyll is extracted using hot methanol may produce results twice those of samples extracted in acetone (O'Boyle, S., Pers. Comm). Various different systems are also used to quantify eutrophication; these may be based on the geographical extent of a particular eutrophication symptom (e.g. Bricker et al., 1999) or the frequency of occurrence of values exceeding the predetermined eutrophication limits (e.g. Toner et al., 2005) or a combination of both temporal and spatial occurrence. The differing cut-off values and analytical methods used to quantify eutrophication mean that no universally applied absolute standard for eutrophication status exists; this reflects the variability in estuarine types as well as the diverse methodologies applied. However eutrophication as defined in the European context has three main elements

1. Enrichment of waters with nutrients
2. Accelerated algal or macrophyte growth
3. Undesirable disturbance.

The response of ecosystems to the pressures of nutrient enrichment differ greatly both quantitatively and qualitatively between systems. Estuarine environments have been shown to demonstrate a range of responses to nutrient pressures (Cloern, 1999) and the responses of marine environments have also been varied. For instance the dramatic shift in magnitude, timing and composition of phytoplanktonic primary producers in the North Sea (Colijn et al., 2002) contrasts with the more equivocal evidence for eutrophication demonstrated in the Irish Sea (Gibson et al., 1997). The variation in the response of an ecosystem to nutrient loading may be attributed to two major categories of phenomena, namely the physical and biological processes. The principal physical factors that influence eutrophication are light availability (which is controlled by vertical water mixing and the attenuation of light) and horizontal advection (which controls the residence time of a particle in a given aquatic ecosystem). These physical processes are driven by topographic, hydrodynamic, climatological and weather conditions, which vary greatly from site to site. Biological processes may mediate the expression of eutrophication through grazing. The interaction of these physical and biological processes result in the unique patterns of eutrophication observed in different estuaries and coastal marine environments within Europe and around the world.

6.1.0 Eutrophication in the Liffey Estuary and Dublin Bay

6.1.1 Enrichment of waters with nutrients

A recent study (Toner, 2005) considers the Liffey estuary to be of "intermediate" trophic status since median measured nutrient and chlorophyll concentrations were in compliance with the limits set out (median values <2.6 mg $N.l^{-1}$, <60 µg $P.l^{-1}$, <15 µg. $Chla.m^{-3}$). Monthly data presented in this study however demonstrate high nutrient concentrations within the estuary. The mean N values in the upper estuary from 2000-2004 exceeded the concentrations ascribed for highly enriched waters (1 $mg.l^{-1}$) by Bricker et al. (2003) and P concentrations near the sewage treatment plant also exceeded the levels considered "high" (0.1 $mg.l^{-1}$). The monthly nutrient data indicate that the Liffey estuary is

hypernutrified with respect to N and P since both N and P were available for uptake at all times during the study period, even when phytoplankton biomass was at its highest. The calculated loads of nutrients both from the riverine and sewage sources were 2309 kg $N.km^{-2}.y^{-1}$ and 311 $kg.P.km^{-2}.y^{-1}$, exceeding the moderately eutrophied category of Hessen (1999) and with higher catchment normalised values than U.K equivalents. The Liffey estuary's short length and shallow depths mean that the nutrient loads are large in terms of relative volume compared to many other estuaries with deeper depths and larger surface areas e.g. the Tay (Dobson, 2005). However the nutrient data indicate no major sinks of nutrients within the estuary which suggests minimal excess production of phytoplankton.

6.1.2 Accelerated microalgal growth

Monthly measured chlorophyll data were generally in the "low" ($\leq$5 $mg.m^{-3}$) to "medium" (5 $mg.m^{-3}$-$\leq$20 $mg.m^{-3}$) range of Bricker (1999) yet sporadically "high" (20 $mg.m^{-3}$-$\leq$60 $mg.m^{-3}$) and "hypereutropic" (< 60 $mg.m^{-3}$) values suggested that the high nutrient loads were stimulating some accelerated growth of the phytoplankton. The sporadically high chlorophyll concentrations indicated that the monthly sampling frequency may not have been adequately capturing some of the eutrophication phenomena occurring. The deployment of the YSI 6600 sondes and the resulting higher frequency data confirmed that high concentrations of chlorophyll can persist in the upper estuary for more than two weeks. The two-week *Crytpomonas* bloom (May 2004) with maximum chlorophyll concentrations (measured by fluorescence) of 193 $mg.m^{-3}$ exceeded the chlorophyll concentration limits set out by Bricker et al. (1999) for "hypereutrophication". This bloom also acted as a considerable source of organic matter to the upper estuary. These blooms have now been detected in both 2003 and 2004 and are likely to continue to occur in the upper estuary due to the abundant supply of nutrients and the strong vertical stratification. The supply of allochtonous organic matter to the upper estuary from these blooms is likely to have consequences for oxygen availability in the area and is comparable to the carbon supply produced during spring bloom conditions in eutrophic systems (Hagy et al., 2005). The Liffey sediments are known to suffer from

anoxia and are thought to be abiotic in terms of infauna (Wilson et al., 1986). As a result they have little capacity for passing additional organic matter further up the food chain. Since in summer the river flow (driven by rainfall) appears to control the duration of these blooms and summer rainfall is predicted to diminish with climate change (Sweeney & Feale, 2002), these blooms may become a more serious contributor to carbon deposition in the upper estuary in the future. The *Cryptomonas* blooms may be seen as a sustained, "press" disturbance, sporadically interrupted by rainfall events. Such phenomena are of greater significance to environmental health than episodic "pulse" disturbances (Tett, 2004). Reduction in the agricultural nutrient loading of the river may help reduce the intensity of this phenomenon.

In the seasonally nutrient-limited waters of north Dublin Bay monthly water column sampling of offshore sites showed little sign of eutrophic effects, though it appears that there may be some stimulation of phytoplankton growth in the extreme north east of the study area. The bathing waters of north Dublin Bay have shown prolonged and spatially extensive blooms of the diatom *Odontella aurita* with cell concentrations reaching $7.5x10^6$ cells.l^{-1} and total phaeopigment concentrations of up to 120.2 mg.m^{-3}. These blooms have only been observed since the upgrading of the Ringsend sewage treatment plant, though they may have been occurring prior to this since sampling for chlorophyll and phytoplankton was not previously conducted in the bathing waters of north Dublin Bay. However the visible discolouration of the water column coincided with the treatment plant upgrade and an increase in oxidised N forms arriving on the shores of north Dublin Bay. The high cell concentrations involved in this bloom exceed the 10^5 cell.l^{-1} concentrations considered to indicate eutrophication (Devlin & Best, 2005) and have been sufficient to cause a visible brown discolouration of the bathing waters reducing the amenity value of the beach to recreational users.

6.1.3 Undesirable disturbances

The river Liffey has been a modified environment for over 1000 years and for much of this time its principal functions have been as a trade route and as a sewer. Its walled nature and long history of human usage means that undesirable disturbance should not be judged against natural, unperturbed conditions (since reference conditions are not known); rather a functional judgement approach is required. While the estuary still contains a busy trading port, the functioning of this industry is little affected by the trophic status of an estuary. In recent years the amenity value of the estuary has been realised and there has been an increasing drive towards the use of the Liffey as an aesthetic resource, particularly in terms of tourism. The recent construction of the Liffey boardwalks, which flank the river on its northern side, and the coming addition of a Liffey water taxi are testament to this shift in the Liffey estuary's urban role. Similarly the principal social functions of Dublin Bay are now recreational. In this context undesirable disturbances may be viewed as anything that diminishes the aesthetic quality of the Liffey estuary or Dublin Bay.

One of the major aesthetic concerns relating to the Liffey estuary ecosystem is the smell of its anoxic sediments, caused by over supply of organic matter to the bottom layer of the stratified part of the estuary. This smell is already of such concern to Dublin citizens that it has even been immortalized in song

> *"I remember that summer in Dublin, and the Liffey as it stank like hell"*
>
> Bagatelle- 1980

The *Cryptomonas* blooms in the Liffey estuary (stimulated by the availability of excess nutrients) act as a considerable source of organic matter to the sediments of the upper estuary and as such they may be seen a contributor to the anoxia in the sediment of this area. In this phenomenon the three elements of eutrophication, nutrient enrichment, accelerated growth and undesirable disturbance are discernible and as such the phenomenon may be classified as eutrophication according to the WFD (EU, 2000).

The bloom of *O. aurita* in the bathing waters of north Dublin also indicates a response to the supply of oxidised N due to the upgrading of the sewage treatment plant. Here again we see enrichment, accelerated algal growth and an undesirable disturbance with respect to the aesthetic quality of bathing waters.

In the lower estuary, near the Ringsend sewage treatment plant, rapid tidal flushing, high diffuse attenuation coefficients, deep water depths and strong vertical mixing limit the extent of microalgal growth. However the high frequency data indicate that pressures caused by organic loading from the Ringsend sewage treatment plant and thermal loading from the Poolbeg power station may combine with natural organic loads to produce sporadic anoxic events. This indicates an environment which is sensitive to anthropogenic disturbance. The frequency of occurrence of such events is not known but such conditions are likely to be detrimental to those fauna existing in the area and represent a further anthropogenic pressure on the system. The river Liffey is a salmonid river and low oxygen conditions could have serious consequences for migrating salmonid fish. The oxygen depletion observed in this study appears to be the result of direct anthropogenic organic loading rather than enrichment with nutrients, however the ecosystems approach demands that such loading be taken in the context of an already nutrient stressed environment.

6.2.0 Management

The European Environment agency advocates the Driving forces, Pressures, State, Impact, Reponse (DPSIR) approach to ecosystem management (Figure 6.1) (EEA, 1999). This model may be seen as a cycle where the changing driving forces exert changing pressures on an ecosystem resulting in altered states and impacts on that ecosystem and requiring management responses. In the Liffey estuary and Dublin Bay ecosystem the principal driving forces are the increasing domestic population in the Liffey catchment, agricultural production and increasing industrial activity. These driving forces exert the pressures of nutrient and organic matter enrichment on the system. These pressures have resulted in

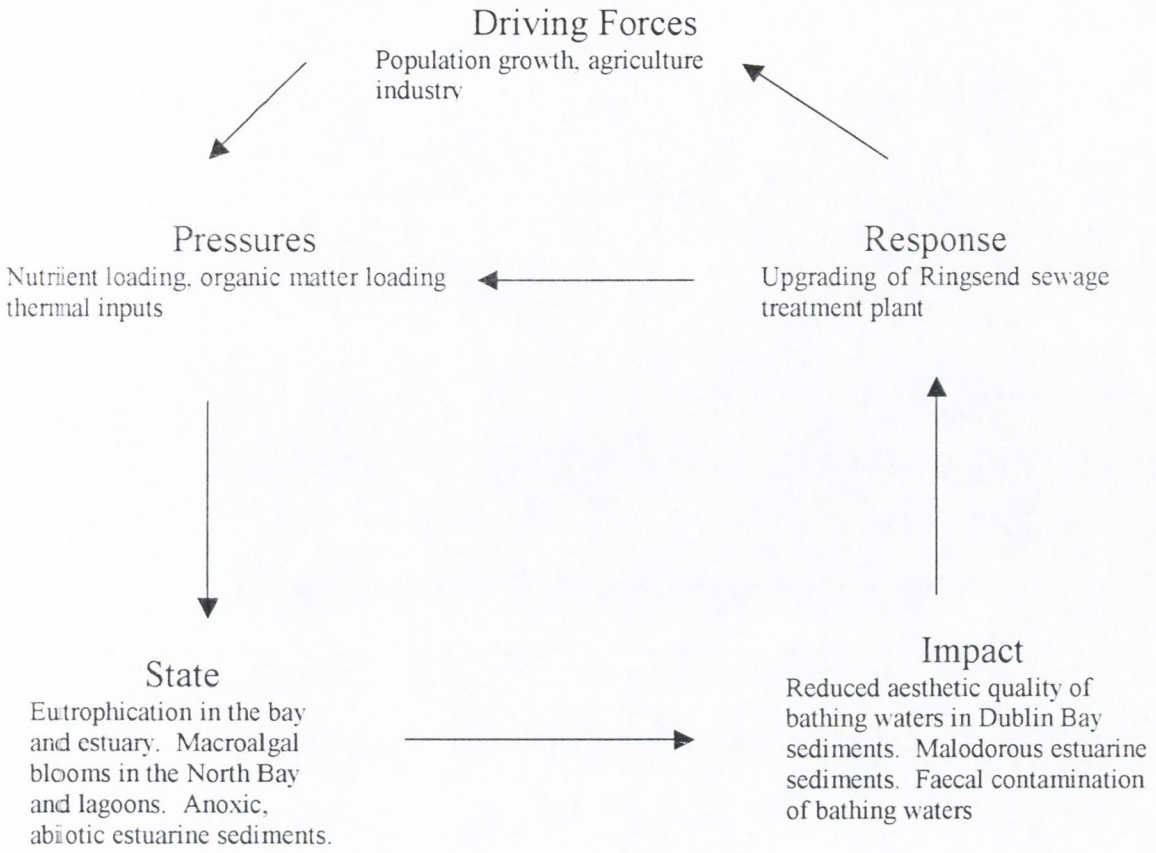


Figure 6.1: Schematic representation of the DPSIR approach to the Liffey estuary and Dublin Bay. The State and Impact are those prior to the upgrade of the Ringsend sewage treatment plant.

an ecosystem which has shown signs of eutrophication for almost 100 years (Adeney, 1908) and had been substantially altered from healthy conditions prior to the upgrading of the Ringsend sewage treatment plant. Indicators of the altered state included anoxic and abiotic estuarine sediments (Wilson et al., 1986); excessive growth of green and brown algae (Jeffrey et al., 1993, 1995, Brennan et al., 1994) and heavy metal pollution (Jones & Jordan, 1979; Wilson et al., 1986). The response to the eutrophication problem has been the upgrading of the sewage treatment plant. This has altered the pressures on the ecosystem by increasing the inputs of TON. The coincidence of a persistent, visible bloom of *O. aurita* on the northern shores of Dublin Bay with the changing nutrient pressure suggests that this may be the response of the system to this new pressure. This phenomenon requires further research as to its extent and controlling mechanisms. Any

new impact will require a new management response. Mitigation of enhanced microalgal growth will require significant reductions in the inputs of the limiting nutrient N to these bathing waters. Under the Urban Wastewater Treatment Directive (EU, 1991a), N effluents which are larger than 100,000 population equivalent, and discharging to designated waters must be reduced by 70-80%. Phosphorus discharges must also be reduced by 80% and these objectives must be fulfilled by June 2008. A reduction in the N flux to the area requires tertiary denitrification treatment of the sewage effluent and is likely to be effective in reducing the symptoms of eutrophication in the Bay.

6.3.0 Conclusions

Overall the data presented here indicate a range of ecosystem dysfunctions present in the study area. The continuous oversupply of nutrients to the system has resulted in a number of eutrophication phenomena. In the upper Liffey estuary, persistently abundant nutrient supply and the highly stratified column favour the formation of phytoplankton blooms. These blooms represent a significant carbon source to the upper stratified tidal reaches of the estuary probably contributing to the already existing anoxic conditions in the sediments there. As such they may be considered undesirable disturbance. Simple mathematical modelling has illustrated the importance of physical factors, tides and flow in determining the timing of the occurrence of bloom formation. While the simplified flushing models illustrate the variability in residence times, the actual processes at work are far more complex. In order to develop a truly predictive model of phytoplankton bloom development a multi-layered vertical model is required and the possibility of laterally differing horizontal flows must also be accounted for. Such a model would require much more detailed physical data regarding current speeds and water column structure and such needs might be met using profiling CTD or ADCP instruments.

In the lower estuary and in Dublin Bay the symptoms of eutrophication are more limited. With the exception of the anoxic incident which appears to have occurred as a result of a combination of natural and anthropogenic factors these areas show limited signs of eutrophication. This is principally as a result of the short residence times and rapid

dilution with the truly saline waters of the Irish Sea. The persistent phytoplankton bloom in the bathing waters of North Dublin Bay appears to be partly associated with microphytobenthic diatoms with their ability to adhere to the sediments increasing their residence time sufficiently to produce the observed discolouration of the waters.

The complex interactions between the physical, biological and chemical processes in aquatic environments, combined with stochastically driven weather processes can lead to highly changeable conditions on timescales from hours to months. This complexity results in problems of determining sampling frequencies adequate to uncover phenomena on the relevant timescales. Meaningful assessment of the trophic status and eutrophic response of a given ecosystem relies on the collection of representative data from the study area which may be difficult when events occur on such short timescales. Since physical processes govern the distribution of the relevant parameters at a given time, an understanding of these processes is essential to the interpretation of data collected. This study illustrates the complexity of events occurring in the estuarine environment on timescales much shorter than those of traditional spot sampling. Both the *Cryptomonas* blooms and the anoxic event in the Liffey estuary are of considerable concern to the environmental manager and both were elucidated through the collection of high frequency data. Under the WFD the specified minimum temporal frequency for the collection of phytoplankton data is six months. This study illustrates that a 1 month interval is barely sufficient to reveal important estuarine processes and it seems clear that data collected on a six monthly interval can yield little useful information in the context of such highly variable aquatic environments. Indeed given the complexity of estuarine systems a measurement interval of six hours might still be sufficient to explain the many processes at work.

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Appendix I

	Latitude			Longitude			Eastings	Northings
	o	'	''	o	'	''		
1	53	20	53	-06	15	17	316273.64	234487.41
2	53	20	53	-06	15	11	316384.51	234476.33
3	53	20	51	-06	14	48	316632.07	234423.93
4	53	20	46	-06	14	13	317461.5	234294.03
5	53	20	42	-06	13	42	317995.29	234175.48
6	53	20	44	-06	13	31	318249.69	234261.6
7	53	20	50	-06	12	56	318891.38	234448.34
8	53	20	43	-06	12	32	319330.54	234251.48
9	53	20	32	-06	11	32	320458.04	233934.71
10	53	20	36	-06	11	09	320884.63	234062.46
11	53	20	31	-06	10	53	321182.54	233921.57
12	53	20	30	-06	10	32	321572.95	233899.98
13	53	20	31	-06	09	46	322418.86	233960.65
14	53	20	34	-06	09	00	323263.07	234086.39
15	53	20	41	-06	10	03	322095.68	234262.28
16	53	20	44	-06	10	32	321555.01	234341.22
17	53	20	44	-06	10	56	321109.07	234320.57
18	53	20	40	-06	07	59	324398.49	234279.27
19	53	20	48	-06	08	42	323587.35	234515.36
20	53	21	00	-06	08	12	324132.34	234901.48
21	53	21	18	-06	08	01	324328.86	235463.4
22	53	21	36	-06	07	54	324436.8	236023
23	53	21	18	-06	06	36	325893.43	235504.57
24	53	21	00	-06	06	48	325686.44	234942.31
25	53	20	40	-06	06	25	326126.65	234322.57
26	53	21	03	-06	05	55	326656.14	235059.35
27	53	20	58	-06	04	35	328148.63	234937.88
28	53	21	18	-06	03	30	329335.72	235586.96
29	53	20	24	-06	04	39	328097.6	233888.61
30	53	20	20	-06	05	48	326828.62	233738.79
31	53	20	23	-06	06	55	325584.05	233798.19
32	53	20	01	-06	07	02	325470.24	233110.34
33	53	19	58	-06	06	02	326594.77	233034.34
34	53	20	00	-06	05	27	327235.86	233140.53
35	53	19	35	-06	07	18	325208.37	232296.11
36	53	18	29	-06	06	25	326244	230300.11
37	53	18	16	-06	08	12	324266.65	229832.74
38	53	18	39	-06	09	05	323264.08	230530.49
39	53	19	26	-06	08	59	323344.34	231962.36
40	53	19	60	-06	08	13	324161.54	233042.6
41	53	20	12	-06	09	42	322505.87	233378.28

Appendix I: Station numbers and coordinates both as latitude and longitude and as Irish National Grid.

Appendix II

Date	Total Oxidised Nitrogen					Orthophosphate				
	n	m	c	r^2		n	m	c	r^2	
17/08/2000	15	-87.54	2899.95	0.871	**	11	-5.646	208.28	0.927	**
05/10/2000	16	-46.14	1637.10	0.862	**	12	-2.264	106.73	0.816	**
30/11/2000	17	-56.35	1984.80	0.911	**	9	-0.265	48.463	0.962	**
13/12/2000	15	-45.54	1768.00	0.957	**	11	-1.295	65.906	0.919	**
11/01/2001	7	-49.02	2035.60	0.736	*	8	0.4833	36.795	0.842	**
14/02/2001	17	-45.81	1682.00	0.885	**	10	-0.483	50.126	0.322	**
22/03/2001	13	-68.68	2512.40	0.917	**	13	-0.113	79.348	0.002	
10/04/2001	9	-94.19	3304.10	0.971	**	7	-1.857	89.237	0.911	**
02/05/2001	17	-52.64	1762.30	0.970	**	9	-0.742	54.47	0.912	**
20/06/2001	15	-56.16	1904.60	0.844	**	11	-8.013	295.76	0.543	**
11/07/2001	17	-14.31	488.91	0.855	**	9	-0.936	39.724	0.970	**
29/08/2001	14	-35.64	1220.90	0.882	**	8	-2.569	107.46	0.991	**
05/09/2001	12	-37.34	1307.40	0.891	**	8	-3.497	141.63	0.984	**
21/11/2001	15	-35.21	1314.10	0.966	**	7	-0.255	41.367	0.744	*
06/12/2001	15	-43.21	1686.00	0.771	**	6	-1.093	62.607	0.994	**
16/01/2002	15	-66.19	2363.20	0.991	**	8	-1.7	88.243	0.992	**
29/01/2002	15	-87.13	3073.60	0.975	**	11	-1.39	71.35	0.890	**
14/02/2002	14	-83.56	2979.60	0.963	**	8	-0.752	54.659	0.955	**
21/03/2002	15	-79.32	2761.20	0.996	**	14	-1.484	70.107	0.937	**
24/04/2002	15	-57.64	2068.00	0.912	**	7	-1.588	84.886	0.967	**
29/05/2000	15	-29.57	1045.30	0.862	**	8	-1.254	63.991	0.936	**
12/06/2002	17	-41.36	1501.40	0.938	**	12	-1.328	75.365	0.986	**
03/07/2002	15	-50.39	1713.90	0.906	**	12	-1.984	93.36	0.875	**
14/08/2002	15	-58.88	1950.40	0.989	**	-	-	-	-	
11/09/2002	14	-55.70	1832.10	0.754	**	8	-2.047	98.73	0.897	**
09/10/2002	17	-47.86	1645.20	0.810	**	12	-2.17	96.983	0.902	**
07/11/2002	15	-37.69	1457.30	0.895	**	6	-0.936	72.457	0.908	**
18/12/2002	14	-44.01	1645.90	0.963	**	15	0.0285	86.962	0.000	
09/01/2003	15	-60.70	2319.10	0.983	**	6	2.4606	47.521	0.829	**
17/02/2003	11	-72.50	2626.70	0.995	**	7	-1.149	91.05	0.879	**
03/03/2003	15	-48.50	1890.90	0.871	**	6	-0.181	72.256	0.252	-
16/04/2003	15	-76.47	2600.80	0.859	**	5	-0.634	63.734	0.710	-
01/05/2003	15	-55.95	1989.30	0.499	**	8	0.403	16.989	0.027	-
05/06/2003	14	-47.68	1752.40	0.866	**	7	-3.438	124.34	0.753	**
23/07/2003	15	-49.35	1788.10	0.904	**	6	-1.729	94.422	0.938	**
21/08/2003	15	-51.53	1769.50	0.899	**	6	0.3185	47.558	0.029	-
04/09/2003	17	-49.59	1791.60	0.931	**	6	-1.616	97.926	0.650	*
16/10/2003	15	-87.42	3067.20	0.981	**	6	-3.137	136.19	0.934	**
19/11/2003	15	-42.34	1606.90	0.837	**	6	-0.102	41.154	0.204	-
10/12/2003	15	-64.80	2375.40	0.964	**	6	-0.434	50.081	0.909	**
21/01/2004	15	-66.79	2597.70	0.936	**	6	-0.395	65.209	0.510	-
18/02/2004	15	-60.76	2334.60	0.954	**	6	-0.418	74.762	0.279	-
11/03/2004	8	-81.06	2999.30	0.892	**	8	-0.906	74.226	0.902	**
01/04/2004	15	-69.17	2688.10	0.956	**	6	-0.109	70.337	0.0310	-
27/05/2004	16	-33.26	1505.60	0.357	*	7	-1.58	71.73	0.688	*
10/06/2004	-	-	-	-		8	-2.135	99.326	0.977	**

Appendix II: Results of estuary TON and PO_4 mixing curves. n, number of samples. m, slope of mixing curve, c, constant ($\mu g.l^{-1}$), r^2 , * indicates $p<0.05$, ** indicates $p<0.001$

Date	Ammonia n	m	c	r^2	
17/08/2000	8	-3.1389	163.33	0.648	*
05/10/2000	8	1.2373	31.55	0.430	-
02/11/2000	8	-6.0061	173.97	0.024	-
30/11/2000	8	2.356	89.299	0.386	-
13/12/2000	6	0.8193	85.134	0.660	*
14/02/2001	8	0.1526	46.032	0.006	-
22/03/2001	6	6.0296	77.144	0.699	*
02/05/2001	8	3.3899	13.643	0.939	**
20/06/2001	6	0.3357	148.72	0.000	-
11/07/2001	8	-2.314	138.76	0.392	-
29/08/2001	6	4.1415	23.96	0.862	**
05/09/2001	8	1.8763	68.138	0.611	*
21/11/2001	6	1.2446	62.575	0.315	-
06/12/2001	6	-0.7361	95.097	0.236	-
16/01/2002	6	-2.5973	161.22	0.615	-
29/01/2002	6	-0.0789	47.553	0.009	-
14/02/2002	6	0.9868	47.212	0.586	-
21/03/2002	6	0.9162	47.004	0.351	-
24/04/2002	6	1.6805	11.542	0.790	*
29/05/2002	6	-4.5049	209.77	0.683	*
12/06/2002	8	-1.0184	107.7	0.158	-
03/07/2002	6	-1.019	140.02	0.125	-
14/08/2002	8	-0.6951	120.49	0.020	-
11/09/2002	6	-3.83	184.44	0.561	-
09/10/2002	8	0.9761	104.41	0.440	-
07/11/2002	6	1.5095	39.877	0.932	**
18/12/2002	6	-1.2638	114.53	0.250	-
09/01/2003	6	5.2528	89.311	0.455	-
17/02/2003	3	-0.0137	92.591	0.001	-
13/03/2003	6	0.7751	70.68	0.069	-
16/04/2003	6	1.1248	103.16	0.277	-
01/05/2003	4	5.2833	112.62	0.892	-
05/06/2003	6	0.5655	74.772	0.061	-
23/07/2003	6	0.0547	54.709	0.010	-
21/08/2003	6	0.0246	51.314	0.001	-
04/09/2003	6	-2.6299	170.16	0.221	-
16/10/2003	6	2.3753	70.418	0.841	**
19/11/2003	6	0.0816	51.069	0.254	-
10/12/2003	6	1.5517	66.032	0.981	**
21/01/2004	6	0.4347	36.819	0.576	-
18/02/2004	6	2.8234	29.8	0.918	**
11/03/2004	-	-	-	-	-
01/04/2004	6	5.011	21.382	0.887	-
27/05/2004	6	0.1234	24.133	0.005	-
10/06/2004	-	-	-	-	-

Appendix II: Results of estuary ammonia mixing curves. n, number of samples. m, slope of mixing curve, c, constant ($\mu g.l^{-1}$), r^2 , * indicates $p<0.05$, ** indicates $p<0.001$

Date	Total Oxidised Nitrogen					Orthophosphate				
	n	m	c	r^2		n	m	c	r^2	
28-Jun-00	20	-20.342	701.87	0.491	**	20	-73.27	2515	0.849	**
27-Jul-00	-	-	-	-	-	-	-	-	-	-
24-Aug-00	7	-55.035	1862	0.890	**	-	-	-	-	-
28-Sep-00	-	-	-	-	-	21	-13.333	468.67	0.181	*
23-Nov-00	24	-50.632	1828.7	0.996	**	24	-4.7849	184.98	0.975	**
18-Jan-01	24	-95.247	3472.9	0.941	**	24	-3.4054	140.63	0.652	**
8-Feb-01	23	-67.951	2522.2	0.984	**	24	-2.8048	122.74	0.403	**
21-Feb-01	24	-35.087	1375.2	0.592	**	24	-4.8587	187.13	0.059	-
14-Mar-01	24	-65.318	2398.1	0.371	**	24	-19.372	685.36	0.737	**
19-Apr-01	24	-60.053	2199.7	0.863	**	24	-13.866	493.99	0.730	**
26-Apr-01	24	-54.57	1860.5	0.344	**	24	-13.556	463.06	0.394	**
23-May-01	4	2.1053	-56	0.011	-	24	0.1953	-3.5772	0.001	-
6-Jun-01	-	-	-	-	-	24	1.1215	33.14	0.028	-
25-Jul-01	3	-25	856	0.250	-	14	-21.949	757.45	0.757	**
2-Aug-01	-	-	-	-	-	5	-47.5	1627	0.586	-
11-Oct-01	23	-44.728	1584.5	0.793	**	23	-22.788	794.93	0.587	**
14-Nov-01	24	-50.65	1843.2	0.838	**	24	-8.8422	325.27	0.720	**
11-Dec-01	23	-54.679	1986.8	0.989	**	23	-8.7444	320.16	0.792	**
21-Feb-02	22	-56.736	2084.9	0.905	**	23	-3.9633	159.58	0.410	**
5-Mar-02	19	-58.876	2174.4	0.882	**	19	-5.4011	201.61	0.659	**
11-Apr-02	23	-38.903	1447.3	0.663	**	23	-3.8963	158.02	0.081	-
15-May-02	-	-	-	-	-	-	-	-	-	-
20-Jun-02	19	-32.309	1113.6	0.889	**	18	-8.0507	281.74	0.664	**
18-Jul-02	10	-43.683	1484.5	0.950	**	22	-17.815	614.28	0.860	**
22-Aug-02	13	-0.8621	41.914	0.000	*	22	18.571	637.85	0.197	*
25-Sep-02	23	-29.053	1001.2	0.483	**	23	3.1498	82.062	0.007	-
13-Nov-02	23	-79.279	2734.8	0.981	**	23	-4.9714	199.55	0.589	**
5-Dec-02	24	-48.672	1805.9	0.544	**	24	-2.6553	109.23	0.028	-
23-Jan-03	23	-66.707	2428.9	0.902	**	23	-5.0609	203.32	0.223	*
6-Mar-03	24	-42.4	1595.3	0.467	**	24	-0.4	36.987	0.000	-
9-Apr-03	21	-64.554	2242.3	0.790	**	20	-23.085	793.47	0.787	**
8-May-03	12	-54.598	1879.5	0.729	**	18	-11.727	406.2	0.795	**
25-Jun-03	5	-80	2743.7	0.494	-	-	-	-	-	-
03/07/2003	12	-25.488	870.33	0.608	**	23	-13.919	477.91	0.664	**
12/11/2003	24	-107.9	3760.4	0.926	**	24	-33.398	1155	0.819	**
04/12/2003	18	-61.965	2230.4	0.645	**	18	-7.1725	281.19	0.807	**
28/01/2004	9	-78.721	2865.2	0.936	**	9	-2.9	128.89	0.140	-
12/02/2004	23	-85.471	3075.6	0.935	**	23	-10.733	381.48	0.772	**
12/05/2004	13	-37.289	178.86	0.480	**	12	-51.753	1746.2	0.907	**
30/06/2004	15	-83.22	2851.1	0.590	**	6	-4.7368	170.98	0.029	-

Appendix II: Results of Dublin Bay TON and PO_4 mixing curves. n, number of samples. m, slope of mixing curve, c, constant ($\mu g.l^{-1}$), r^2 . * indicates $p<0.05$, ** indicates $p<0.001$

	Ammonia				
Date	n	m	c	r^2	
27/07/2000	20	-103.36	3553.4	0.239	*
24/08/2000	10	-30.7	1050.8	0.679	**
28/09/2000	17	-136.67	4674.3	0.521	**
26/10/2000	8	-2.6026	47.5	0.148	-
23/11/2000	24	-30.414	1048.3	0.932	**
18/01/2000	24	-31.063	1103.1	0.829	**
14/03/2001	24	-87.825	3009.8	0.589	**
19/04/2002	23	-61.813	2124.4	0.774	**
26/04/2001	9	-17.879	626.31	0.053	-
25/07/2001	11	-98.673	3391.1	0.825	**
02/08/2001	6	-218	7452	0.886	**
11/10/2001	23	-92.687	3190.8	0.508	**
14/11/2001	24	-42.525	1486.3	0.867	**
11/12/2001	9	-41.43	1445.4	0.810	**
21/02/2002	23	-21.769	777.89	0.394	**
05/03/2002	19	-35.89	1246	0.715	**
20/06/2002	12	-34.244	1199.1	0.618	**
18/07/2002	21	-99.254	3380.2	0.964	**
22/08/2002	23	-80.714	2754.1	0.224	*
25/09/2002	23	-133.08	4537.6	0.796	**
13/11/2002	23	-27.329	953.17	0.780	**
23/01/2003	19	-23.471	809.58	0.588	**
09/04/2003	19	-75.536	2585.1	0.782	**
08/05/2003	13	-24.098	838.19	0.586	**
25/06/2003	4	-96.667	3316	0.289	-
03/07/2003	-	-	-	-	-
07/08/2003	11	-10.859	384.12	0.788	**
24/09/2003	13	-35.068	1208.3	0.951	**
12/11/2003	10	-100.02	3431	0.791	**
04/12/2003	18	-46.526	1606.6	0.851	**
28/01/2004	9	-9.3023	348.02	0.138	-
12/02/2004	20	-27.111	933.76	0.756	**
12/05/2004	7	-97.363	3282.1	0.825	**
30/06/2004	14	-33.349	1149.9	0.152	-

Appendix II: Results of Dublin Bay ammonia mixing curves. n, number of samples. m, slope of mixing curve, c, constant ($\mu g.l^{-1}$), r^2 , * indicates $p<0.05$, ** indicates $p<0.001$

Appendix III

Station 36	08/05/2003
Diatoms	Cells l^{-1}
Leptocylindrus danicus	15700
Eucampia zoodiacus	200
Chaetoceros densum	200
Rhizosolenia stoltherfotii	300
Proboscia alata	800
Thalassionema nitzchoides	600
Nitzschia delicatissima	400
Lauderia borealis	300
Guinnardia flaccida	200
Centric 20um	400
Dinoflagealltes	
Protoperidinium islandicum	100
Gymnodinium variabile	100
Prorocentrum minimum	400
Gyrodinium glaucum	500
Gyrodinium aureolum	100

Appendix III: Phytoplankton counts from station 36 in Dublin Bay

Station 36	25/06/2003
Diatoms	Cells.l^{-1}
Rhiosolenia stolterfotii	12000
Proboscia alata	1700
Stauroneis membranacea	700
Pseudo-nitzchia delicatissima	2200
Leptocylindrus minimus	2700
Centric 60x20	100
Navicula 80x12	300
Fragilariopsis sp. 25x10	100
Odontella sinensis	100
Dinoflagealltes	
Glenodinium danicum	100
Protoperidinium brevipes	100
Gymnodinium simplex	200
Prorocentrum dentatum	100
Ceratium furca	400
Prorocentrum micans	500
Gyrodinium aureolum	100
Gymnodinium variabile	300
Protoperidinium pellucidum	300
Protoperidinium oblongum	100
Dinophysis acuta	100
Cryptomonas sp.	100

Appendix III: Phytoplankton counts from station 36 in Dublin Bay

Station 36	03/07/2003
Diatoms	Cells.l^{-1}
Odontella alterans	80
Odontella regia	40
Odontella sinensis	40
Melosira numuloides	80
Melsoira moniliformis	80
Paralia sulcata	3440
Pseudonitzchia seriata	160
Proboscia alata	40
Stauroneis membrancea	40
Thalassionema nitzschoides	520
Unkonwn 30µm	40
Centric 25x10µm	80
Centric 30x10µm	360
Centric 50x10µm	40
Centric 60x20µm	40
Centric 60x30µm	200
Centric 80x10µm	40
Centric 90x20µm	80
Navicula 20x6µm	200
Navicula 78x18µm	40
Pennate 120x8µm	40
Dinoflagellates	
Prorocentrum aporum	40
Gyrodinium pepo	80
Scripsiella sp.	80
Ceratium furca	40

Appendix III: Phytoplankton counts from station 36 in Dublin Bay

Station 36	07/08/2003
Diatoms	Cells.l^{-1}
Rhiosolenia stolterfotii	200
Proboscia alata	100
Stauroneis membranacea	100
Pseudo-nitzschia seriata	35200
Leptocylindrus danicus	44700
Chaetoceros densum	500
Cylindrotheca closterimn	2400
Rhizosolenia setigera	200
Centric 40µm	300
Centric 90µm	100
Dinoflagealltes	
Protoperidinium brevipes	100
Scripsiella sp.	100
Prorocentrum micans	400
Ceratium fusus	200
Ceratium minutum	100
Gyrodinium lachryma	100
Gyrodinium conicum	100

Appendix III: Phytoplankton counts from station 36 in Dublin Bay