Pilot Water Quality Monitoring Station in Dublin Bay North Bank Monitoring Station (NBMS) MATSIS Project Part 1

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Pilot Water Quality Monitoring Station in Dublin Bay

North Bank Monitoring Station (NBMS)

MATSIS Project Report Part 1

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Executive Summary

The lack of short-term temporal resolution associated with traditional spot sampling for monitoring water quality of dynamic coastal and estuarine waters has meant that many organisations are interested in autonomous monitoring technologies to provide near real-time semi-continuous data. Such approaches enable capturing short term episodic events (which may be missed or alternatively skew datasets when using spot samples) and provide early warning of water quality problems. New policy drivers such as the Water Framework Directive (WFD) provide added impetus to develop this field. Therefore, as part of the Interreg IIIa funded MATSIS project the Marine Institute undertook to develop and pilot an autonomous monitoring station in Dublin Bay (North Bank Monitoring Station NBMS). This report presents the outcome of this pilot study.

The site chosen for the monitoring station was the North Bank lighthouse within the confines of the East and Bull walls. This provided a practical working platform and was a good test site with appreciable freshwater influence of the rivers Liffey, Tolka and Dodder. A number of commercially available sensors were selected and deployed for testing. This included a novel optical sensor for measuring nitrate (Satlantic ISUS) as well as more established sensors for measurement of salinity, temperature, fluorescence and dissolved oxygen. The sensors were integrated and data transmitted in near real-time via a Black Box™ (Techworks Marine) to a base station where it could be graphically displayed on a webpage. Automated water samplers were also incorporated to collect nutrient and phytoplankton samples. The pilot system enabled automated periodic, remote triggered and event triggered sampling (e.g. by elevated chlorophyll as measured by fluorescence sensor).

Validation of the sensors was carried out by cross comparison with other sensors and for the nitrate sensor by comparing data over a number of deployments with laboratory analysis of spot samples. Although this indicated some analytical limitations, including a small bias, the value of high frequency measurements at this variable site to detect trends outweigh the analytical limitations of the instrument, once quality control procedures are in place so that these limitations are established.

An initial consideration of water quality at the site was made using data from four separate deployments: October–November 2005, April-May and July–September 2006 and March–July 2007. Data showed a tidally dynamic site with nutrient concentrations varying by as much as an order of magnitude over a tidal cycle and nitrate generally <10μmol l^{-1} at high tide. The highest nitrate concentration of 58.9μmol l^{-1} was recorded on 9th September 2006 close to low tide, although 4 hours later with the incoming tide the nitrate concentration recorded was <3μmol l^{-1} Chlorophyll levels were generally low although there was some evidence of short lived blooms. Phytoplankton species recorded, albeit from very few samples, were typical of coastal and estuarine waters.

This pilot project demonstrated the advantages of autonomous systems as cost-efficient water quality monitoring tools to complement traditional monitoring techniques, although they do require substantial operational support. The advantages of these techniques are that they provide near real-time data and avoid under-sampling and potentially misrepresenting water quality, with potentially substantial consequential costs. As reliable sensors are only commercially available for a limited number of parameters, integration of smart automated water samplers provided a useful tool for collecting data on additional parameters, such as nutrients and phytoplankton, and also collecting samples for laboratory analysis to validate sensor performance. Such monitoring systems require validation and ongoing quality control to ensure data is of known accuracy and precision and is "fit-for-purpose". Autonomous water quality monitoring systems should be considered for wider application in selected coastal and transitional waters, for example in the context of Water Framework Directive monitoring, and it is further recommended that the NBMS station is maintained as a key test site in any such network.

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1. Background and objectives

1.1 MATSIS Project

The MATSIS project (Methods of Assessment of the Trophic Status of the Irish Sea) was an Irish Wales Interreg IIIa funded collaboration between University of Wales Bangor, the Marine Institute and the Irish Environmental Protection Agency (EPA). The project consists of two parallel work packages. Firstly seasonal interdisciplinary surveys were carried to study particular areas of the Irish Sea. This project relates to the second part in which the Marine Institute undertook to develop and pilot an autonomous water quality monitoring station in Dublin Bay.

1.2 Autonomous water quality monitoring station – Background and objectives

The requirement for coastal and transitional *in situ* water quality monitoring systems that collect high frequency data is self-evident, given that such water bodies are often highly dynamic and that it is difficult to capture episodic events such as phytoplankton blooms using conventional spot sampling. An important element of the MATSIS project was the establishment of a pilot autonomous monitoring station in Dublin Bay. While the SmartBuoy network exists in the UK (http://www.cefas.co.uk/products-and-services/environmental-monitoring-equipment/smartbuoy.aspx), including the site in Liverpool Bay, there has been no counterpart in Irish waters with the exception of the Northern Ireland Department of Agriculture and Rural Development's mooring in the north western Irish Sea. As part of the MATSIS project the Marine Institute, in collaboration with the EPA, undertook to set-up and pilot an integrated cost-effective water quality monitoring station in Dublin Bay using off-the-shelf equipment. A key objective was to gain experience in using such systems for water quality monitoring in Ireland.

The proposed system was to include a water quality probe collecting continuous salinity, temperature, fluorescence, turbidity and dissolved oxygen measurements with data telemetry, a nitrate analyser and water sampler. The pilot deployment was intended to:

- test and validate (through comparisons with water samples) an *in situ* nitrate analyser;
- integrate smart sampling capabilities and trial *in situ* water samplers with telemetry for remote and/or event triggering of samples;
- test an *in situ* multi-parameter probe encompassing the measurement of temperature, salinity, dissolved oxygen, fluorescence and turbidity measurements.

The water samplers would collect samples for subsequent laboratory nutrient analysis and phytoplankton speciation. The communication and telemetry would allow remote triggering of the water samplers and automatic triggering based on measurements taken by the multi-parameter probe. In addition, data from the multi-parameter probe and the nitrate analyser would be viewed in real time on a website. A schematic representation of this system is shown in Figure 1.

1.3 Deployment location and platform

With the permission of Dublin Port Company, the North Bank lighthouse (NBL) in Dublin Bay was selected as a platform for deployment of the system. The lighthouse stands on stilts and is in the outer reaches of Dublin port, within the Bull and East walls, and is only accessible by boat. This area is within the outer River Liffey estuary, and also influenced by the inflow of the two smaller rivers, the Dodder and Tolka. It is very close to the primary wastewater treatment plant for Dublin City. This plant was commissioned in 2004 and provides tertiary treatment for a population equivalent of 1.7 million to improve water quality in Dublin Bay. The NBL site was selected as it afforded security and provided a cost-effective platform with good access. Furthermore, this location has been used in the past by Dublin City Council and the EPA to collect continuous monitoring data through deployment of a YSI 6600 sensor. Figure 2 shows the location of the NBL in Dublin Bay.

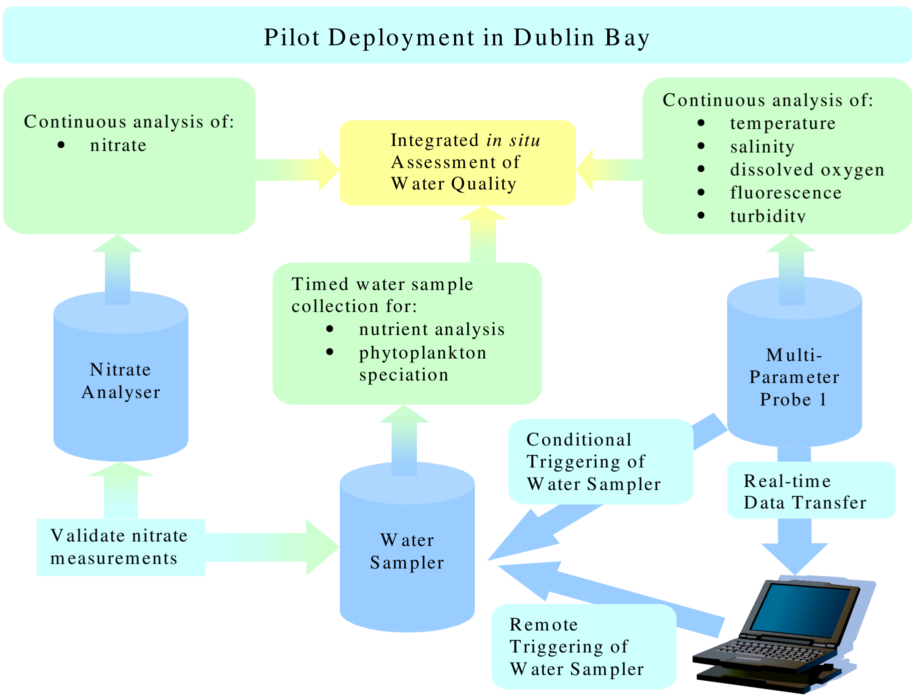


Fig. 1. Schematic for the pilot water quality monitoring station in Dublin Bay.

2. Integration and deployment of equipment and instrumentation

2.1 Instrumentation and system integration

Following a tender, the equipment and instrumentation listed in Table 1 was deployed in the integrated system.

The instrument package, data logger and water samplers were powered by three 12 volt car batteries in series, which were re-charged via a 40 watt solar panel. The sensors also had internal batteries as a back-up power supply.

A key element of the project was the testing of a nitrate sensor. There are various autonomous nutrient analysers on the market, mostly based on "wet chemistry" i.e. reagent based systems. While such systems have been routinely deployed, for example on the Smartbuoy network, it was decided to trial the Satlantic MBARI-ISUS, a novel optical nitrate sensor. This system developed by Monterey Bay Aquarium Research Institute (US) measures nitrate using its UV absorption spectrum (Johnson and Colletti, 2002). The advantages of the ISUS are that it does not require regular replacement of reagents, it does not require pumps or moving parts so theoretically is less likely to encounter mechanical problems in a difficult working environment, and it has a broad linear working range and reasonable sensitivity.

The ISCO water samplers were set up so they could collect samples for subsequent phytoplankton analysis and also samples for analysis of dissolved inorganic nutrients (total oxidised nitrogen (TOxN), nitrite, ortho-phosphate, silicate). This was achieved by placing Lugol's iodine in the water bottles designated for phytoplankton and mercuric chloride ($HgCl_2$) in bottles designated for nutrient testing.

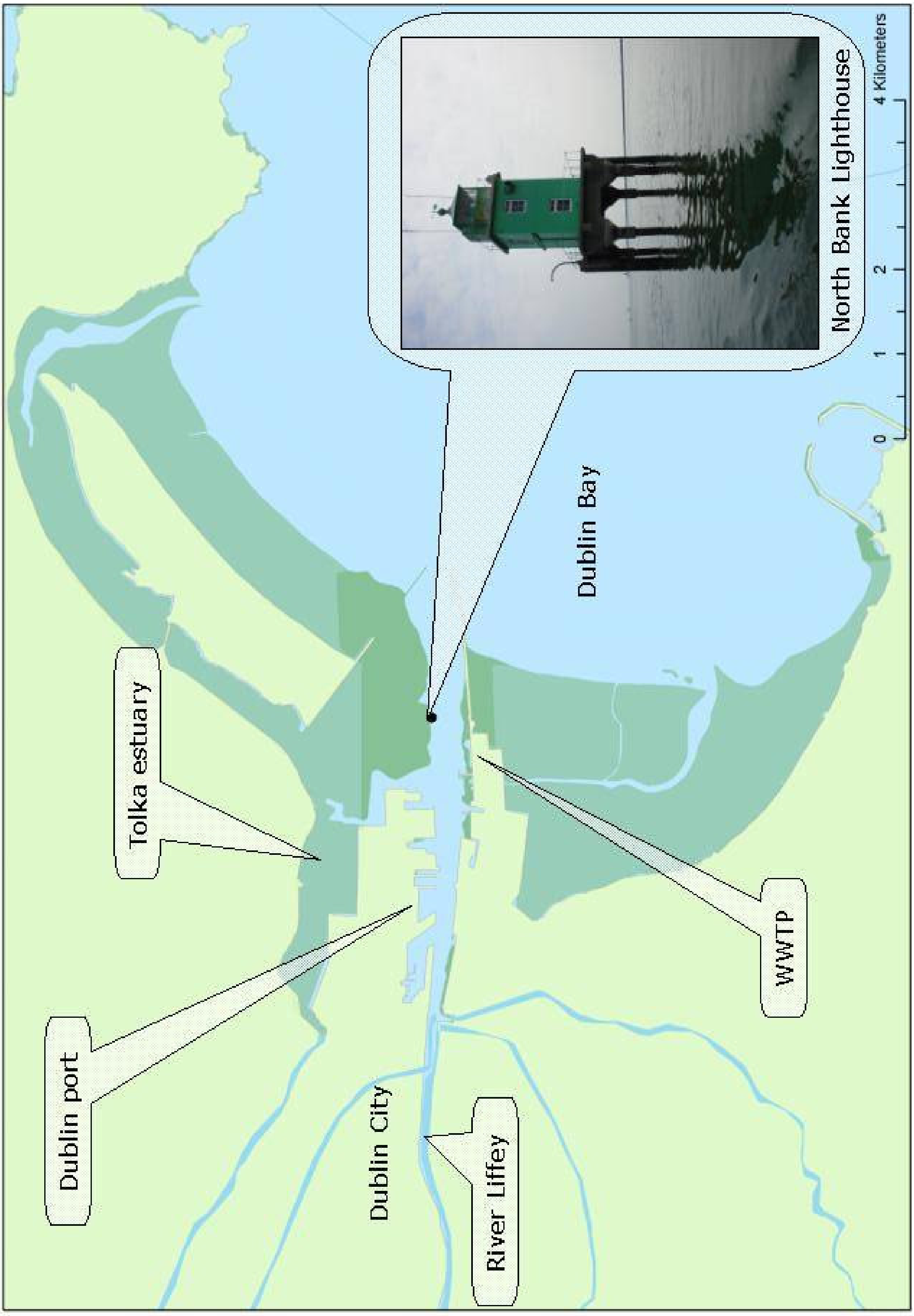


Fig.2: North Bank lighthouse. Location of MATSIS pilot monitoring station in Dublin Bay (WWTP = Ringsend waste water treatment plant)

Table 1: North Bank monitoring station instrumentation

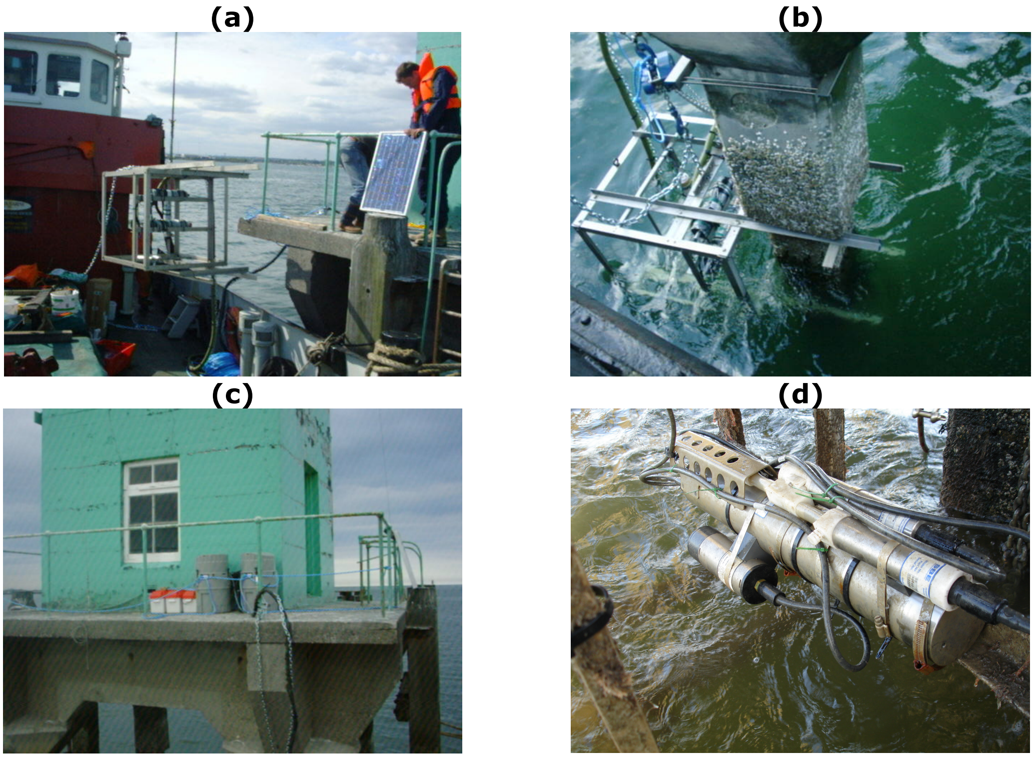
Instrument/Sensor		**Measurement (Units)**
Seabird SBE16		Temperature (°C), salinity (psu)
Seabird SBE43		Oxygen concentration (mg l^{-1})
WetLabs ECO FLNTU		Chlorophyll (µg l^{-1}), turbidity (ntu)
Satlantic MBARI ISUS nitrate sensor		Nitrate concentration (µmol l^{-1})
2 ISCO 6712C automated water samplers		Samples collected, preserved and stored for subsequent lab analysis of nutrients and phytoplankton
TechWorks Marine Black Box^{TM} (including base station)		Data acquisition and transmission

Notes: A Hydrolab Datasonde 4X multi-parameter probe, supplied by the EPA, was initially deployed, but due to technical issues, including difficulties in integrating with the data acquisition system, this was replaced by the Seabird sensors and Wetlab chlorophyll sensor supplied by the Marine Institute. Later in the project the Datasonde was deployed as a standalone instrument alongside for comparison.

2.2 Deployment

Sensors were deployed on a specially constructed stainless steel frame. The frame was built so that it could be manoeuvred up and down one of the legs of the lighthouse using a block and tackle in order to access the sensors for servicing. The water samplers, batteries, data logger and solar panel were all mounted on the deck of the lighthouse. Water samples were pumped up from depth with a source close to the sensor package. With the exception of the solar panel this equipment was housed in a garden storage box for security. The frame was first deployed in August 2005 and this operation is depicted in plates 1 a-d.

Plate 1: (a, b) Deployment of sensors in customised stainless steel frame. Note solar panel for regeneration of power supply. (c) ISCO automated water samplers on deck of lighthouse. (d) Sensor package ready for deployment.



2.3 Communication

Techworks, a Dublin-based SME worked with MI to build and maintain the North Bank Monitoring Station (NBMS). The data acquisition system was TechWorks Marine Black Box^{TM}. Data was collected by the sensors every 20 minutes, communicated via GSM to a base station and updated hourly on the password protected Techworks webpage. A webpage was also designed to display the data in near real-time on the Marine Institute web page, although this requires some upgrading following a Marine Institute website upgrade.

The system was constructed to enable smart water sampling with the following functionality successfully achieved:

- periodic water sampling intervals can be reset remotely from the base station;
- water sampling can be triggered remotely from the base station;
- conditional triggering was set up based on near real-time information from the sensors.

3. System validation

A validation plan was prepared for the North Bank Monitoring Station in line with the Marine Institute quality system. The results are outlined below.

3.1 ISUS Nitrate Analyser

The nitrate analyser was tested in the laboratory using reference solutions of known nitrate concentration and in the field by comparing sensor measurements against laboratory nitrate measurements for water samples collected alongside the system**.**

The *Limit of Detection* (LoD) and *Limit of Quantification* (LoQ) were determined by analysing seawater reference solutions with known low nitrate concentrations. The calculated LoD of 0.73 µmol l^{-1} and LoQ of 2.44 µmol l^{-1} accords well with the manufacturer's specifications of 0.5 µmol l^{-1} and 2 µmol l^{-1} respectively.

The certified nitrate concentrations in two certified reference materials (CRMs) were measured using the senor to assess the *accuracy* or *trueness* of the instrument. The CRMs were a coastal (salinity 35 psu) and an estuarine (salinity 11.1 psu) water. The results indicated a mean measured concentration 7.56 µmol l^{-1} nitrate for the coastal water CRM (certified value 5.25 µmol l^{-1}). This is a bias of +44% and would be outside the acceptable range for a laboratory analysis at this concentration, for example as defined by the QUASIMEME laboratory proficiency testing scheme (lZl = 6.79). The mean measured nitrate concentration of 10.58 µmol l^{-1} for the estuarine sample is in very close agreement with the certified value of 10.53 µmol l^{-1}. With a lZl score of 0.08 this would be well within the acceptable range for laboratory analysis.

The same data was also used to determine *precision*. A coefficient of variation (CV) of 5.52% (n=60) for the coastal sample and a CV of 4.74% (n=60) for the estuarine sample was determined.

Replicate measurements were also carried out for other seawater samples of known concentrations (i.e. QUASIMEME samples with assigned values for proficiency testing). The results of these and CRM measurements are summarised in Table 2.

Table 2: Summary statistics for measurement of nitrate in CRM and QUASIMEME samples (QNU). (EW = estuarine; SW = Seawater)

Sample	Mean value µmol l^{-1} nitrate	CV	n	Assigned value	% difference	z score
CRM SW 4.1 (35 psu)	7.56	5.52	60	5.25	+44%	6.79
CRM EW 3.1 (11.1 psu)	10.58	4.19	60	10.53	+0.05	0.08
QNU 162EW	34.2	0.99	27	38.3	-10.8	-1.76
QNU 163 EW	8.68	0.94	28	7.2	+20.6	3.24
QNU 159 SW	12.6	0.80	33	10.87	+15.8	2.54

Overall the results suggest a positive bias for the instrument in 3 out of 5 samples. These results show that the QUASIMEME acceptance criteria holds true for only two of the samples (QNU 162EW and CRM EW 3.1).

Field testing was also carried out for the ISUS. The ISUS was deployed in Rinville Bay, Co. Galway on three occasions (23rd May 2006, 25th February 2007 and 1st March 2007) with water samples being taken alongside for laboratory analysis every 15 minutes. The ISUS was also deployed at the test site in Dublin over a 24-hour period on the 15th August 2006. Discrete water samples were collected every hour for laboratory nutrient analysis using the ISCO water sampler. Overall these tests provided comparative data in two different environments at a range of concentrations. In general there was reasonable agreement between laboratory and sensor measurements and similar trends for the varying concentrations over each deployment period. However, during all deployments the ISUS appeared to generally overestimate the nitrate concentration compared with quality controlled laboratory measurements, i.e. there is a positive bias. The performance of the ISUS in all the above field trials compared with laboratory-measured nitrate concentrations are plotted in Figure 3. This indicates a good correlation (R^2=0.94) across a concentration range of approximately 5 – 35 µmol l^{-1} nitrate but with a slope of 1.08 and an intercept of 2.39. This indicates a small constant error and also a proportional error, which should be considered and possibly corrected for when using this equipment. The manufacturer's literature indicates that coloured dissolved organic matter (CDOM) may interfere with nitrate measurements but chemical analysis of water samples collected at NBMS in 2007 suggests CDOM in Dublin Bay to be low.

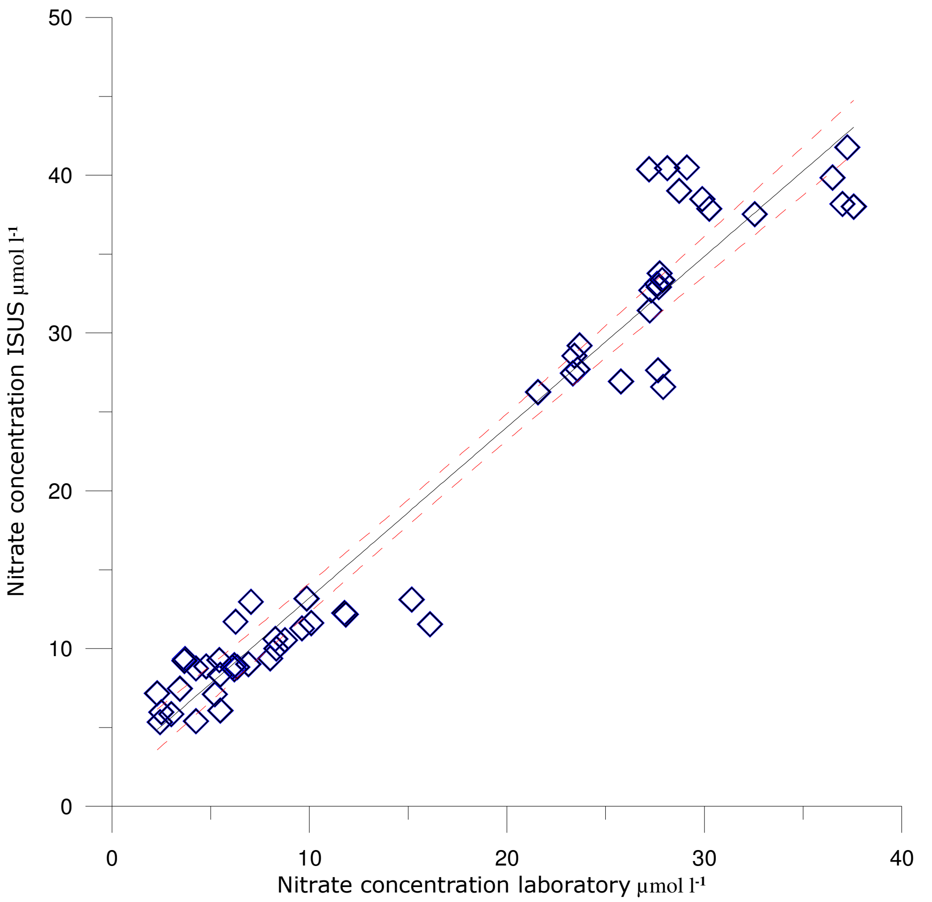


Fig. 3: Regression plot of nitrate concentrations measured by the ISUS in the field against values for discrete samples collected alongside and measured in the laboratory using an autoanalyser.

There were some reliability issues with the ISUS and there were problems when redeployed during 2007. The instrument was returned to Satlantic for checking and recalibration. It is noted that the version deployed in MATSIS is the ISUS V1 and this has been upgraded since then (currently V3).

3.2 Validation of telemetry and communications

Plotting a subset of Seabird (SBE 16) temperature data and Wetlabs chlorophyll instrument-logged data against the data temperature and chlorophyll data recorded on the Base Station (telemetered) showed a perfect match, indicating no issues with data transferral. However, there was a slight discrepancy when ISUS logged nitrate data was plotted against the data held on the base station. Although the error was very small, the reason is not clear.

Remote triggering of the water sampler was also validated on site by witnessing a sampling event while a colleague triggered sampling from the base station. Automatic and conditional event triggering (e.g. temp > 10°C and DO > 8 mg l^{-1}) was verified from the record log.

3.3 Comparison of standalone Hydrolab Datasonde 4 with Seabird sensors

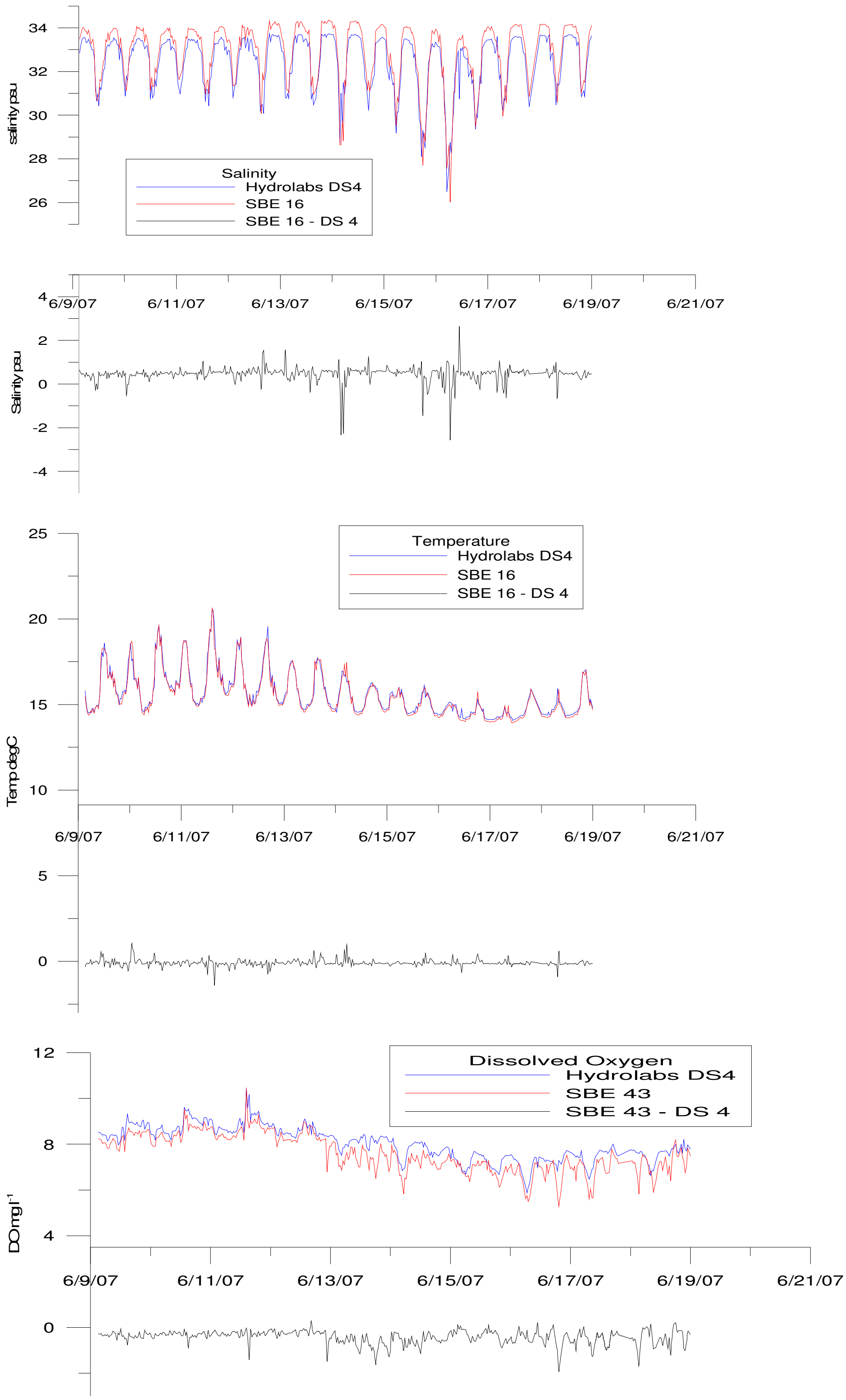
While the Seabird equipment is well established and routinely used in offshore ocean moorings, such as the MI weather buoy network, the use of cheaper multiparameter probes offers the potential for economical inshore deployments. With this in mind a Hydrolabs Datasonde 4 was deployed as a standalone system between June 9th and 24th 2007 before heavy fouling and battery failure caused the Datasonde to stop recording. Comparisons of the Datasonde against the Seabird equipment are presented in Figure 4. This generally showed good agreement for temperature, salinity and to a lesser extent dissolved oxygen over the period tested.

4. North Bank Monitoring Station – Issues encountered and lessons learned

As anticipated, there was substantial *biofouling* of the underwater equipment especially in summer 2006. However, the actual sensors generally remained relatively free of fouling as each has their own antifouling mechanisms (e.g. copper guard on the ISUS). Bird fouling of the solar panel leading to a reduced power output was overcome by building a ledge above the panel. Use of sacrificial anodes reduced corrosion of chains attaching the frame to the lighthouse.

Various *data collection and communication* issues were encountered, especially in the early stages of the project. These problems were ironed out over the course of the project.

While the NBL offered many advantages as a work platform one drawback was that access to the sensors was limited to the period around low spring tides due to the structure of the lighthouse pillars. This greatly limited the accessibility as a convergence of low spring tides during daylight hours were required. Good weather, personnel availability and boat availability were also required to carry out a full service visit.



a)
Salinity
Datasonde DS 4x compared with Seabird SBE 16

b)
Temperature
Datasonde DS 4x compared with Seabird SBE 16

c)
Dissolved Oxygen
Datasonde DS 4x compared with Seabird SBE 43

Fig. 4: Comparison of Hydrolabs Datasode DS4 and Seabird measurements of a) Salinity (psu), b) Temperature (°C) and, c) dissolved oxygen (mg l^{-1})

5. Dublin Bay assessment

There have been four successful deployments to date:

- October – December 2005
- April – May 2006
- July – September 2006
- March – July 2007

The data from these deployments are summarised in Tables 4-7 in Appendix 1 and also presented graphically for each deployment period in figures 8-13 in Appendix 2. For 2007 data, actual tidal height data from the Dublin Port Tide Gauge (Marine Institute) is plotted. For 2006 predicted tides are derived from Tideplotter software.

5.1 Salinity and temperature

Temperature and salinity show a pattern that reflects the tidal cycle at the sampling site. The greatest extremes in temperature and salinity coincide with spring tides. For example, lowest salinity values can be seen at the highest tidal elevations. Seasonal variations are also evident. For example, mean temperature varies from 8.5ºC in November – December 2005 to 16.1ºC in summer 2006 (with a maximum of 20.5ºC). Likewise, salinity also shows a seasonal variation. Lowest salinities are recorded in October – December 2005 (mean: 30.9 psu; minimum 22.3 psu) with highest salinities in summer 2006 (mean 32.6 psu), reflecting the greater freshwater input from the River Liffey in winter.

These data compare well with data recorded by Dublin City Council using a YSI multi-parameter probe at the same site in April 2005. The following mean values were recorded: temperature 10.2ºC; salinity 32.7 psu.

5.2 Nutrients

ISUS Nitrate data is only available for October 2005 and July – September 2006 with nitrate levels slightly higher in summer than in winter. Data presented are as measured and are not corrected. Nitrate concentrations show a strong tidal signal with an inverse relationship with salinity confirming a freshwater source for nitrate. These tidal fluctuations in nitrate concentrations with the tidal cycles were observed during both deployments and there was often more than an order of magnitude in concentration difference between high and low tides. Nitrate concentrations at high tide (i.e. in higher salinity water) tended to be less than 10 µmol l^{-1}. At low tide (lower salinity water) more variable nitrate concentrations were evident. The highest concentration measured was 58.9 µmol l^{-1} on the 9th September 16:08, 2006, (salinity 31.1 psu). This was approximately one hour before measured low tide. It is worth noting that within four hours after this with the incoming tide the nitrate concentration had dropped to <3 µmol l^{-1} (salinity 33.4 psu). The nitrate results clearly indicate the inadequacy of spot sampling in the context of such a high degree of variability.

TOxN and phosphate data from discrete samples collected are available for the following periods: November-December 2005 and June 2007. The data are presented in Figures 5 and 6 and like the sensor data show a pattern that reflects the tidal influences of the test site. Nitrate data from the ISUS are not available to compare with the TOxN results from the samples collected. TOxN data do compare favourably with nitrate data from the ISUS for the period 16th August 2006.

In an earlier study (O'Higgins and Wilson, 2005), mean surface and bottom values for TOxN of 19 µmol l^{-1} (min: 0.57 µmol l^{-1}; max: 82 µmol l^{-1}) and 9.7 µmol l^{-1} (min: 0.64 µmol l^{-1}; max: 47.6 µmol l^{-1}) were measured at the same site during the period June 2000 – June 2003. Phosphate values are representative of those expected for this site. O'Higgins and Wilson (2005) recorded mean surface and bottom values for phosphate of 2.3 µmol l^{-1} (min: 0.30 µmol l^{-1}; max: 9.8 µmol l^{-1}) and 1.0 µmol l^{-1} (min: 0.20 µmol l^{-1}; max: 3.8 µmol l^{-1}) in Dublin Bay during June 2000 – June 2003.

5.3 Chlorophyll, Dissolved Oxygen, and Phytoplankton

5.3.1 Chlorophyll and dissolved oxygen - Sensor data

There is no strong seasonal variation in chlorophyll evident. Chlorophyll levels are low in November – December 2005 as expected, but there is no substantial increase in chlorophyll levels in April – May 2006. It could be possible that the sensor deployments did not coincide with the expected Spring phytoplankton blooms. However, maximum values of 24.5 and 48.2 µg l^{-1} in April – May and July – September 2006, respectively, would suggest the presence of possible short-lived phytoplankton blooms. Most obvious are the higher levels of chlorophyll seen during July 2006. The chlorophyll shows a strong tidal signal inversely related to salinity suggesting an upstream phytoplankton bloom being washed in and out with the tide. The chlorophyll levels were typically > 10 µg l^{-1} for lower salinity water (low tide) between the 20th and the 23rd July with maximum values of 48 µg l^{-1}. Chlorophyll minima during this period and at this location were observed in higher salinity water (high tide) and were low (< 2 µg l^{-1}). The higher levels of chlorophyll seen in 2006 were not apparent in 2007. It is not clear whether this is due to genuine low levels of chlorophyll or instrument problems and this is being investigated.

Dissolved oxygen (DO) levels were variable and more complicated as both tidal and diurnal cycles were evident and often superimposed. DO solubility is a function of water temperature and salinity and consequently will reflect tidal cycles. In July 2006 concentrations were between 3 and 7 mg l^{-1} with tidal cycling evident and higher DO associated with higher chlorophyll levels at low tide. DO levels dropped marginally after the bloom. DO concentrations between 5 and 8 mg l^{-1} were recorded during the April–May 2006 deployment but higher concentrations were observed in March–May 2007 deployment with concentrations > 100% saturation. This is surprising as the chlorophyll sensor suggests very low activity. In the period around the 4th April 2007 the concentrations reached over 12 mg l^{-1} and diurnal patterns were evident. The high DO may have been an issue with sensor calibration although it is noted that in July 2007 the concentrations reduced substantially. The following mean values were recorded by Dublin City Council using a YSI multi-parameter probe at the same site in April 2005: DO 10.2 mg l^{-1}; chlorophyll 3.8 µg l^{-1}.

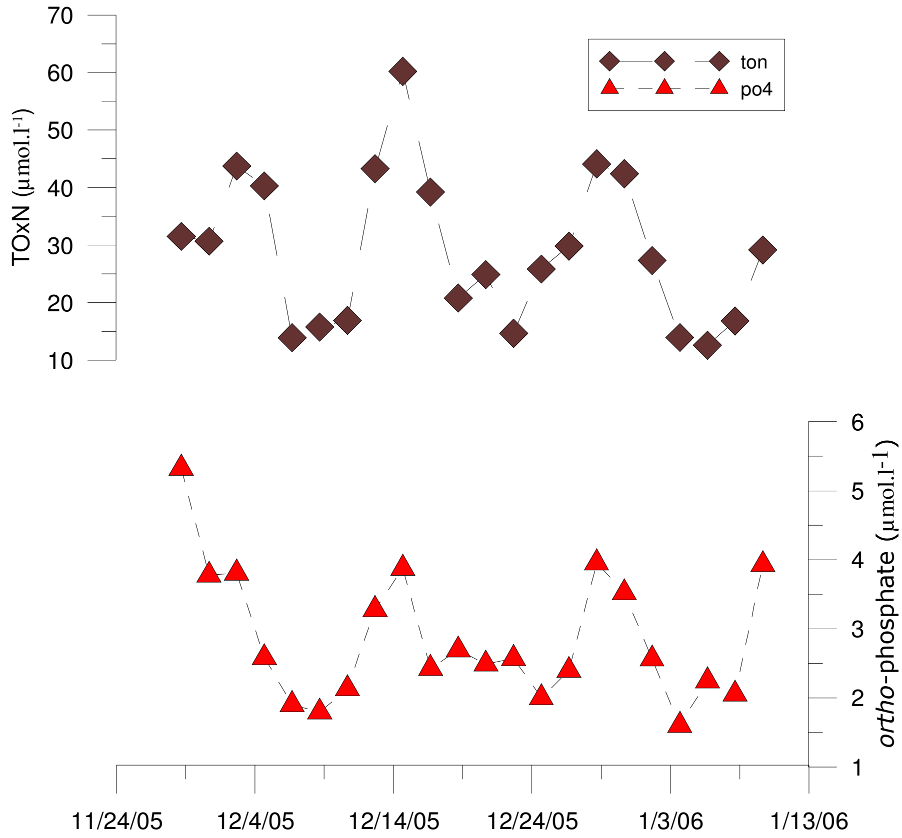


Fig. 5: Total oxidized nitrogen and orthophosphate concentrations in laboratory analyzed discrete water samples collected in using November 2005–January 2006 using the automatic water sampler.

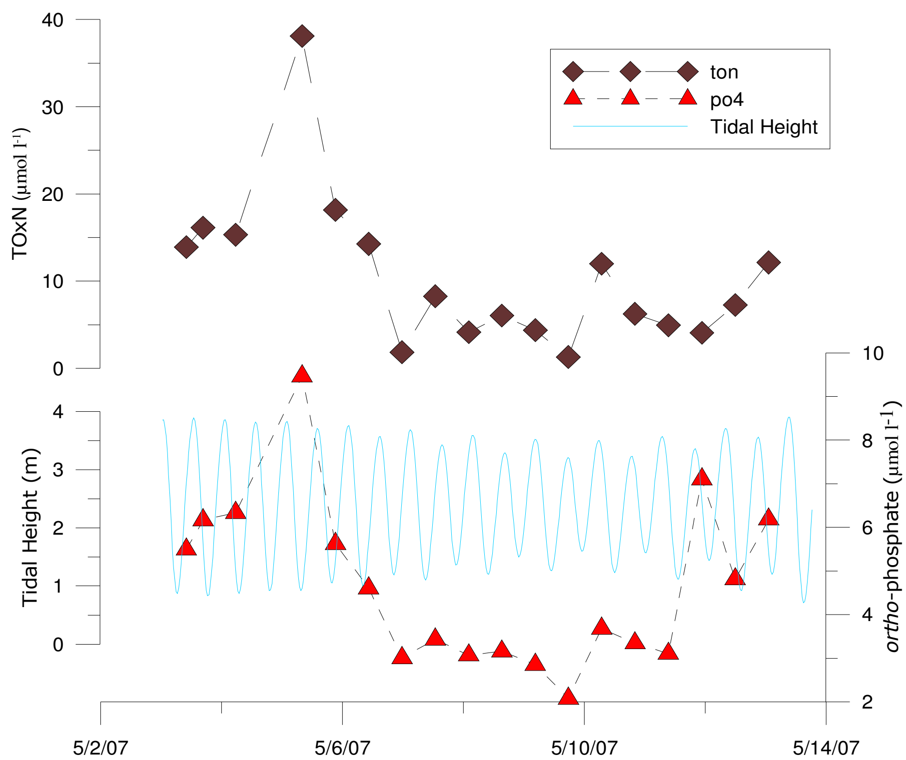


Fig. 6: Total oxidized nitrogen and orthophosphate concentrations in laboratory analyzed discrete water samples collected in May 2007 using the automatic water sampler. Tidal height data collected by Dublin Port Tidal Gauge (North Wall).

5.3.2 Discrete samples for phytoplankton analysis

A group of samples collected by the auto-sampler in Dublin Bay were taken during the period 21st July – 4th September in 2006. The samples were taken in duplicate in order to have a sample suitable for phytoplankton identification and enumeration analysis.

The phytoplankton species identified in this group of samples tended to be dominated by diatoms, and there were very few high counts. The composition of the population was typical summer mixed, and there were no monospecific blooms observed in these samples. The highest count was in the last sample taken on 4th September with a count of 24000 *Cylindrotheca closterium* which is an oligohaline species typical of coastal embayment. Other species of diatoms observed at moderate levels were *Rhizisolenia sp*. (*pungens* and *setigera*), again both species associated with brackish waters, and would be expected in this coastal site.

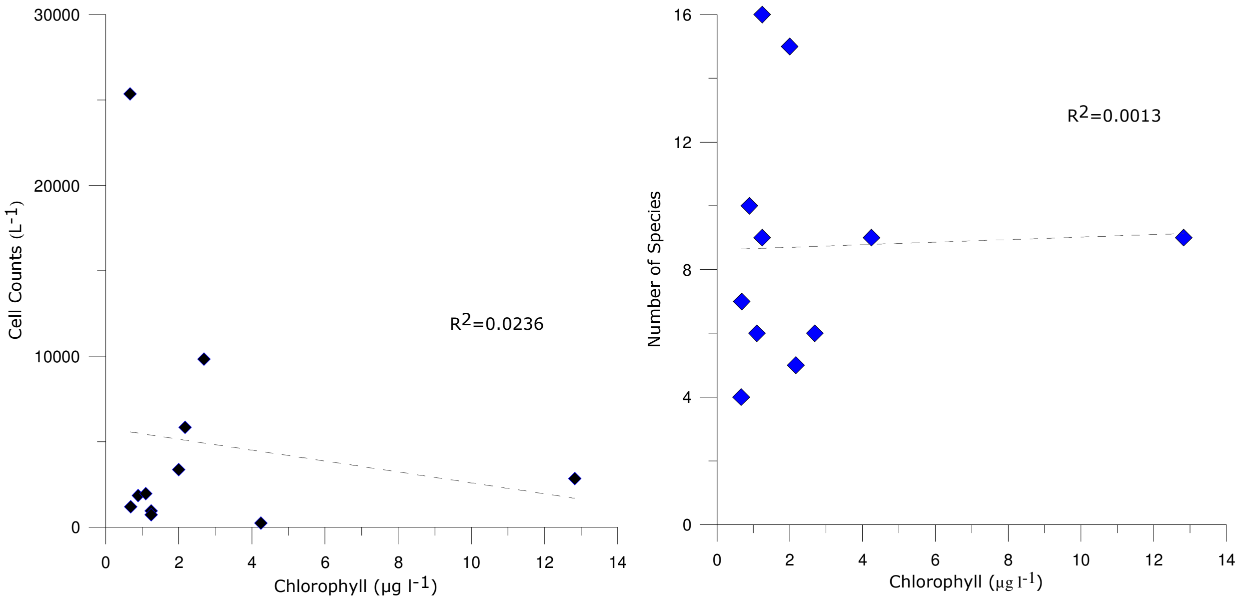
Dinoflagellates were neither represented at high counts or diversity in these samples. There were some low counts of *Protoperidinium sp., Prorocentrum sp., Miniscula sp., Gymnodinium sp. and Dinophysis sp.* observed but in each case at low cell counts. Despite the low counts their presence does at least indicate that the phytoplankton population is mixed and healthy and there were no signs of eutrophication seen in the phytoplankton population.

The chlorophyll levels as determined using the fluorometer were also typical for this time of the year. Measurements ranged from 0.663 µg l^{-1} to 12.827 µg l^{-1}. The single high concentration was not explained by the phytoplankton counts with low numbers of *Dinophysis acuminata*, *Pseudo-nitzschia delicatissma* group, *Rhizosolenia imbricate* and *Ceratium tripos* present. There may have been undetected micro flagellates present which might explain the high chlorophyll.

In any case, the correlation for chlorophyll and cell counts was not good suggesting that chlorophyll is not a good proxy for phytoplankton quantification. This is also the case between chlorophyll and the number of species present. The reason for this is probably explained by: 1) the low number of samples; 2) presence of heterotrophic species that contain little chlorophyll, and 3) small species that contain chlorophyll but are not readily counted by light microscopy.

Table 3 Phytoplankton sample details and results

Date	Phytoplankton ID	Chlorophyll ID	Chl (μg l^{-1})	Total Phytoplankton Cell Count (L^{-1})	No of species
21/07/2006	PHY0722022	210706-03	12.827	2840	9
23/07/2006	PHY0722023	230706-04	4.244	240	9
29/07/2006	PHY0722024	290706-07	0.887	1840	10
31/07/2006	PHY0722025	310706-08	1.241	960	16
02/08/2006	PHY0722026	020806-09	1.996	3360	15
12/08/2006	PHY0722037	120806-14	1.242	720	9
16/08/2006	PHY0722038	160806-16	2.689	9840	6
18/08/2006	PHY0722039	180806-04	2.168	5840	5
24/08/2006	PHY0722040	240806-10	1.097	1960	6
30/08/2006	PHY0722041	030806-16	0.678	1200	7
04/09/2006	PHY0722042	040906-21	0.663	25362	4



a) Chlorophyll fluorescence vs. Cell Count

b) Chlorophyll fluorescence vs. Number of species

Fig.7: Chlorophyll fluorescence vs cell count and number of species. July – September 2006.

6. Future plans for autonomous inshore monitoring infrastructure in Ireland

The EPA is responsible for WFD monitoring of physico-chemical and phytoplankton quality elements in transitional waters and the MI has been requested to implement monitoring of these quality elements in coastal waters. It is anticipated that the MI will maintain the NBMS as key monitoring infrastructure within this programme. In the interim the system was redeployed in July 2008 as an ongoing test platform linking into the SmartBay programme currently being developed by the Marine Institute.

The Marine Institute has tendered for the supply of an inshore data-buoy network. The experience gained during MATSIS was instrumental to the development of this work programme and to drawing up tender specifications. Subject to resources the MI intends to expand the use of autonomous inshore water quality monitoring systems and this directly builds on the experience gained in MATSIS.

The EPA and Marine Institute are funding a number of research activities to develop new sensors and autonomous monitoring technologies. This includes the SmartCoast project, led by the National Centre for Sensor Research (NCSR) at Dublin City University.

The MATSIS team have been in regular communication with the project to provide an end-user perspective and have given presentations on NBMS at a Sensor Technology workshop run by the MI in 2007.

7. Conclusions and recommendations

An autonomous Water Quality monitoring station was successfully piloted in Dublin Bay. Instrumentation and equipment was integrated in accordance with the project plan.

- A relatively new to the market optical nitrate analyser, the Satlantic ISUS, was tested and validation showed a good correlation with laboratory analysed samples. Although there was clear evidence of a positive bias for nitrate concentration as measured by the ISUS it may be possible to correct for this. While the analytical performance was short of what would be obtained for laboratory analysis, the high temporal variability observed for field data showed that there is an important role for semi-continuous nutrient sensors in transitional and coastal water monitoring. There were some reliability problems with the ISUS over the course of the project and consequently on the basis of the MATSIS project there are still outstanding questions on the suitability of the system for use in inshore monitoring stations or mooring deployments. It is recognized that due to the high capital cost only one instrument was tested and the technology has been refined since the system was purchased.

- The Seabird 16 CT sensor and the Seabird 43 DO sensor were found to be reliable and easy to integrate with the data acquisition system.
- A Hydrolabs Datasonde 4x deployed alongside generally provides good quality data for a period of time although there was some disagreement between sensors.
- Remote and smart water sampling capabilities were successfully included in the system.
- The data acquisition system (Techworks Marine Black Box^{TM}) performed well and data could be displayed and accessed by a web interface in real-time.

Data from four deployments showed a strong tidal signal for most of the parameters, including DO, chlorophyll fluorescence, and especially nitrate concentrations which could vary by as much as an order of magnitude over a tidal cycle. The high temporal variability indicates the important role for semi-continuous monitoring as spot sampling will almost certainly lead to under-sampling and potentially a misrepresentation of water quality.

Use of the North Bank lighthouse as a platform made this a cost-effective system. The experience gained during MATSIS has directly supported the development of Irish national monitoring plans for inshore waters, including the establishment of an inshore buoy network, and has fed into other research initiatives.

It is recommended that the NBMS is maintained in the context of WFD monitoring and the use of autonomous inshore monitoring stations be extended in Ireland. While the MATSIS NBMS provides an excellent model, it is recognized that the precise configuration will depend on site-specific requirements. Further roll-out of such systems will require developments in data management and processing capabilities. As with any monitoring measurements should be subjected to rigorous validation and ongoing quality control to ensure data is of known quality and "fit-for-purpose".

An additional set of sensors that could be exchanged at service visits would provide efficiencies and result in fewer data gaps. The use of smart automated water samplers is recommended to provide routine quality control checking of sensor data and to provide data on additional parameter

8. Abbreviations

CDOM	Coloured dissolved organic matter
Chl	Chlorophyll
Chl.Flu	Chlorophyll Fluorescence
CRMs	Certified reference materials
CV	Coefficient of variation
DO	Dissolved oxygen
EPA	Environmental Protection Agency
EW	Estuarine
$HgCl_2$	Mercuric chloride
L^{-1}	Per litre
LoD	Limit of Detection
LoQ	Limit of Quantification
lzl	Absolute value of Z score
MATSIS	Methods of Assessment of the Trophic Status of Irish Sea
$mg\ l^{-1}$	Milligrams per litre
MI	Marine Institute
n	Number of analysis
NBL	North Bank Lighthouse
NBMS	North Bank Monitoring Station
NSCR	National Centre for Sensor Research
NTU	Nephetometric turbidity unit
PSU	Practical salinity units
R^2	Correlation coefficient
SW	Seawater
Tur	Turbidity
$\mu g\ l^{-1}$	Micrograms per litre
$\mu mol\ l^{-1}$	Micromoles per litre
V	Volts
WFD	Water Framework Directive
WWTP	Waste water treatment plant

9. References

Johnson, K., Coletti, L., 2002. In situ ultraviolet spectrometry for high-resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep sea Research* I, 49, 1291-1305.

O'Higgins, T.G., Wilson, J.G., 2005. Impact of the River Liffey discharge on nutrient and chlorophyll concentrations in the Liffey estuary and Dublin Bay (Irish Sea). *Estuarine, Coastal and Shelf Science*, **64**, (2-3), 323-334

Appendix 1: MATSIS NBMS data Summary

Table 4. October–December 2005

	Temp (ºC)	Salinity (psu)	DO (V)	Chl. Flu. (µg l^{-1})	Tur. (ntu)	Nitrate (µmol l^{-1})
Mean	8.456	30.928	2.565	0.786	7.475	9.804
SD	0.339	2.618	0.033	0.200	3.646	8.420
Median	8.477	32.280	2.572	0.760	6.381	6.420
Min.	7.582	22.329	2.414	0.396	2.479	-0.390
Max.	10.766	33.421	2.624	1.456	22.395	30.660
n	594	594	594	594	594	212

Notes: Nitrate data is for period 3rd – 12th October 2005. Seabird data is for period 29th November– 6th December 2005.

Table 5. April–May 2006

	Temp (ºC)	Salinity (psu)	DO (mg l^{-1})	Chl. Flu. (µg l^{-1})	Tur. (ntu)
Mean	11.056	31.452	6.478	2.388	11.644
SD	1.297	1.742	0.439	2.686	9.498
Median	11.183	32.031	6.542	1.495	6.617
Min.	7.997	23.719	3.959	0.121	1.070
Max.	16.111	33.538	8.762	24.527	24.015
n	2672	2672	2672	2672	2672

Note: No nitrate data available for this period.

Table 6. July–September 2006

	Temp (ºC)	Salinity (psu)	DO (mg l^{-1})	Chl. Flu. (µg l^{-1})	Tur. (ntu)	Nitrate (µmol l^{-1})
Mean	16.328	32.586	4.611	2.036	14.356	11.422
SD	0.861	0.819	0.355	2.730	9.972	7.401
Median	16.133	32.813	4.604	1.385	19.071	9.245
Min.	14.932	28.507	2.611	0.459	0.943	0.470
Max.	20.470	33.539	6.974	48.198	24.022	58.860
n	4323	4323	4323	4323	4323	4385

Table 7. March – July 2007

	Temp (°C)	Salinity (psu)	DO (mg l^{-1})	Chl. Flu. (µg l^{-1})
Mean	12.796	32.140	9.270	0.848
SD	2.522	1.288	1.761	0.306
Median	12.943	32.540	9.758	0.774
Min.	7.985	25.833	2.083	0.409
Max.	20.598	33.820	12.943	4.403
n	3561	3561	3561	3561

Note: No nitrate or turbidity data available for this period.

Appendix 2: NBMS data plots

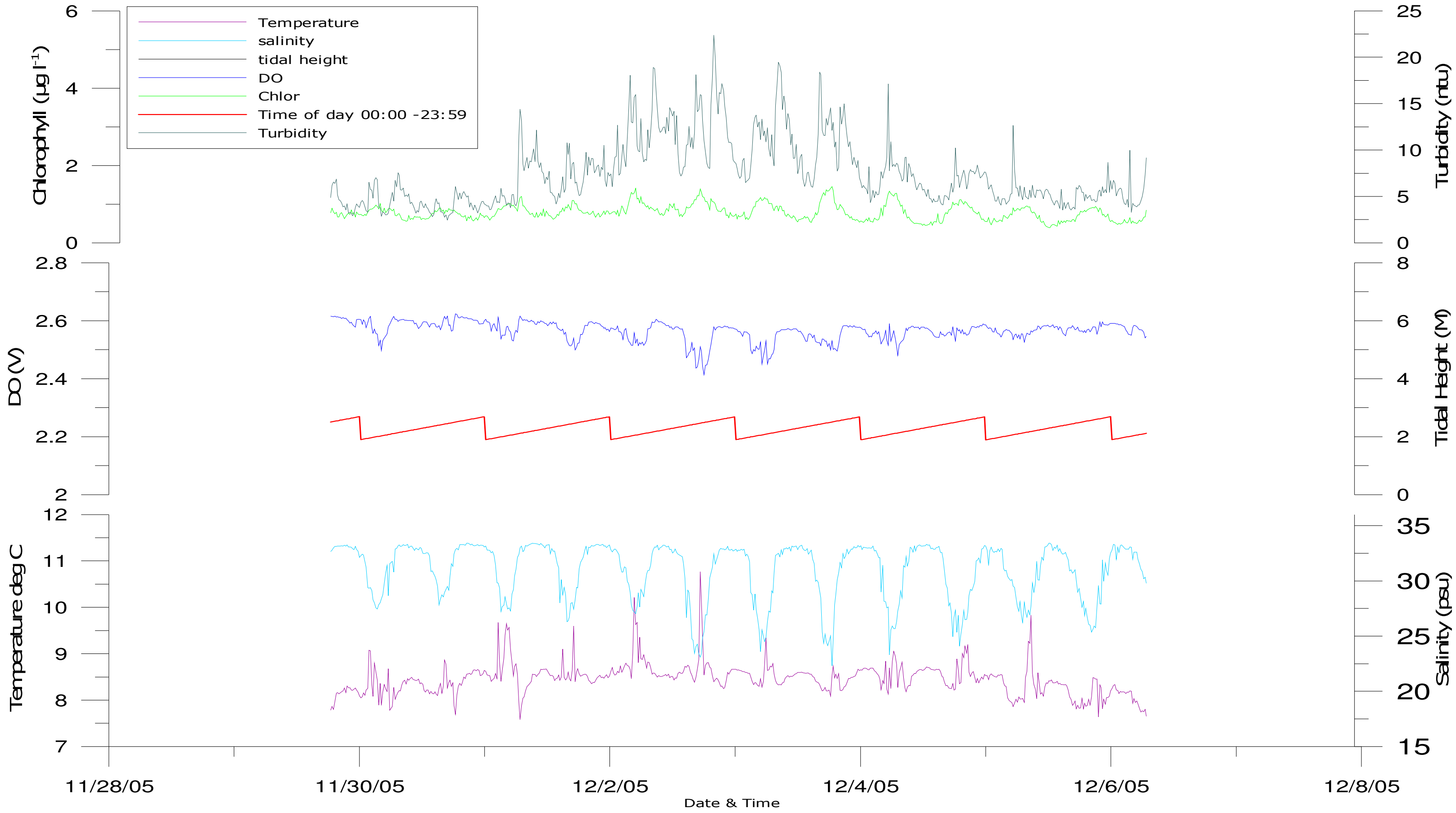


Fig. 8. North Bank monitoring station data, November–December 2005: Salinity (psu), temperature (°C), DO (v), turbidity (ntu) chlorophyll fluorescence (µg l^{-1}), time of day (24h).

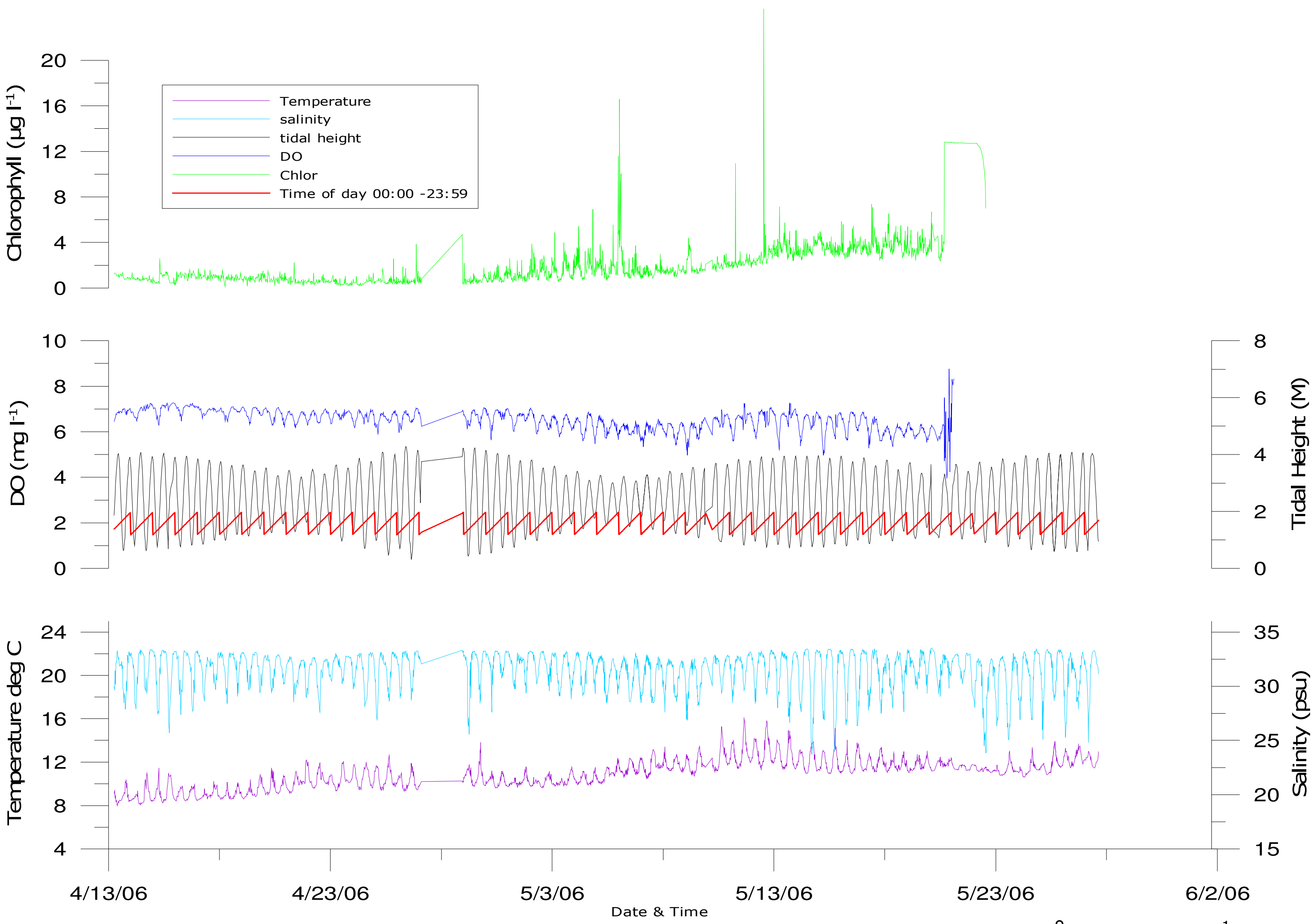


Fig. 9. North Bank monitoring station data (Apr – May 2006): Salinity (psu), temperature (°C), DO (mg l^{-1}), chlorophyll fluorescence (µg l^{-1}), predicted tidal height (m), time of day (24h).

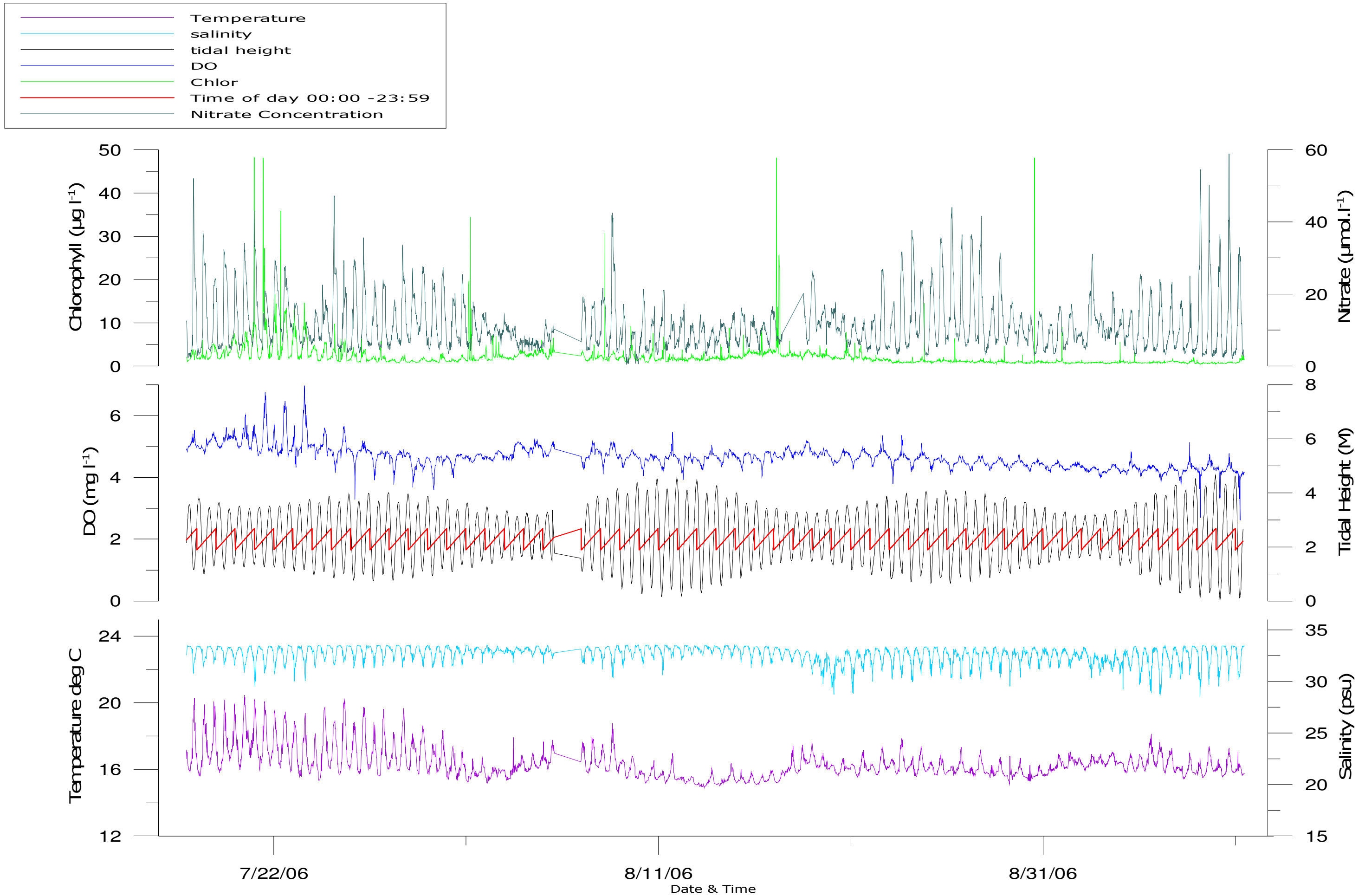


Fig. 10. North Bank monitoring station data. July – September 2006: Salinity (psu), temperature (°C), DO (mg l^{-1}), nitrate ISUS (µmol l^{-1}), chlorophyll fluorescence (µg l^{-1}), time of day (24h), predicted tidal height (m).

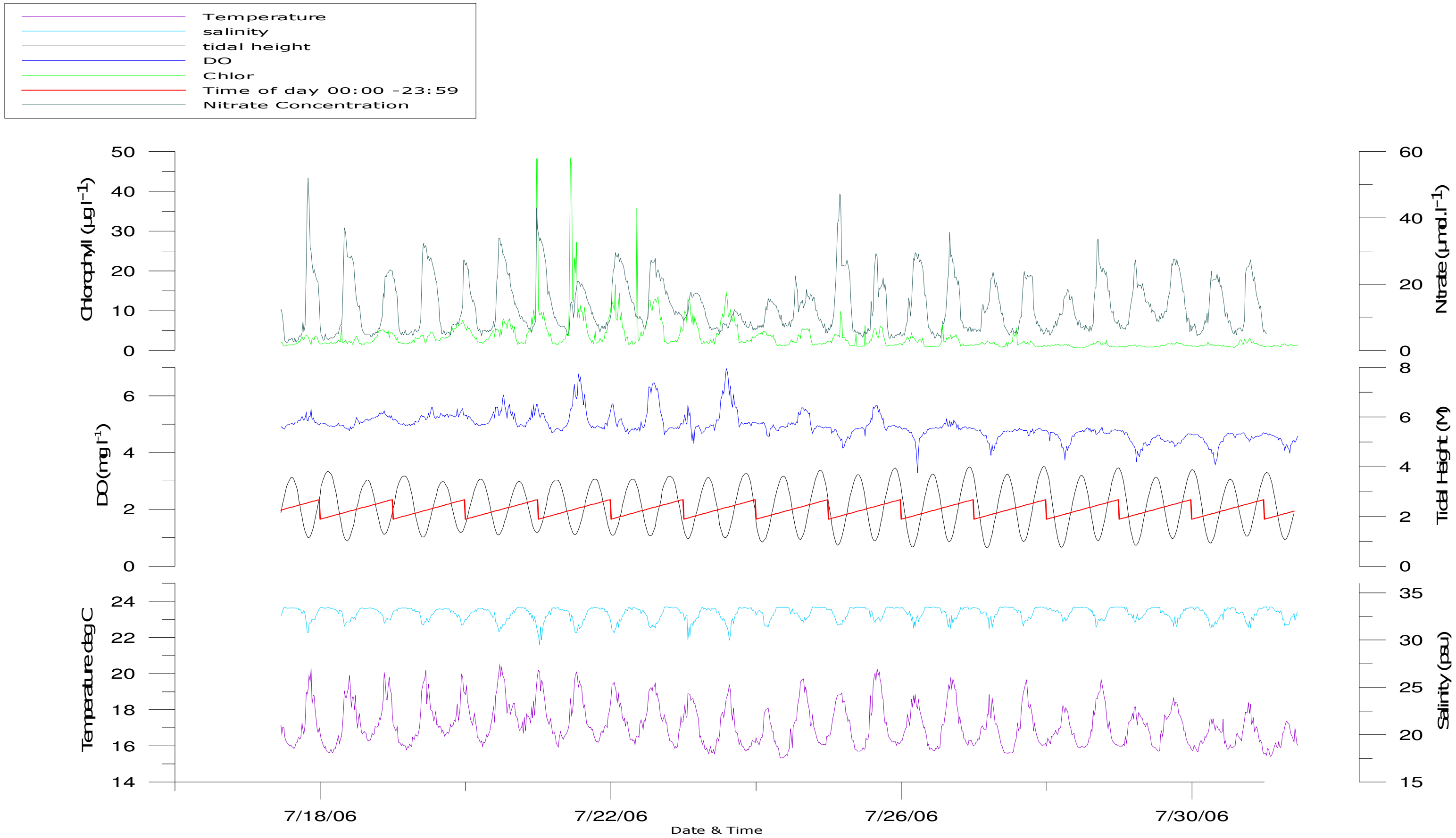


Fig. 11. North Bank monitoring station data. July 17th – 31st 2006: Salinity (psu), temperature (°C), DO (mg l^{-1}), nitrate ISUS (µmol l^{-1}) chlorophyll fluorescence (µg l^{-1}), time of day (24h), predicted tidal height (m).

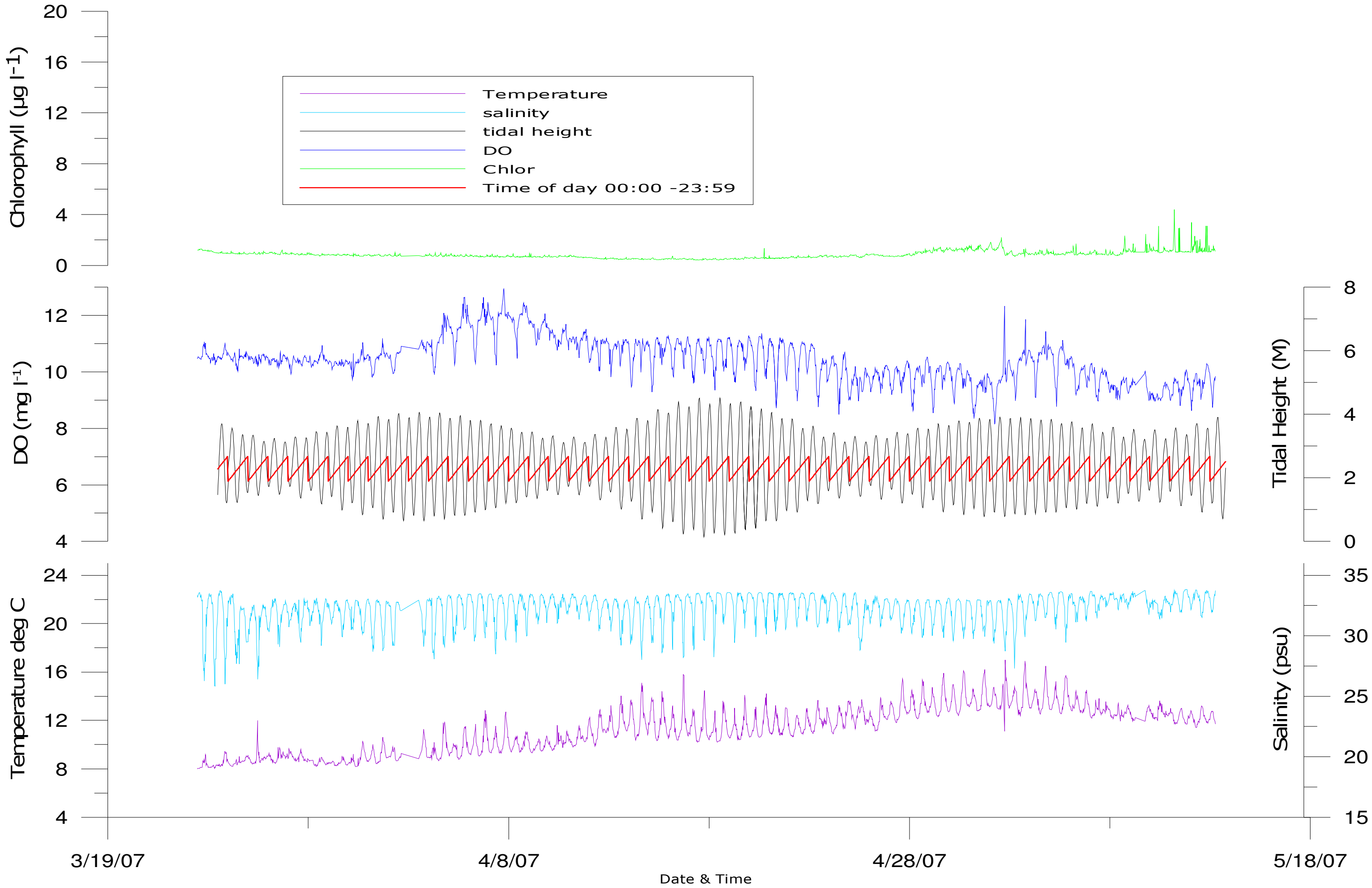


Fig. 12. North Bank monitoring station data. March – May 2007: Salinity (psu), temperature (°C), DO (mg l^{-1}), chlorophyll fluorescence (µg l^{-1}), time of day (24h); tidal height (m) from Dublin Port tidal gauge.

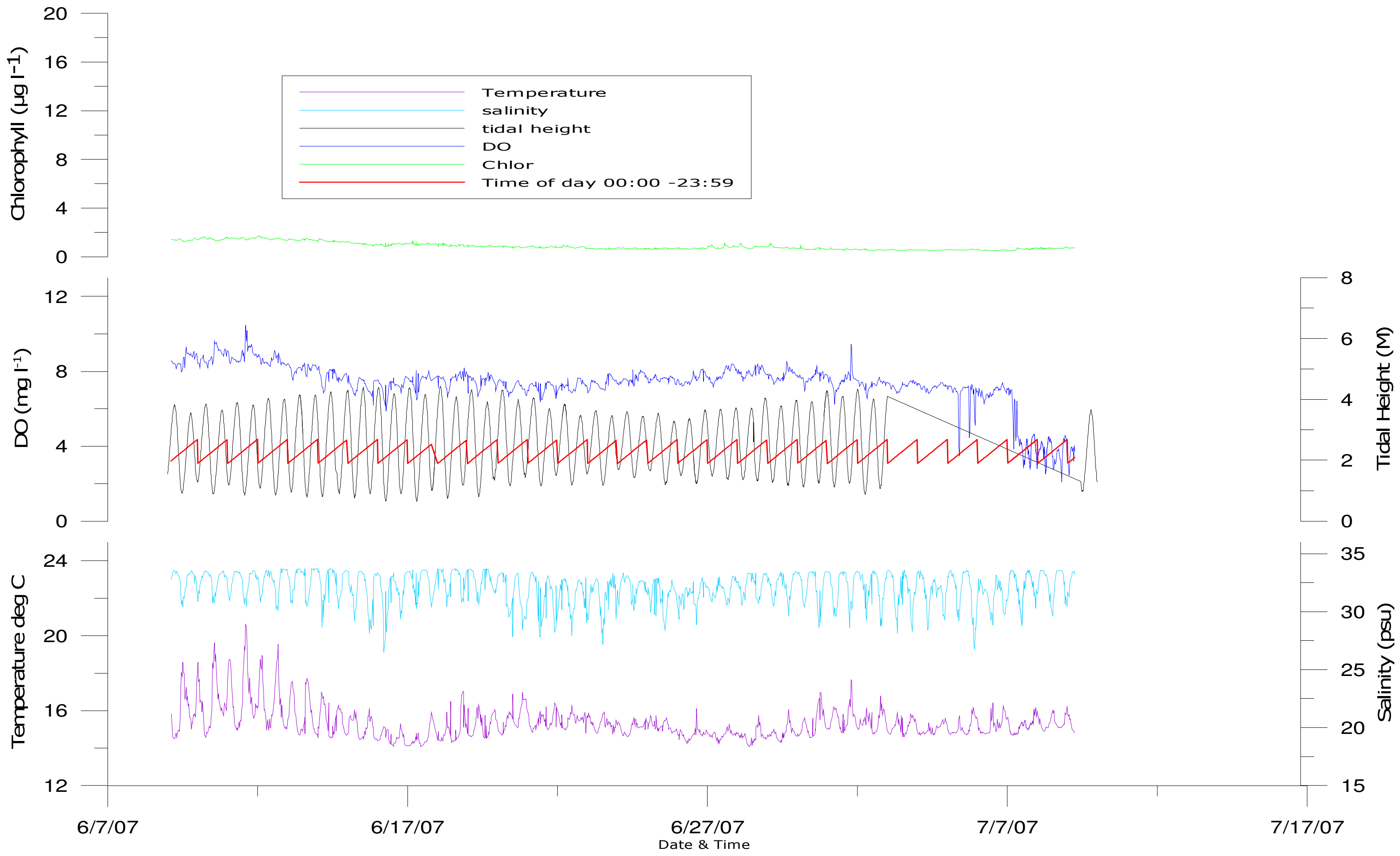


Fig. 13. North Bank monitoring station data. June – July 2007: Salinity (psu), temperature (°C), DO (mg l^{-1}), chlorophyll fluorescence (µg l^{-1}), time of day (24h), tidal height (m) from Dublin Port tidal gauge

Appendix 3: Cell Identifications and Counts in Cells per litre

	21/07/2006	23/07/2006	29/07/2006	31/07/2006	02/08/2006	12/08/2006	16/08/2006	18/08/2006	24/08/2006	30/08/2006	04/09/2006
Centric Diatom sp.									160	40	80
Cerataulina pelagica										280	
Ceratium fusus	40										
Ceratium symmetricum	40										
Ceratium tripos		40									
Chaetoceros (Hyalochaete) *sp*						200		1000			
Cilliate sp											40
Cylindrotheca closterium/Nitzschia longissima						80					24242
Dactyliosolen sp										80	
Dinoflagellate cysts (smooth)						80			40	80	
Dinoflagellate cysts (spiny)						80			80		80
Dinophysis acuminata		40									
Diplopsalis lenticula									40		
Eucampia zoodiacus								120			
Fragilariopsis sp				80							
Fragilidium sp									40		
Guinardia flaccida								160			
Gymnodinium sp									40		40
Gyrodinium britannicum							40				
Lauderia / Detonula sp										160	
Leptocylindrus minimus	360										
Licmophora sp				80		40					40
Minuscula bipes								80			
Naked Dinoflagellate sp.				40					120		40
Navicula sp	40		40				200				
Nitzschia sp					280						
Odontella sp								480	160	80	80
Paralia sulcata			280								40
Pennate Diatom sp.				40					40		200
Pleurosigma / Gyrosigma sp				40		40					40
Proboscia alata							480				
Prorocentrum micans				40				480	40	40	40
Protoperidinium mariaelebourae								40			
Pseudo-nitzschia delicatissma group	1280	120	480		1480		800				
Pseudo-nitzschia seriata group			960	480	240		1760		120	280	
Rhizosolenia imbricata		40									
Rhizosolenia pungens			40				3520				
Rhizosolenia setigera					320		3040	3000			
Rhizosolenia sp				80		80			600		280
Rhizosolenia styliformis			40					480			
Scrippsiella sp				80					120		
Skeletonema costatum	1080				1040						
Striatella sp						40				40	40
Striatella unipunctata									200		
Thalassiosira sp						80			80		
Trachelomonas Sp.									80	120	80
Grand Total	2840	240	1840	960	3360	720	9840	5840	1960	1200	25362