MULTI-YEAR HIGH FREQUENCY NUTRIENTS MEASUREMENTS IN AN OPERATIONAL DATA BUOY NETWORK

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1. ABSTRACT

Until relatively recently nutrient measurements were only possible using ship-based monitoring techniques with samples analysed on board or in the laboratory using traditional chemical methods. The Cefas SmartBuoy measures nutrients using a NAS-3X in-situ nutrient analyser and an automated water sampler. In-situ data are also compared to the results of discrete water samples which are collected during mooring service cruises. This paper presents measurements made since 2001 at sites in the SmartBuoy network (www.cefas.co.uk/monitoring) which reveal variability at a wide range of temporal and spatial scales. Nutrient enriched coastal sites exhibit up to four fold variability in TOxN over tidal cycles. Strong interannual variability is also evident as well as episodic events associated with increased rainfall. The rapid draw down of nutrients during the spring bloom is a recurrent feature of the time-series as is the increase in nutrients during the winter period.

2. INTRODUCTION

Cefas has run an operational SmartBuoy (data buoy) network since November 2000 [1], designed to provide high frequency surface measurements of certain physical, biological and chemical parameters which are published in near real-time to the internet (www.cefas.co.uk/monitoring). The network currently contains seven SmartBuoys, the data from which contribute to robust assessments of water quality and ecosystem health such as the eutrophication assessment required by OSPAR [2], the ecological status assessment for the Water Framework Directive and, in the future, the environmental status assessment for the Marine Strategy Framework Directive [3].

The supply of energy to higher trophic levels in open marine ecosystems is dependant on primary production of phytoplankton which is limited by the supply of light and nutrients, which vary over time. Until relatively recently sampling for nutrient analysis was only possible using low-frequency ship-based monitoring techniques with subsequent analysis using traditional chemical methods such as continuous flow analysis (CFA). Developments in instrumentation technology have enabled robust measurements of nutrients to be made in situ.

3. METHODS

The Cefas SmartBuoy provides measurements of nutrients using two different approaches. High frequency measurements (typically 2 hourly) of TOxN (nitrate + nitrite) are made using a NAS-3X (NAS-2E prior to 2006) in situ nutrient analyser (EnviroTech, USA). This instrument uses the traditional chemical method within a robust submersible casing. Instruments are checked for linearity prior to deployment and calibration is achieved in situ by use of an on board standard. Prior to deployment, a pre-deployment seawater standard (PDS) with a known concentration of TOxN as analysed by continuous low analysis (CFA) is repeatedly run through the NAS-3X. Results from the PDS are used to derive accuracy and precision of the NAS-3X. The second method uses an automated waters sampler (AquaMonitor, EnviroTech, USA) which collects water samples which are stored in blood transfusion bags pre-loaded with mercuric chloride. When the mooring is serviced, these samples are retrieved and returned to the laboratory for filtration and analysis using standard CFA techniques. The concentrations of nitrate, phosphate (only if negligible suspended particulate matter present) and silicate can be determined using this approach. Data obtained from the in situ measurements are compared with results of discrete samples collected alongside the buoys during mooring service visits. The use of two different methods also ensures that redundancy is built in to avoid complete loss of data in case of instrument failure.

4. QUALITY ASSURANCE

Nutrients data from the SmartBuoy programme are used for the assessment of water quality therefore guidance on the required accuracy is taken from the OSPAR Eutrophication Monitoring Guidelines for nutrients [4]. These guidelines state a desired accuracy of ± 25% at low TOxN concentrations (where low is defined as within a factor of 20 of the limit of detection) and ± 12% at medium to high concentrations.

There are several procedures and checks carried out to ensure the quality of nutrients data from the SmartBuoy programme:

1. A linearity check of the NAS-3X is carried out to verify the linear range of the instrument and a limit of detection calculated.
2. Within the quality assurance procedure, the accuracy of the NAS-3X is assessed by comparing the results of the TOxN in the PDS from the NAS-3X to the concentration of TOxN as analysed by the Skalar and the precision assessed by calculating the variability of the results of the PDS from the NAS-3X.
3. The accuracy of NAS-3X is ensured by use of on-board calibration standard throughout deployment.
4. The concentration of TOxN in the samples collected by AquaMonitor (WMS) are compared to the results from the NAS-3X.
5. Both in situ data sets are compared to the results of discrete water samples which are collected alongside the buoy by a rosette sampler during mooring service cruises.
6. The accuracy and precision of CFA is assessed from the results of external check standards.

5. RESULTS

The accuracy and precision of each of the methods is summarised in Table 1. Analysis of the NAS-3X results for the PDS from 57 deployments showed that the accuracy of the NAS-3X was ±10.6% and the precision was 5%. The accuracy and precision of CFA are ±3.0% and 2.7% respectively. The accuracy and precision of the NAS-3X is therefore lower than for the traditional CFA method but falls within the guidelines given by OSPAR [4].

Table 1 Methods of nutrients analysis within the SmartBuoy programme

Sample type	Method	Parameters	Measurement frequency	Accuracy	Precision
NAS-3X (EnviroTech, USA)	*in situ*, wet chemistry; on-board calibration standard run every 6 samples; pre-deployment standard run repeatedly to check accuracy and precision	TOxN (1)	typically every 2 hours	±10.6 % (3)	5 % (3)
Aqua Monitor (EnviroTech, USA)	samples collected and stored in sample bags pre-loaded with mercuric chloride, analysed in laboratory by continuous flow analysis	TOxN Silicate Phosphate (2)	typically daily	±3.0 % ±3.9 % ±3.1 % (4)	2.7 % 3.1 % 3.8 % (4)
Rosette samples collected during mooring service trips	Continuous flow analysis	TOxN Silicate Phosphate	Monthly	±3.0 % ±3.9 % ±3.1 % (4)	2.7 % 3.1 % 3.8 % (4)

(1) TOxN (nitrate + nitrite); (2) if negligible suspended particulate matter; (3) relative to pre deployment standard
(4) relative to laboratory standard

Data from SmartBuoy have provided greater understanding of the variability in nutrients concentrations in UK coastal waters over a variety of temporal scales. It is important to understand and quantify this variability in order to make accurate assessments of water quality such as under the OSPAR Comprehensive Procedure [2].

5.1. Inter annual variability

There is a large inter annual variability in the concentrations of nutrients in UK coastal waters as shown in the Thames Estuary (Fig. 1) and Liverpool Bay (Fig. 2). Variability is greater at the Thames than at Liverpool Bay (Table 2); maximum over winter nutrient concentrations during the past nine years have ranged between 32.7 μmol l^{-1} in 2004/2005 to 109.8 μmol l^{-1} in 2000/2001 in the Thames and between 36.4 μmol l^{-1} in 2004/2005 and 60.2 μmol l^{-1} in 2003/2004 in Liverpool Bay. Winter is defined within the OSPAR Comprehensive Procedure as November to February inclusive [2] although it is interesting to note that data obtained by SmartBuoy show that concentrations of TOxN at UK coastal locations frequently continue to increase during March and April (Fig. 1 and Fig. 2). In order to describe the inter annual variability in nutrient concentrations for assessment purposes, a level of confidence is attached to the assessment of nutrient enrichment, based on how many of the years exceed the nutrient assessment threshold [2]. This measure of confidence therefore reflects the variability observed in the average winter TOxN concentration between years.

Table 2 Minimum, maximum and average concentration (µmol l^{-1}) of TOxN at Thames and Liverpool Bay between November and February

	Thames				Liverpool Bay			
winter	**minimum**	**maximum**	**average**	**n**	**minimum**	**maximum**	**average**	**n**
00/01	11.5	109.8	48.2	76	-	-	-	-
01/02	7.7	39.2	20.6	498	-	-	-	-
02/03	5.9	88.8	32.1	758	5.9	45.2	16.6	397
03/04	0.6	44.8	16.5	840	0.2	60.2	22.7	337
04/05	4.0	32.7	17.1	705	2.8	36.4	16.9	696
05/06	4.3	46.5	15.9	491	6.7	50.2	23.5	921
06/07	3.6	64.2	28.2	1364	3.3	39.3	14.1	1628
07/08	5.5	69.9	25.8	1357	6.2	49.4	15.1	1753
08/09	10.2	36.2	15.1	337	0.2	43.6	19.5	719

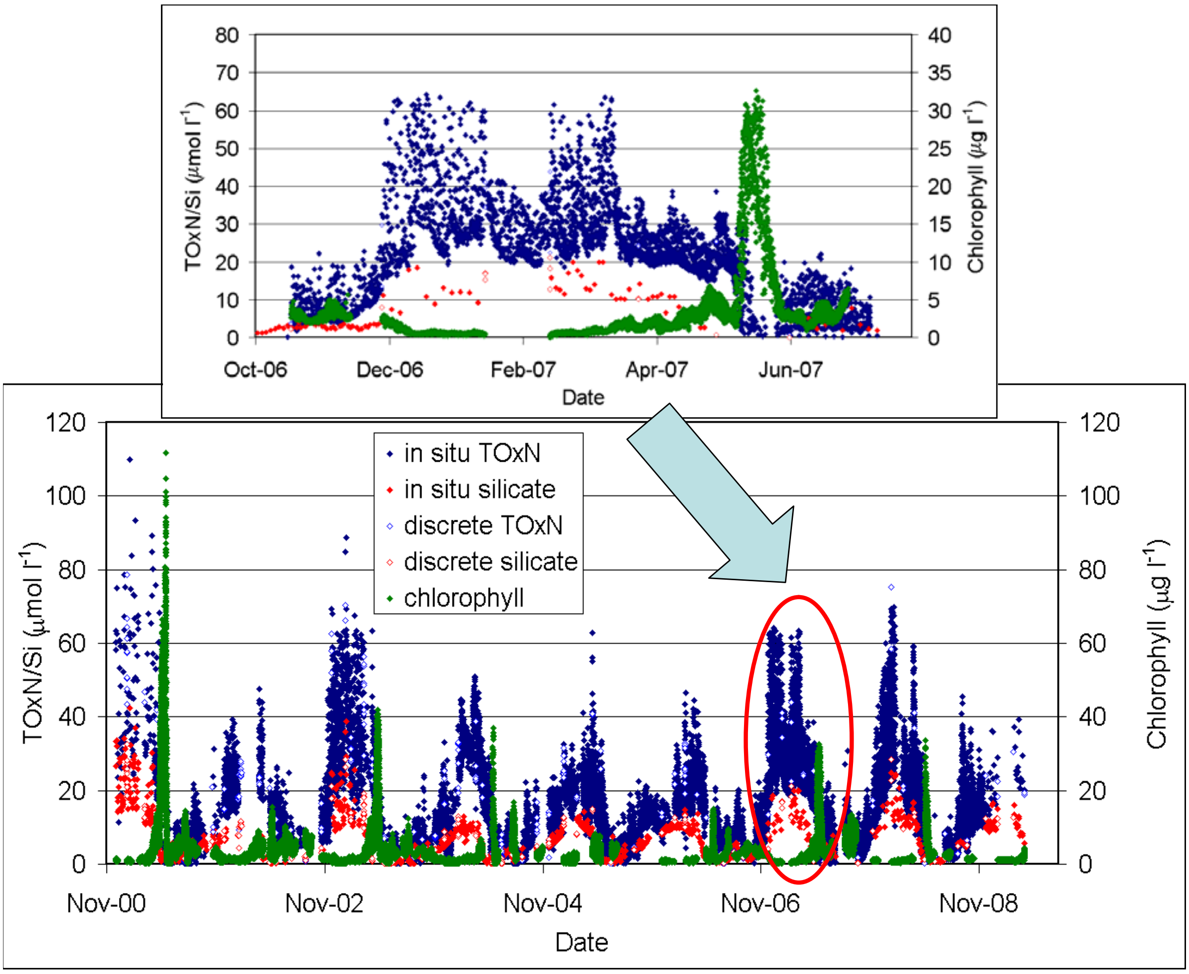

Figure 1. Time series of TOxN and silicate at the Warp in the Thames Estuary, UK. Chlorophyll data from calibrated chlorophyll fluorescence, in situ TOxN is combined data from NAS-3X and WMS, in situ silicate is from WMS samples. Discrete TOxN and silicate are results from samples collected by rosette and analysed by continuous flow analysis. Strong inter annual and seasonal variability in nutrient concentrations is evident. The expanded section is from 1/10/2006 to 01/08/2007; the strong seasonal signal of increasing nutrients during the autumn/winter and the draw down of nutrients with the simultaneous increase in chlorophyll biomass are evident.

5.2. Seasonal variability

There is a strong seasonal signal in the nutrients data from the moorings with concentrations of TOxN and silicate increasing during the autumn and winter (Fig. 1 and Fig. 2). There is a rapid draw down of nutrients in the spring coincident with the spring bloom which varies in its timing and magnitude each year. Within the OSPAR assessment, average winter TOxN concentrations are calculated and compared to a threshold to assess nutrient enrichment. The biological response to nutrients is assessed as the mean growing season (March to September) chlorophyll concentration relative to assessment thresholds. Data from SmartBuoys have been used to investigate the controls on the timing and amplitude of the spring bloom and simultaneous depletion of nutrients in these coastal locations [5]. The underwater light conditions and the physical structure of the water column have been shown to be important controlling factors in Liverpool Bay [5].

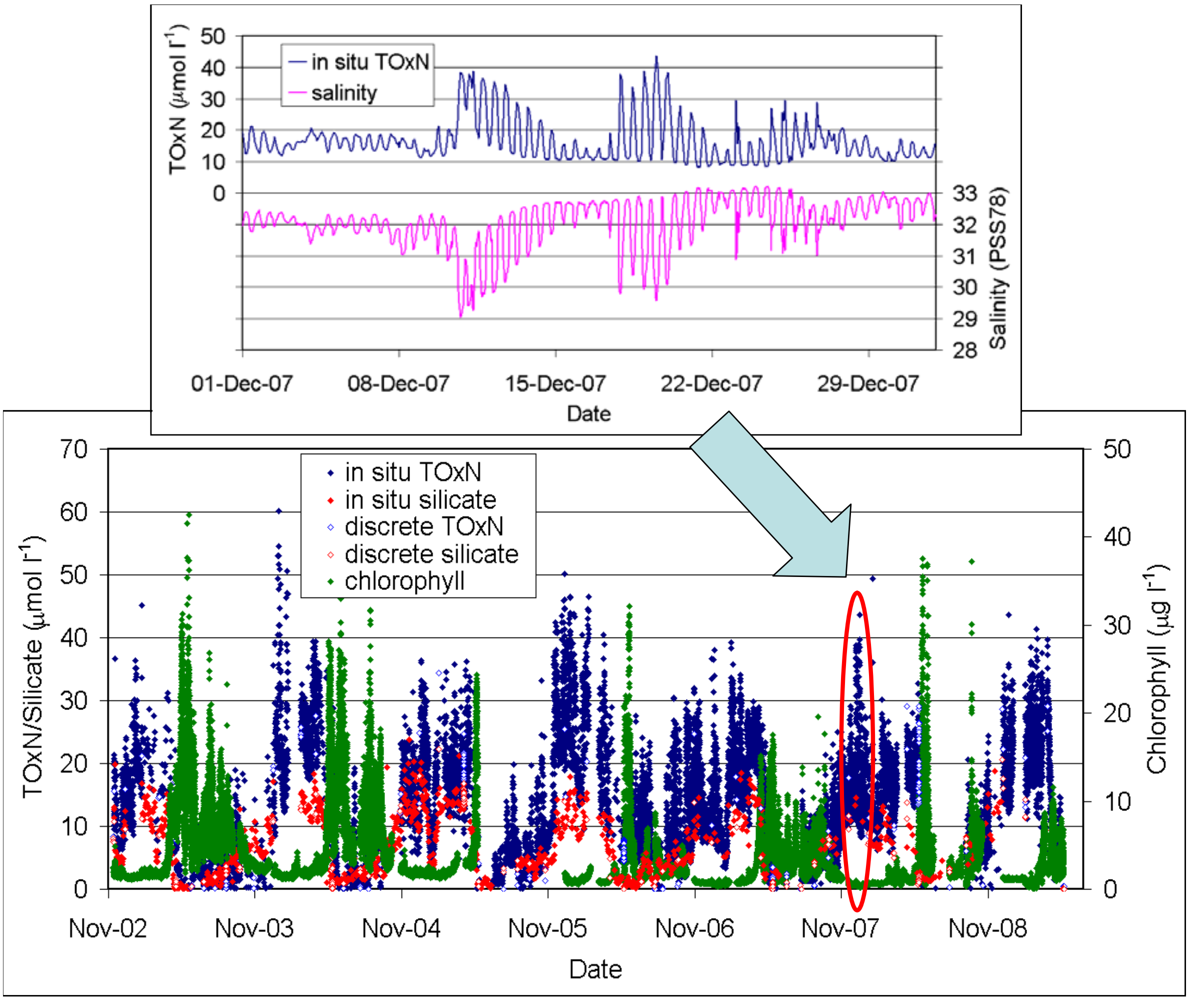

Figure 2. Time series of TOxN and silicate at Liverpool Bay, UK. Chlorophyll data from calibrated chlorophyll fluorescence, in situ TOxN is combined data from NAS-3X and WMS, in situ silicate is from WMS samples. Discrete TOxN and silicate are results from samples collected by rosette and analysed by continuous flow analysis. Expanded section shows TOxN and salinity from 1/10/2006 to 01/08/2007; the strong tidal signal evident in both parameters, with TOxN concentration showing a four fold increase over a tidal cycle. An increase in rainfall brings lower salinity water and elevated TOxN concentrations at the site.

5.3. Tidal variability

There is a strong tidal signal in the nutrients data from the moorings, particularly those in nutrient enriched coastal locations (Fig. 2). In order to allow for varying freshwater inputs of TOxN, mixing diagrams of TOxN against salinity are constructed for assessment purposes [2]. TOxN concentrations are then normalised to a specific salinity when assessing nutrient enrichment; samples with a salinity between 30 and 34.5 are considered ‘coastal’ and are normalised to a salinity of

32, samples with a salinity of greater than 34.5 are considered offshore and normalised to a salinity of 34.5. Such a normalisation process allows a consistent assessment procedure to be applied across different water bodies.

5.4. Short term episodic ‘events’

Short term episodic ‘events’ such as increased rainfall are also observed in the TOxN timeseries. For example, at Liverpool Bay increased rainfall is observed as a lowering in the salinity observed at the site and an increase in the TOxN as measured by the NAS-3X (Fig. 2). Such short term events are captured with in situ monitoring but may well be missed by ship-based surveys. In spring and summer such ‘events’ may be important in delivering additional nutrients which fuel biomass growth. The episodic input of nutrients throughout the year in Liverpool Bay supports continued algal growth from April to October (Fig. 2) and could increase the mean growing season chlorophyll concentration increasing the risk of eutrophication

6. LESSONS LEARNT

Sustaining a network of high frequency in situ observations with SmartBuoy has presented many challenges. The importance of maintaining a clear audit trail from instrument preparation to data quality assurance and archive must not be under estimated. The use of an integrated SmartBuoy database has enabled such an audit trail to be maintained. Standard procedures for instrument service and preparation have been developed to ensure continued consistent performance across SmartBuoy locations. The team involved with the SmartBuoy programme includes software developers, electronics engineers, chemists, laboratory technicians and field technicians and the need to communicate effectively in such a multi disciplinary team is essential for the programme to run effectively. The SmartBuoy network is designed to provide quality assured data on a routine basis and therefore any changes to its operation, including addition to the payload or altering the configuration of instruments, must be carefully tested to ensure quality is not compromised.

7. CONCLUSIONS

In situ measurements made by SmartBuoy reveal the variability in the nutrient concentrations at a range of UK coastal sites. Understanding the nature of the variability enables more accurate assessments of water quality to be made. The SmartBuoy network is a key component of the UK marine monitoring strategy and in combination with model outputs and remote sensing, the data from the network provide a greater understanding of the effects of anthropogenic nutrient inputs and enable a more robust assessment of water quality to be made.

8. REFERENCES

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