

Multi-year high frequency nutrients measurements in an operational data buoy network



N. Greenwood, D. K. Mills, D. B. Sivyer, D. J. Pearce, S. J. Malcol, J. Keable, T. A. Hull, N. S. Needham and H. E. Lees
Centre for Environment, Fisheries and Aquaculture Science, Lowestoft, UK
www.cefas.co.uk

Overview

Cefas has run an operational SmartBuoy (data buoy) network since November 2000 (Mills *et al.*, 2005), 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 (Figure 1), the data from which contribute to robust assessments of water quality and ecosystem health such as the eutrophication assessment required by OSPAR (Foden *et al.*, accepted), the ecological status assessment for the Water Framework Directive and, in the future, the environmental status assessment for the Marine Strategy Framework Directive.

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*.



Figure 1. Locations of SmartBuoys denoted by triangles, data are presented for locations highlighted in red

Methods

The Cefas SmartBuoy provides measurements of nutrients using two different approaches which allow for comparison of datasets and builds in redundancy to avoid complete loss of data (Table 1). The NAS-3X uses a traditional wet chemistry method in a robust submersible casing to determine TOxN (nitrate + nitrite) *in situ*. Use of an on-board calibration standard provides a calibration every six samples and a pre deployment nitrate standard is run before deployment to assess accuracy and precision. The Aqua Monitor collects samples and stores them in bags pre loaded with mercuric chloride. These samples are analysed on return to the laboratory for TOxN, silicate and phosphate (only when negligible suspended particulate matter). In addition, discrete samples are collected during mooring service cruises and analysed by continuous flow analysis.

Sample type	Method	Frequency	Accuracy	Precision
NAS-3X (SmartBuoy, UK)	<i>in situ</i> , wet chemistry, submersible, continuous flow analysis (CFA) using a pre-deployment standard for nitrate to check accuracy and precision	TOxN (1)	±1.8 %	±1 %
Aqua Monitor (SmartBuoy, UK)	samples collected and stored in sample bags pre-loaded with mercuric chloride, analysed in laboratory by continuous flow analysis	TOxN, Silicate, Phosphate	±0.8 %	±1.1 %
Mooring service cruises	continuous flow analysis	TOxN, Silicate, Phosphate	±0.6 %	±1.1 %

Table 1. Methods of nutrients analysis within the SmartBuoy programme
(1) TOxN (nitrate + nitrite) (2) if negligible suspended particulate matter (3) relative to pre deployment standard (4) relative to laboratory standard

Acknowledgements
This work was funded by Defra as part of the UK Marine Monitoring and Assessment Strategy (UKMMAS) through contract SLA25. The SmartBuoy in Liverpool Bay forms a part of the Liverpool Bay Coastal Observatory (www.cobs.pol.ac.uk) coordinated by the Proudman Oceanographic Laboratory.

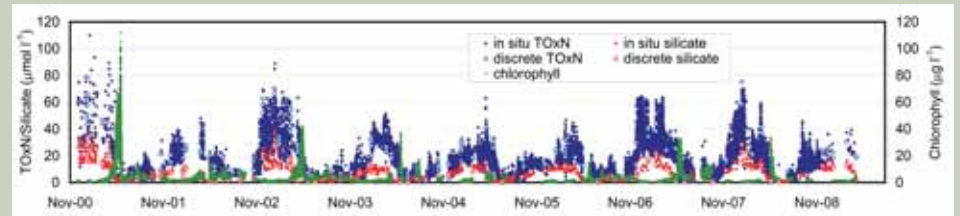


Figure 2. Time series of nutrients and chlorophyll biomass (from calibrated chlorophyll fluorescence) in the Thames Estuary, UK. Inter annual and seasonal variability in nutrient concentrations are evident

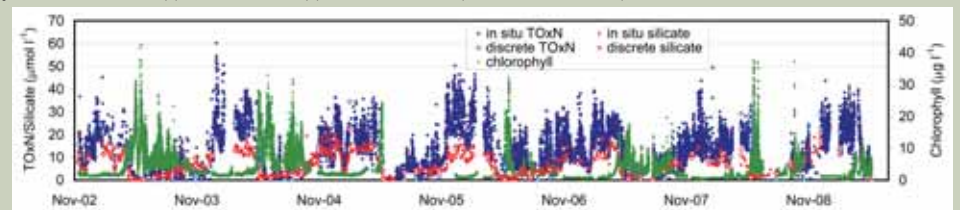


Figure 3. Time series of nutrients and chlorophyll biomass (from calibrated chlorophyll fluorescence) in Liverpool Bay, UK. Inter annual and seasonal variability in nutrient concentrations are evident

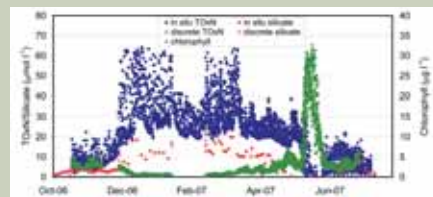


Figure 4. Expanded section from Thames Estuary time series which highlights the strong seasonal signal of increasing nutrients during the autumn/winter and the draw down of nutrients in the spring with the simultaneous increase in chlorophyll biomass

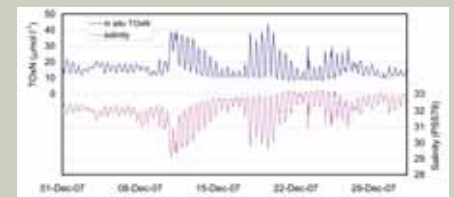


Figure 5. Expanded section from the Liverpool Bay time series shows the strong tidal signal evident in TOxN and salinity, with TOxN concentration showing a four fold increase over a tidal cycle. An increase in rainfall brings lower salinity water and elevated TOxN concentrations at the site

Quality assurance

- A linearity check of the NAS-3X is carried out to verify the linear range of the instrument and a limit of detection calculated
- Accuracy and precision of NAS-3X nutrient analyser assessed from results of pre-deployment standard
- Accuracy of NAS-3X ensured by use of on-board calibration standard throughout deployment
- Results from Aqua Monitor compared to results from the NAS-3X
- Results from Aqua Monitor and NAS-3X compared to results from discrete water samples
- Accuracy and precision of CFA assessed from results of external check standards

Results

Data from SmartBuoy have provided greater understanding of the variability in nutrients concentrations in UK coastal waters over a range of temporal scales.

- **Inter annual variability** in the concentrations of nutrients in UK coastal waters as shown in the Thames Estuary and Liverpool Bay (Figures 2 and 3). Such variability is reflected in a level of confidence which is attached to the assessment of nutrient enrichment, based on how many of the years exceed the nutrient assessment threshold.
- **Seasonal variability**; concentrations of TOxN and silicate increase during the autumn and winter (Figure 4) followed by 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 (November to February) 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.
- **Tidal variability** in nutrients concentrations, particularly those in nutrient enriched coastal locations (Figure 5). TOxN concentrations must be normalised to a specific salinity to allow for varying freshwater inputs of TOxN when assessing nutrient enrichment.
- **Short term episodic 'events'** such as the effects of increased rainfall are observed in the nutrients time series (Figure 5). Such short term events are captured with high frequency *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.

Conclusions

In situ measurements made by SmartBuoy reveal the variability in the nutrient concentrations at a range of UK coastal sites. In combination with model outputs and remote sensing, these data provide a greater understanding of the effects of anthropogenic nutrient inputs and enable a more robust assessment of water quality to be made.

References

Foden, J., Devlin, M. J., Mills, D. K., and Malcol, S. J. (accepted). Searching for undesirable disturbance: The OSPAR eutrophication assessment method applied to marine waters of England and Wales, Biogeochemistry.
Mills, D. K., Greenwood, N., Krüger, S., Devlin, M., Sivyer, D. B., Pearce, D., Cutchey, S., Malcol, S. J. (2005) New Approaches to Improve the Detection of Eutrophication in UK Coastal Waters. Environmental research, engineering and management, 2(32), 36-42.