

Characterising the seasonal cycle of dissolved organic nitrogen using Cefas SmartBuoy high-resolution time-series samples from the southern North Sea

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Received: 14 April 2011 / Accepted: 5 April 2012 / Published online: 9 May 2012
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Abstract The Cefas SmartBuoy network provides a unique insight into the biogeochemical dynamics of the Northern European shelf seas, particularly the North Sea, through high-resolution automated off-shore water sampling. We present total dissolved nitrogen and dissolved organic nitrogen (DON) from the Dowsing SmartBuoy site (53.531° N, 1.053° E) from January to October 2010, the first high resolution seasonal (winter-autumn) cycle of DON from the open North Sea. On top of a refractory background DON concentration of approximately 5 μM , a rapid increase in DON of a further $\sim 5 \mu\text{M}$ is observed over the course of the spring bloom. This rapidly produced DON declines at an estimated net decay rate of between 0.6 and 1.8 $\mu\text{M month}^{-1}$. The slow decay suggests that the majority of the additional DON produced during the spring bloom is of semi-labile nature and has a lifetime of weeks to months. The dataset allows us to tightly constrain the budget for water column nitrogen over the winter, spring and summer of 2010 and clearly demonstrates the

‘sawtooth’ nature of the seasonal cycle of DON in the open North Sea, which has been impossible to resolve with a more traditional ship-based mode of operation. This work highlights the importance of autonomous sampling approaches in better understanding shelf sea biogeochemistry in the future.

Keywords Dissolved organic nitrogen · North Sea · Ammonium · Total dissolved nitrogen · SmartBuoy

Introduction

Understanding the cycling of nitrogen (N) compounds in the marine environment is important in our understanding of new and recycled primary productivity in surface waters (e.g. Eppley and Peterson 1979; Yool et al. 2007). It is also important in relation to the production of climate-active gases such as nitrous oxide, ammonia and alkyl nitrates throughout the water column (e.g. Bange et al. 2009; Johnson et al. 2007; Hughes et al. 2010). The microbial nitrogen cycle is complex, with multiple oxidation states and transformation pathways. In its simplest form, the marine microbial N cycle consists of the reduction of nitrate (NO_3^-) to particulate organic nitrogen (PON; within the cells of living organisms and in detrital and fecal material), which is then either remineralised to ammonium (NH_4^+) by heterotrophic

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activity (ultimately by bacterial breakdown, although commonly considered to be related to zooplankton grazing) or exported from the water column. After drawdown of NO_3^- , N is cycled between PON and NH_4^+ until it is ultimately nitrified back to nitrate, which is a dominant N transformation below the thermocline in the deep ocean; and in the sediments or lower water column of well mixed shallow seas (e.g. Lohse et al. 1993). N may also be removed from the system by denitrification of nitrate (or removal of ammonium by anammox) to N_2 gas in low oxygen conditions (e.g. Brandes and Devol 2007). In coastal and shelf seas, nitrogen cycling is further complicated by riverine and atmospheric inputs, which are substantial forcings in (e.g.) the southern North Sea (SNS) system (e.g. Jickells 1998, 2005).

Dissolved organic nitrogen (DON) in the marine N cycle is an important intermediary in the remineralisation of PON, and a potentially significant sink of N if the DON becomes part of the refractory DON pool (e.g. Berman and Bronk 2003). The composition of the marine DON pool is poorly characterised; and will vary considerably with season, location and biogeochemical regime. DON is predominantly of biotic origin (McCarthy et al. 1997) and has a wide compositional range, from long-lived, almost completely bio-inert material such as degradation-resistant bacterial cell wall materials (e.g. Bronk 2002) through to highly biologically labile materials which can be directly assimilated by primary producers, such as amino acids and primary amines (e.g. Berman and Bronk 2003; Lønborg et al. 2009; Van Engeland 2010). A recent review has suggested that some parts of the ‘semi-labile’ and refractory DON pools may also be accessible to phytoplankton under certain conditions (Bronk et al. 2007), but the primary turnover of these pools is probably due to heterotrophic bacterial activity. Bacteria may assimilate DON as a C and N source, releasing or assimilating NH_4^+ to balance their internal C:N ratios (e.g. Kirchman 2000; Johnson et al. 2007), or directly metabolise DON for energy, yielding NH_4^+ . As well as multiple sink terms, there are undoubtedly multiple sources of DON as well. Phytoplankton will exude DON, either through leakage or release for particular purpose e.g. biosignalling, defense etc; the nature and quantity of DON released being dependent on conditions and phytoplankton species. Intracellular DON (in phytoplankton and bacteria) will be released by maceration during

grazing, and bacterial action will release DON from PON in dead and dying cells and detritus. Furthermore, photolysis of large biologically inert N-containing organic molecules has been shown to yield smaller, bio-available DON molecules (Bushaw et al. 1996); but there is also photochemical mineralisation of organic nitrogen to NH_4^+ (Kitidis and Uher 2008). Thus the dynamics of DON on short timescales (days to weeks) is extremely complex.

On longer timescales, the characteristic marine seasonal cycle of DON is rather poorly known both in terms of DON composition and total concentration. It is commonly found that there is a sizeable ‘baseline’ concentration of refractory DON which comprises a significant proportion of the total fixed nitrogen in the water column, which is assumed to be roughly constant throughout the year (Bronk 2002); presumably with loss terms (photolysis, slow bacterial breakdown, export) balanced on an annual timescale by a modest background production term. In oligotrophic open-ocean water there appears to be little seasonality in the datasets from the Hawaii Ocean Time Series (Church et al. 2002) and the Bermuda Atlantic Time Series (Hansell and Carlson 2001; Knapp et al. 2005), with similar concentrations observed in the surface and deep oceans, suggesting a lifetime for this refractory pool of hundreds of years or more. To our knowledge there are no studies of the seasonal cycle of DON in the temperate or high-latitude open-ocean, so in the absence of a data compilation and synthesis effort the nature of such is unknown. However, recent temperate and high-latitude coastal and shelf sea studies have presented a number of seasonal DON datasets which suggest a possible coherent characteristic seasonal cycle (discussed below), and these have provided the impetus for this study.

Coastal seas are one of the most valuable habitats on the planet (Costanza et al. 1997) but are threatened by numerous global change pressures including increasing nutrient loads (Jickells 1998). This is particularly true for some regions of the North Sea, which is surrounded by dense population centres with associated industrial, domestic and agricultural pollution. The effective management of these pressures requires an understanding of the nitrogen cycle and the transport and fate of nutrients in coastal seas. Temperate coastal waters such as the shallow southern North Sea (SNS) are characterised by a strong

biological seasonal cycle with relatively high nutrient concentrations and low (light limited) primary productivity and phytoplankton biomass in winter (Weston et al. 2004; Capuzzo 2011). In the SNS, a strong spring bloom results in almost complete draw-down of inorganic nutrients, leading to a summer season with low inorganic nutrient concentrations, and moderate productivity sustained by nutrient recycling (Weston et al. 2004).

The fate of the nitrate-N lost from the water column during the spring bloom is uncertain. Weston et al. (2004) noted that there appears to be little long-term sedimentation of organic matter in the SNS, hence the nitrogen must either be lost from the system through denitrification or be stored temporarily as PON, NH_4^+ or DON. Weston et al. (2004) showed that about half of the lost nitrate is transformed to PON and ammonium. The potential importance of DON in this role as a temporary reservoir for N over the seasonal cycle and its poorly characterized nature have been emphasised by several authors (e.g. Berman and Bronk 2003; Van Engeland et al. 2010). Model studies suggest that the majority of primary production in the North Sea system is driven by recycled nutrients, although the relative contributions of NH_4^+ and DON to recycled production is unresolved (Proctor et al. 2003). Hydes et al. (1999) and Van Engeland et al. (2010) emphasise the need for better measurements of DON to improve our understanding of this recycling. Suratman et al. (2010) recently presented data that suggest that 5–10 μM of nitrate may be rapidly converted to DON during the spring bloom, but their results do not include the post-bloom summer recycling period so it is unclear whether the DON increase they observed was a transient spike or a more long-lived feature of the post-bloom recycling regime. Furthermore, they did not measure ammonium concentrations in their samples so their DON estimate relies on the assumption that NH_4^+ is low relative to DON.

Van Engeland et al. (2010) have presented 10 years of 1-month resolution time series data from a number of stations on the eastern side of the southern North Sea. This mature dataset has provided substantial insight into the dynamics of DON in the SNS. They find that DON at their coastal stations (all <12 m deep and immediately adjacent to land and strongly river-influenced) shows very strong seasonality, with DON peaking at (on average) $\sim 15 \mu\text{M}$ within 1 month of the spring bloom chlorophyll peak and then decreasing

steadily over the rest of the productive part of the year to return to winter values of ~ 8 to $10 \mu\text{M}$. Rapid increase in DON associated with the spring bloom seems in good agreement with the observations of Suratman et al. (2010). However in the ‘open sea’ sites studied by Van Engeland et al. (2010), away from immediate coastal influence but south of the Dogger Bank, such sharp transitions in DON and seasonality are weak or absent in multi-year averaged data. In the coastal Arctic however, Simpson et al. (2008) find a near doubling of DON concentration over the spring bloom and subsequently a gradual decrease over the rest of the year. A similar, ‘sawtooth’ pattern of DON concentration is also observed in UK coastal and estuarine data by Lønborg et al. (2009) and Agedah et al. (2009) respectively.

We hypothesise that this sawtooth pattern is characteristic of the cycle of DON in productive, shallow seas. We suggest that the increase in DON concentration over the spring bloom has already been partly captured by Suratman et al. (2010); and that the lack of clear seasonality in the open sea site investigated by Van Engeland et al. (2010) is due to low resolution (monthly) sampling being unable to resolve these events, rather than the absence of a cycle. Furthermore we set out to test the assumption made by Suratman et al. (2010) that NH_4^+ is a small component of total dissolved nitrogen in the North Sea throughout the productive period of the seasonal cycle.

The Cefas (Centre for Environment, Fisheries and Aquaculture Science) SmartBuoy network of moorings in the shelf seas surrounding the UK (e.g. Mills et al. 2003, 2005; Greenwood et al. 2010) provides a unique opportunity for observing such processes at a high resolution unachievable by conventional oceanographic fieldwork, with continuous measurement of key physical and biogeochemical parameters and high frequency autonomous water sampling. We take advantage of a near unbroken time-series of water samples from February to October 2010 from the Dowsing SmartBuoy site (Fig. 1) to test the above hypotheses. We build upon the core chemical measurements of TOxN (total oxidised inorganic nitrogen; the sum of NO_3^- and NO_2^-) conducted routinely on SmartBuoy water samples; making additional measurements of total dissolved nitrogen (TDN) and NH_4^+ concentrations to derive DON. As well as evaluating the hypotheses laid out above we find that the dataset produced allows us to infer the lifetime of the DON

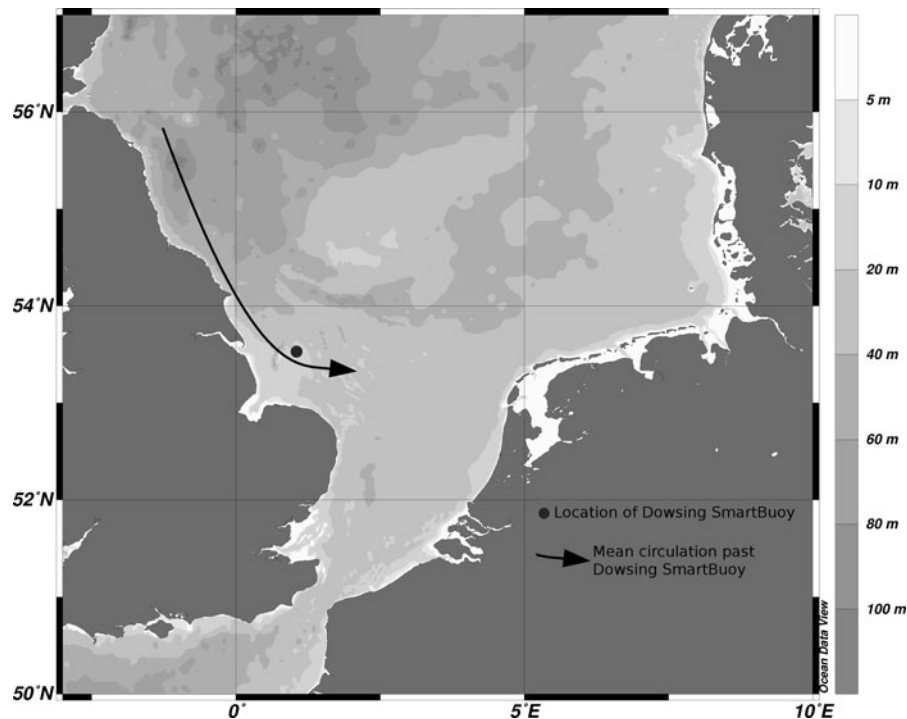


Fig. 1 Location of the Dowsing SmartBuoy and the general circulation responsible for water movement past the Dowsing site. This is part of the wider general circulation of the North Sea, which is characterised by southward transport down the east

coast of the UK changing to eastward transport at around the latitude of the Dowsing site (Queste 2011; Winther and Johannessen 2006)

accumulated over the seasonal cycle and we are able to close the budget for water column N at the Dowsing site, answering the question of how the nitrogen lost from the nitrate pool is divided between the other N reservoirs and sinks over the summer period.

Methods

Sampling site

The Dowsing SmartBuoy (53.531° N, 1.053° E) is situated approximately 40 miles east of the Humber Estuary in 22 m of water (sampling depth at 1m). The water column is tidally mixed throughout the year with no seasonal stratification (Elliott et al. 1991; Ducrotoy et al. 2000) and typically more than 99 % of the water at Dowsing is of North Atlantic origin, advected down the East coast of the UK (Ducrotoy et al. 2000, Queste 2011, this issue). There is a contribution of water from the outflow of the Humber and the Wash, but based on salinity data from the Dowsing site, freshwater sources

contributed at most 1 to 1.5 % of the surface water mass in 2010. The net circulation at the Dowsing site is of the order of 1 km per day or less in summer (Ducrotoy et al. 2000; Winther and Johannessen 2006), suggesting that in situ (biological) processes in summer would be sufficiently rapid relative to advection and thus would be the major controls on biogeochemistry.

SmartBuoy moorings and sample collection

The SmartBuoy moorings include in situ sensors for salinity, temperature, chlorophyll fluorescence, optical backscatter and photosynthetically active radiation at the surface and at 2m depth (Mills et al. 2005). In addition, automated water samplers operate by pumping samples into polyethylene bags pre-injected with 5 ml of 1.4 g/l mercuric chloride (HgCl_2 , in ultrapure water) as a preservative. SmartBuoys are regularly serviced; at least every 2 months each mooring is retrieved for full overhaul and new buoys are deployed in their place, maximising the return of continuous

high precision data. Thus these moorings provide unique temporal coverage of biogeochemical parameters and water samples for time-series based biogeochemical investigations. In this study we use (unfiltered) water samples (150 ml) collected using Enviro-tech AquaMonitor water sampling units mounted at 1m depth on Dowsing SmartBuoys and preserved with mercuric chloride (HgCl_2).

Inorganic nutrients

SmartBuoy bag samples were filtered on return to shore using 0.2 μm pore size Whatman CycloPore polycarbonate filters and analysed at the Cefas laboratory for TOxN using a Skalar SAN plus segmented flow autoanalyser, by standard spectrophotometric methods (Kirkwood 1996). Unpreserved samples taken during mooring changeover cruises (also at 1m depth) were analysed for phosphate (PO_4^{3-}), which is not measured routinely in SmartBuoy sample analysis due to possible preservation issues associated with adsorption and desorption to/ from particulate matter in unfiltered bag samples (Suratman et al. 2010). Calibration was conducted using in-house standards prepared in nutrient-depleted natural seawater and checked against commercial seawater nutrient standards (Ocean Scientific International Ltd (OSIL), UK). Quality control of results for discrete samples analysed for inorganic nutrients is assured by participation in the Quality Assurance for Marine Environmental Measurements (QUASIMEME) scheme. Repeat measurements of blanks and top standards assures that the analytical precision of TOxN measurements is better than 5 % in all cases.

Ammonium concentration was measured using the manual fluorimetric method, broadly following the technique outlined by Holmes et al. (1999), but accounting for improvements to estimates of background fluorescence (BF) effects presented by Taylor et al. (2007). In brief, the Holmes et al. (1999) working reagent (WR) containing the fluorescent compound ortho-phthalaldehyde (OPA) was added to samples, which were analysed on a Jasco-FP750 spectrofluorometer at 380nm (excitation) and 420nm (emission) after between 3 and 12 h incubation. Matrix effects and fluorescence change over time were mitigated by conducting calibration by standard additions to every sample. It was found that the presence of HgCl_2 substantially inhibited

fluorescence, the reasons for which are currently being investigated. However to mitigate this in these samples, large WR:sample volume ratios (3:1) were used which improved sensitivity by dilution (and reduced sample volume requirement) over lower ratios. Measurements of low ammonium seawater indicate a precision of ± 60 nM and a detection limit of ~ 150 nM, which is substantially higher than that achievable using the same method in fresh (i.e. unpreserved) samples (Johnson et al. 2007, 2008). It is possible that addition of HgCl_2 may rupture cells in the stored samples prior to filtering, leading to overestimation of NH_4^+ ; however preliminary tests show that there was no significant difference between fresh samples collected at sea and analysed immediately and samples treated with HgCl_2 and stored for up to 4 weeks in sample bags. For the purposes of the analysis presented here it is sufficient to consider the NH_4^+ data as an upper estimate of in situ concentration. However, the pattern of ammonium concentrations measured in this study (mostly low concentrations with occasional spikes) is very similar to that observed in the SNS by Asman et al. (1994), although absolute concentrations are roughly a factor of two lower in this study, which suggests that the NH_4^+ measurements from the stored preserved SmartBuoy samples are probably not overestimates.

Total dissolved nitrogen and DON

Total dissolved nitrogen (TDN) was quantified by high temperature catalytic oxidation on a Skalar Formacs HT instrument with a CoCr/CeO₂ catalyst at 850°C; and subsequent measurement by chemiluminescence detection online using a Skalar ND20 analyser. Calibration was conducted by standard additions of potassium nitrate solution to 5 ml aliquots of repeat samples. During each run of up to 60 samples, at least 2 high TDN (DSR 05/10) certified reference seawater samples (Hansell 2005) were used to monitor instrument performance for quality control purposes. Analytical precision was better than 2 % in all cases. Repeat measurements of the DSR 05/10 certified reference samples across all runs averaged 33.2 ± 1.7 μM compared to the inter-laboratory consensus value of 32 ± 2 μM . The uncertainty in absolute concentrations varied between sample runs due to the uncertainty associated with calibration by standard additions.

Table 1 Summary of uncertainties in the measurement of TDN

Sample run	Analytical uncertainty (%)	Calibration uncertainty (μM)	CRM scaling factor
18/01/11	<2	± 0.82	1.08
25/01/11	<2	± 0.69	0.94
21/02/11	<2	± 3.4	0.93
15/03/11	<2	± 4.7	0.99
22/03/11	<2	± 1.8	0.93

Certified reference material (CRM) scaling factor refers to the degree of scaling required to fit the measured CRM concentrations with their mean consensus value (Hansell 2005), as described in the main text

A summary of the uncertainties associated with measurement of TDN is presented in Table 1. In order to ensure consistency between sample runs, each run was scaled so that the measured value of DSR 05/10 certified reference seawater matched the consensus value of $32 \pm 2 \mu\text{M}$.

Preliminary storage experiments compared fresh seawater samples with the same water treated in the same way as the SmartBuoy samples (i.e. inoculated with HgCl_2 in sample bags). These showed no significant difference after 0 and 4 weeks of storage for TDN and TOxN (i.e. to within the uncertainty in repeat measurements, fresh and stored sample concentrations were equivalent). Hence we assume that the TDN and TOxN data from stored samples are representative of in situ concentrations at the time of sampling.

DON was calculated as the difference between TDN and the sum of TOxN and NH_4^+ . Maximum uncertainty in the DON estimate propagated through from individual measurements was $< \pm 3 \mu\text{M}$ in all cases.

Ancillary parameters

Values of chlorophyll fluorescence, dissolved oxygen and salinity recorded by the SmartBuoy sensors are presented. Full details of the oxygen sensors and calibration method can be found in Greenwood et al. (2010). Fluorescence is presented in arbitrary units as the sensors were uncalibrated. However, when calibrations are applied to such sensors they are routinely linear calibrations and as such uncalibrated values are

sufficient for the comparative analysis we conduct. Similarly, raw chlorophyll-a from MODIS-Aqua data retrievals (also in arbitrary units) is presented as a first order validation of the in situ chlorophyll, confirming the bloom/transition period of maximum chlorophyll (Fig. 2).

Results and discussion

Seasonal cycle

The seasonal cycle of water column nitrogen is shown in Fig. 2 along with ancillary in situ and satellite parameters. The plot is divided into three time periods by vertical dashed lines, which are based on the TOxN and in situ fluorescence data: i) ‘pre-bloom’ conditions prior to the spring chlorophyll maximum and the start of nitrate depletion (up to 31/03/2010); ii) ‘transition’, the period from 01/04/2010 to 28/04/2010 where the spring bloom develops, and nitrate drawdown and maximum fluorescence occurs (so called because it is the period over which nitrate concentration changes rapidly and therefore the system transitions between light and nutrient limitation); and iii) subsequent ‘post-bloom’ conditions where nitrate is exhausted, a nutrient recycling regime presumably dominates and fluorescence decreases to a more steady level.

Prior to the spring bloom and sharp drawdown of NO_3^- , TDN and TOxN are strongly correlated ($R^2 = 0.92$, $n = 22$, $p < 0.0001$), with TOxN composing on average 58 % of TDN. The remaining TDN is composed primarily of DON, with up to 10 % contribution from NH_4^+ . There is only a weak relationship between TDN and DON ($R^2 = 0.36$, $n = 22$, $p < 0.1$) during the same period, suggesting that the strong covariance in TDN and TOxN is not due simply to the interaction of two differing water masses. In fact, the large decrease in TDN and TOxN in early March is associated with increased chlorophyll and a peak in DON of up to 80 % of TDN; whereas the two peaks in TDN and TOxN in late March immediately before the onset of the spring bloom are not associated with substantial changes in chlorophyll, but with decreases in salinity, suggesting that mixing and circulation effects may have been responsible for these changes, e.g. increased contribution from English Channel water or advection from the Southern Bight

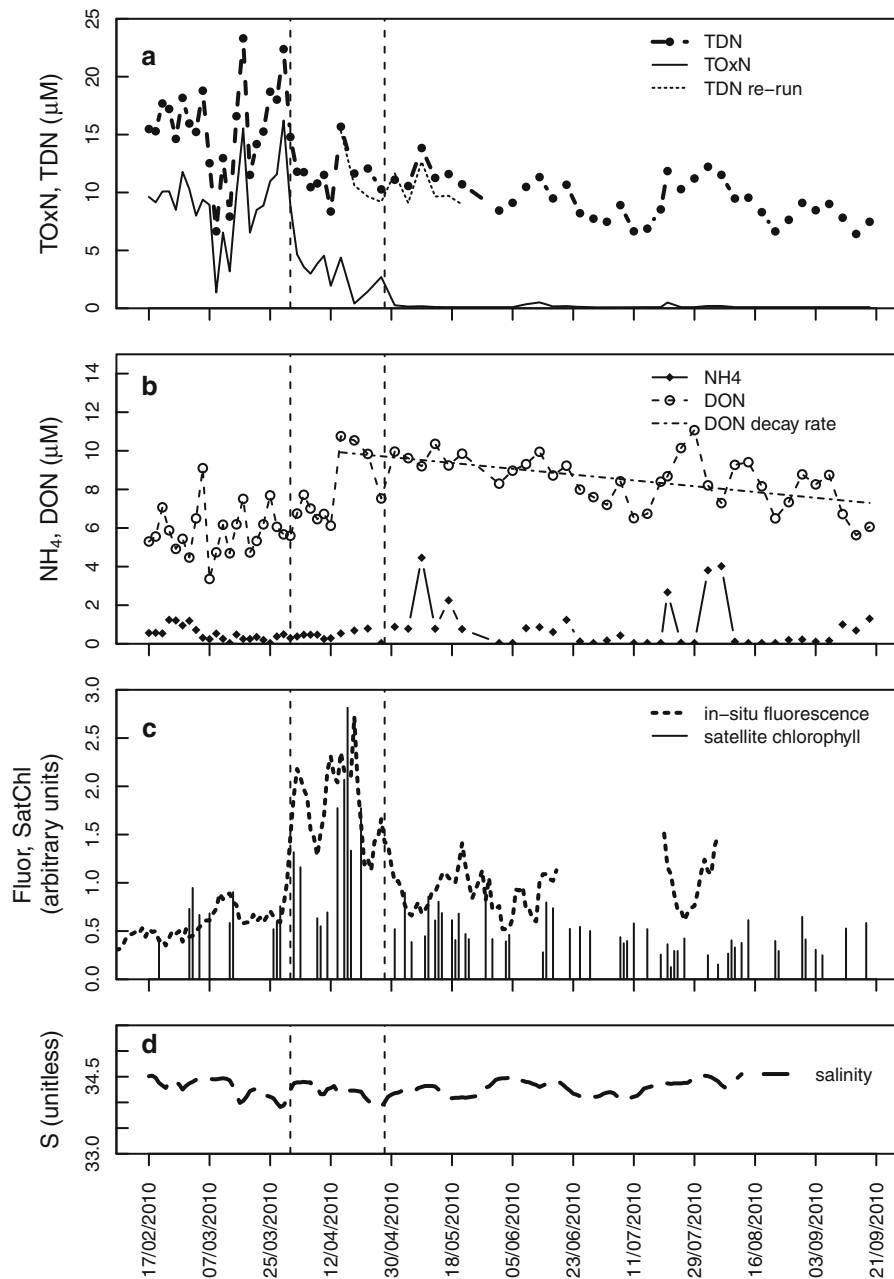


Fig. 2 January to September data from the Dowsing Smart-Buoy site for 2010 focusing on nitrogen cycle parameters: **a** TDN (total dissolved nitrogen), TOxN (total oxidisable nitrogen, $\text{NO}_3^- + \text{NO}_2^-$); **b** DON (dissolved organic nitrogen) and NH_4^+ ; **c** in situ fluorescence and satellite derived chlorophyll-*a*; **d** in situ salinity. Vertical dashed lines delineate the pre-bloom, transition and post-bloom regimes. Repeat measurements of samples from one SmartBuoy deployment (Dowsing

10) on a separate run of TDN analyses shows good agreement (TDN re-run in **a**) with data from the initial run ($R^2 = 0.84$, systematic difference of $\sim 8\%$ and average residual difference of $\sim 1.6\%$). The DON decay rate plotted in **b** is the result of linear regression analysis of the change in DON over time from the peak DON during the spring bloom to the end of the dataset in late September (see text for details)

Table 2 Summary of changes in mean concentrations of N reservoirs over the study period (median values in parentheses)

Form of N	Pre-bloom	Bloom/transition	Post-bloom	Net change
TDN	15.4 (15.6)	11.4 (11.6)	9.5 (9.3)	−5.9 (− 6.1)
TOxN	9.3 (9.3)	3.0 (3.3)	0.2 (0.1)	−9.1 (− 9.1)
NH ₄ ⁺	0.50 (0.43)	0.44 (0.47)	0.80 (0.21)	+0.37 (− 0.22)
DON	5.8 (5.6)	7.9 (7.3)	8.4 (8.6)	+2.9 (+3.0)
DON as percentage of TDN	39 % (35 %)	74 % (73 %)	90 % (95 %)	+51 (60)

All data in μM except percentage DON. Where mean values are presented in bold text, they are statistically significantly different from the mean concentrations of the same N reservoir from the other two time periods (Student's *t* test, $p < 0.001$)

of the North Sea, possibly along with a changing contribution from the riverine system.

As the spring bloom rapidly removes nitrate from the water column in mid-April, TDN and TOxN start to become decoupled. There is poor correlation between TDN and TOxN within the transition and post-bloom periods ($R^2 = 0.12$ and 0.26 respectively). TDN decreases over the course of the spring bloom by $\sim 6 \mu\text{M}$ (Fig. 2) and there is clearly substantial conversion of NO_3^- to other forms (principally DON) during the transition period and post-bloom periods, representing the return of nitrogen to the dissolved phase from the particulate, lessening the overall decrease in TDN due to nitrate uptake by primary producers. As shown by Suratman et al. (2010), an increase in DON can be discerned during the transition period, associated with drawdown of nitrate and either direct release of DON by photosynthesisers or the heterotrophic breakdown of photosynthetic cells. The contribution of DON to TDN increases from 35 % in pre-bloom conditions to 95 % post-bloom and there is an associated absolute increase in concentration of DON from ~ 6 to $\sim 9 \mu\text{M}$ (Table 2). Table 2 demonstrates that the pre-bloom and post-bloom concentrations of DON are statistically significantly different (as are those of TDN and TOxN, but not NH_4^+); providing a formal proof of the hypothesis that there is a discernible seasonality to the DON signal.

NH₄⁺ concentrations

Ammonium remains relatively low ($< 1 \mu\text{M}$) throughout most of the study period with occasional peaks of up to $5 \mu\text{M}$, which are likely to be associated with transient decoupling of uptake and regeneration processes (Johnson et al. 2007), or possibly with

resuspension events (Caetano et al. 1997; Morin and Morse 1999). The latter is unlikely as DON is thought to be released in resuspension events in greater concentrations than NH_4^+ (Fitzsimons et al. 2006), and associated DON spikes are not observed in this dataset. Although concentrations remain predominantly low in the post-bloom period it is likely that ammonium supports the majority of the primary productivity over this period as found previously (e.g. Proctor et al. 2003; Weston et al. 2004) and is turned over rapidly; on the order of a few days at most (Johnson et al. 2007). Thus a regime can be envisaged where, over the course of the productive period of the year following the spring bloom, there is rapid recycling of ammonium via labile components of the DON pool, which would be similarly short-lived and at similar or lower concentrations to NH_4^+ (i.e. making a minor contribution to DON/TDN on average). Furthermore, any direct uptake of labile DON by primary producers as an N source may induce a further tight coupling between heterotrophic and autotrophic N cycling. However, as with ammonium it is possible that the decoupling of source and sink processes (heterotrophic or autotrophic) might lead to substantial transient peaks in this labile DON, particularly at times of regime change (e.g. spring bloom/crash, end of the recycling-dominated summer period). Thus labile DON may be making a significant contribution to the observed noise in the total measured DON concentration.

However, we suggest that there must be a less labile pool of N that is subject to net accumulation at the most productive periods in the seasonal cycle and net loss at other times. Indeed, following the initial sharp increase in DON concentrations of approximately $5 \mu\text{M}$ over the spring bloom (between 31/03/2010 and 15/04/2010), mean DON decreases over the course of

the post-bloom period. Linear regression analysis of the DON concentrations against time yields a rate of decrease of DON of $1.7 \times 10^{-2} \mu\text{M d}^{-1}$ ($0.5 \mu\text{M month}^{-1}$). This relationship is weak (time explaining 33 % of the variance in the data), but statistically significant ($p=0.0011$). This represents a *net* rate of DON degradation, integrating the multiple source and sink terms of the spectrum of DON compounds and their lability (since presumably DON production must continue at some reduced level after the spring bloom).

The role of phosphate

Might it be possible that there is accumulation and then gradual degradation of the *labile* DON fraction over the seasonal cycle, with highly bioavailable DON being utilised by neither photosynthesisers nor heterotrophs? This seems rather unlikely, as such compounds must be a rich and easily metabolised energy source for heterotrophs, regardless of other pressures on the ecosystem. However, it is conceivable that phosphate limitation might lead to a situation where the algal N requirement and thus uptake of DON might be inhibited. Samples taken during SmartBuoy servicing/ redeployment cruises are routinely analysed for inorganic phosphate concentration and these data are shown in Fig. 3.

Whilst of lower resolution, these phosphate values give a clear picture of the seasonal cycle and the period over which inorganic phosphate might be limiting to growth. Taking a typical North Sea mixed-community phosphate half-saturation constant of $0.06 \mu\text{M}$ (Moll 1998) as being representative of the concentration below which phosphate is limiting to primary production, inorganic phosphate appears to have been limiting during the period immediately following the spring bloom until the beginning of August. Whilst this broadly coincides with the period of maximum DON increase, it seems unlikely that this is a causal relationship: (i) we would expect to see accumulation of NH_4^+ in the case of phosphate limitation, where heterotrophic remineralisation of organic material outstrips the N demands of phosphorous-limited autotrophs, whereas we see only transient NH_4^+ peaks at the end of P-limited period; and (ii) the factor limiting growth under these conditions would be the rate of phosphate turnover by the heterotrophic community (rather than inorganic phosphate

concentration), hence it is likely that the dominant pathway supporting algal growth on phosphate will also be remineralising DON to NH_4^+ i.e. *moderating* DON concentrations. Interestingly, the post-spring-bloom recycling period appears to be demarked at beginning and end by transient accumulations of NH_4^+ . As shown in Johnson et al. (2007), post-bloom ammonium accumulation can occur when the normally tight coupling between remineralisation and uptake breaks down e.g. when algal populations crash due to grazing or nutrient limitation. Thus, such NH_4^+ peaks at either end of a period of phosphate limitation are consistent with our current understanding of the marine N cycle.

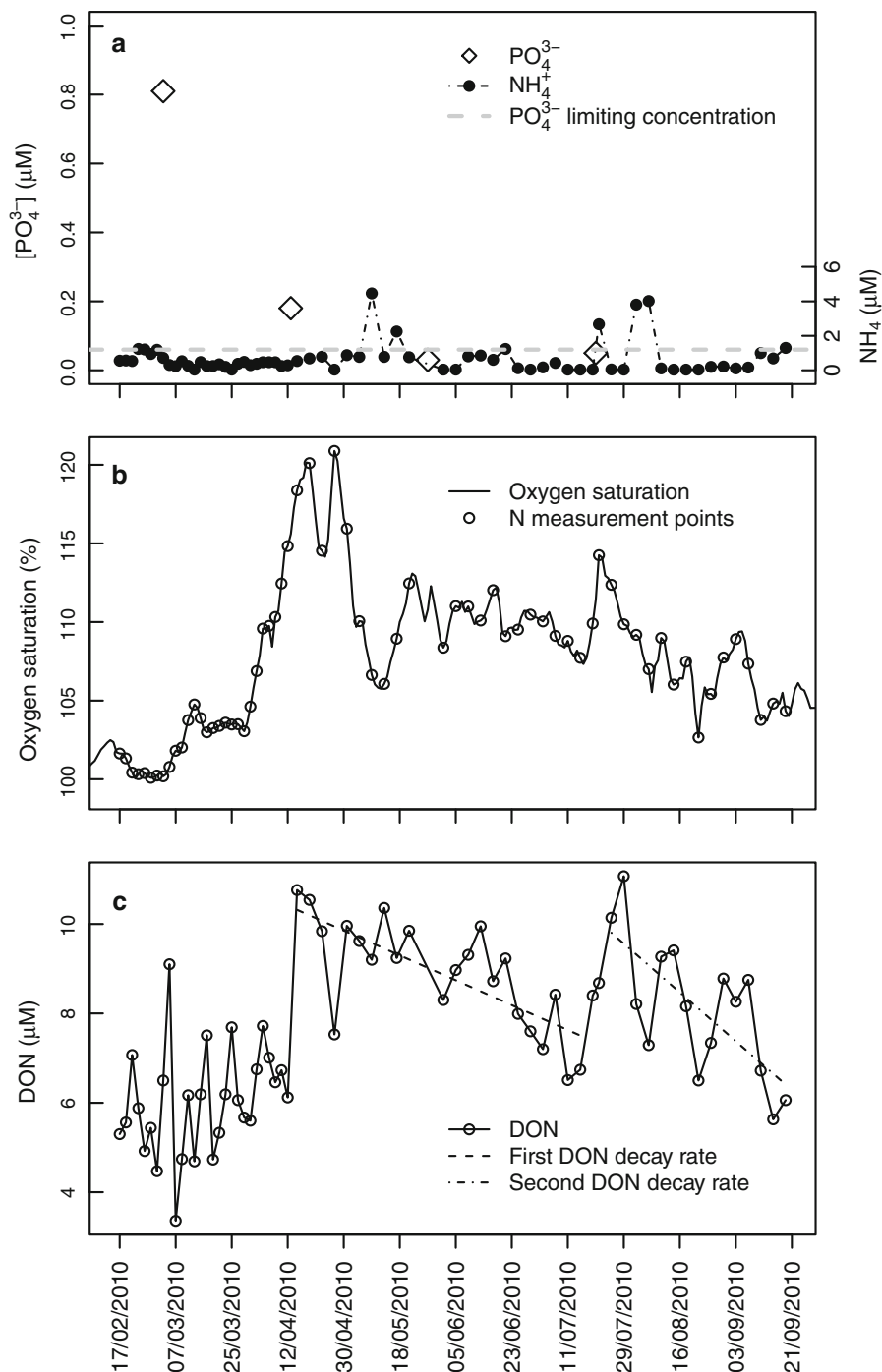
Secondary bloom

If bioavailable DON was accumulating due to phosphate limitation we might expect to see a marked decrease in DON as phosphate limitation is relieved. This does not appear to be the case, in fact there appears to be a marked increase in DON concentration (increasing to its highest measured concentration within the dataset), associated with the relief of phosphate limitation at the end of July.

In the absence of continuous chlorophyll fluorescence data for the period, we turn to dissolved oxygen measurements as an indicator of biological activity (recognising that other effects, particularly air-sea exchange can also be important controls on oxygen concentrations). The spring bloom can be seen clearly as an increase in the oxygen concentration (presented as a saturation value in Fig. 3), coinciding with phosphate drawdown and DON accumulation. It is also quite clear that there is a second peak in oxygen, associated with the relief of phosphate limitation and the second peak in DON, which we suggest is representative of a secondary bloom (a secondary bloom in August in the Dowsing area appears to be a recurring feature, which can be seen in 1988 and 1989 in the North Sea project dataset (Joint and Pomroy 1993)).

The combination of phosphate and oxygen concentrations and historical chlorophyll data provides strong indirect evidence that the second major peak in DON is associated with production during a secondary bloom and thus we reassess the degradation rate of the semi-labile DON fraction by applying 2 separate regressions; one for the period between the spring

Fig. 3 Evidence for a secondary bloom and production of DON: **a** Phosphate and NH_4^+ concentration; **b** Oxygen saturation and **c** DON concentration from the Dowsing site, over the study period. The results from linear regression analysis of DON decay rates is shown as *fit lines* for the post-spring bloom period (15/04/2010–15/07/2010) and the secondary bloom period (25/07/2010–19/09/2010), with gradients of -0.03 and $-0.06 \mu\text{M d}^{-1}$ respectively (see text for details)



bloom and the secondary August bloom and the second for the period following the August bloom. This analysis (the results of which are shown in Fig. 3) yields degradation rates of 0.03 and $0.06 \mu\text{M d}^{-1}$ (0.9 and $1.8 \mu\text{M month}^{-1}$) for the post-spring-bloom and post-secondary-bloom periods respectively. The

relationships were considerably stronger than that found for a single net degradation rate (54 and 50% of the variance accounted for in the first and second period respectively), and are strongly statistically significant ($p=0.0001$ and $p=0.003$). These net rates are of a similar order to the DON degradation rates

estimated from incubated water samples by Lønborg et al. (2009) of $\sim 0.02\text{--}0.3 \mu\text{M d}^{-1}$.

The N cycle overall

With the detailed dataset we present here it is possible to reconcile the budget for water-column nitrogen in waters at the Dowsing SmartBuoy site in 2010. Figure 4 presents a summary of distributions of the each of the N cycle parameters over the three periods and Table 2 summarises the average (mean and median) values. We can see from these data that, of the $\sim 9 \mu\text{M}$ of TOxN stripped from the water column over the course of the productive period, $3 \mu\text{M}$ was converted to DON and the remaining $6 \mu\text{M}$ lost from the TDN pool. The chlorophyll spring bloom in the SNS is of the order of 5 to $15 \mu\text{g/l}$ of chlorophyll (Weston et al. 2004). Van Engeland et al. (2010) suggest that a spring bloom of this magnitude would increase DON by 1 to $3 \mu\text{M}$ (based on extrapolations from the Rhine plume region), which is consistent with the results presented here and those of Suratman et al. (2008). The $6 \mu\text{M}$ of ‘lost’ TDN may have been converted to PON, which may or may not have been lost to sedimentation (probably only a small proportion subject to long-term sedimentation due to strong tidal and storm-driven resuspension events), or denitrified. Weston et al. (2004) find between 3 to $5 \mu\text{M}$ of PON in the water column in the summer in the SNS. This much PON could alone explain the observed decrease in TDN in our data. However, denitrification rates in SNS sediments have been observed to be potentially significant to the N budget, with rates of between 1 and $255 \text{ mmol m}^{-2} \text{ yr}^{-1}$ (Brion et al. 2004, and references therein). Taking an estimate of $50 \text{ mmol m}^{-2} \text{ yr}^{-1}$ and a water depth of 25m this equates to an annual removal of $2 \mu\text{M}$ of water column N via the sediments (assuming the sediments are at steady state and their N must be replenished from the water column annually), so denitrification can clearly be a significant factor and could explain any lost nitrogen which does not remain as PON at the end of the season.

Conclusions

We have demonstrated that there was a discernible, statistically significant seasonal cycle of DON at the

Dowsing SmartBuoy site in 2010. It is broadly similar to that found in the coastal Arctic by Simpson et al. (2008) and in the Rhine Plume region of the North Sea by Van Engeland et al. (2010), with an increase of DON during or shortly after the spring bloom, which persists for the summer period and slowly decreases back towards winter values. This is also in good agreement with the SmartBuoy DON data from the North Dogger site (Suratman et al. 2010), which showed a rapid increase of DON during the course of the spring bloom. We have also shown that in most cases in our dataset it is reasonable to assume that ammonium is insignificant in the calculation of DON from TDN, although at some points transient spikes of ammonium may affect DON estimates if this assumption is made. Furthermore, these ammonium spikes may be indicators of important regime changes in the seasonal N cycle, as previously suggested Johnson et al. (2007).

The sawtooth nature of the cycle is driven by periods of peak productivity leading to the accumulation of DON, which is then degraded over time. We suggest that this pattern is due to the semi-labile fraction of DON which is degraded on the timescale of weeks to months, with the shorter-timescale variability in the data being due to the complex dynamics of the rapid cycling of the more labile fraction of DON. In reality there must be a continuum of lability in DON rather than separate ‘pools’, and under different conditions it is conceivable that different DON compounds may be more or less bioavailable. In spite of this, and the complexity of source and sink terms for DON, statistically significant trends of DON decay over time are observed in the dataset, leading to an estimated net degradation rate of between 0.5 and $2 \mu\text{M month}^{-1}$, or 16 to 67 % of the seasonal DON pool degraded per month, suggesting a lifetime of the order of 1 to 4 months. Comparing these values to other studies is rather difficult due to the range of approaches taken to estimate degradation rate (net vs gross, in situ vs in vitro etc.). Although reasonably good agreement is found with the absolute degradation rates of Lønborg et al. (2009), the degradation rate as a percentage of ambient DON concentration is smaller: 0.5 to 2 % day^{-1} in our study compared to $\sim 9 \text{ % day}^{-1}$ observed by Lønborg et al. (2009). However, the lifetimes estimated here are in the upper half of the range of observed turnover times from a review of studies by Berman and Bronk (2003).

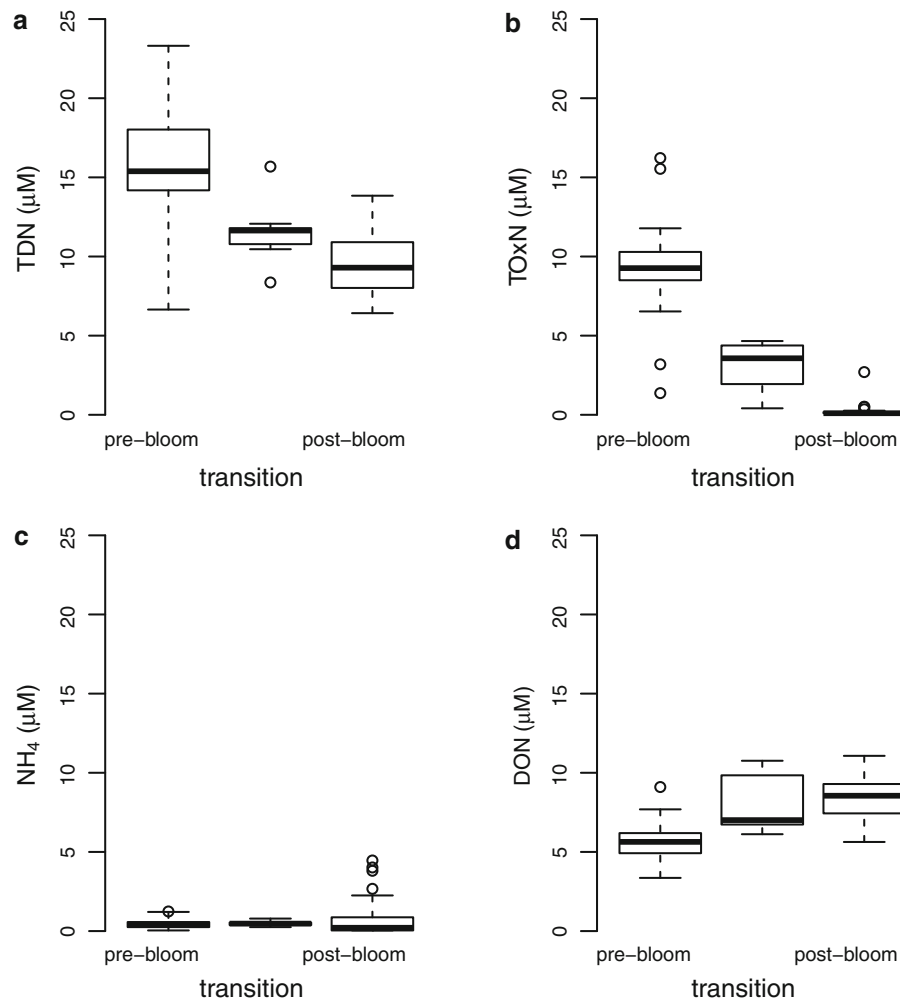


Fig. 4 Summary of concentrations in measured N reservoirs over the study period. For each *box-and-whisker plot*, *thick horizontal lines* represent the median value of each dataset, *boxes* the interquartile range. Whiskers extend to the outermost

DON is actively involved in the seasonal nitrogen cycle in coastal waters, but the timescales over which a major fraction of it changes are much longer than those of the inorganic N components (weeks or months for DON vs days for NH_4^+). At Dowsing, the seasonal growth of phytoplankton removed $\sim 9 \mu\text{M}$ of NO_3^- -N and our data suggests that $\sim 30\%$ of this reappeared as DON, $\sim 30\text{--}50\%$ remained as PON over the summer productive period and the remainder was potentially lost to the sediment where some was denitrified and some recycled. This work and that of others (e.g. Van Engeland et al. 2010; Suratman et al. 2010) emphasises the complex nature of the cycling of

data point which is less than 2 times the interquartile distance from the box, and data points outside this range are marked as individual ‘outlying’ points

DON in shallow coastal seas. The data we present here highlights the potential for significant insight into temporal nitrogen cycle dynamics provided by the unique high resolution time-series of water samples provided by the Cefas SmartBuoy network.

Acknowledgments Thanks are owed to Liz Claxton, Kimberly Wright and Jim Hunter (University of East Anglia, Norwich) for technical support with TDN analysis. Thanks are also due to the Cefas SmartBuoy team particularly Dave Pearce, Jennie Keable, Tom Hull and Chris Read. The officers and crew of RV Cefas Endeavour and THV Alert are to be commended for their skillful handling of the SmartBuoys. TDN sample analysis was funded by the Natural Environment Research Council of the United Kingdom under grant NE/F017359/1. The SmartBuoy at

Dowsing and measurement of core parameters was funded by Defra contract ME5304.

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