DISSOLVED ORGANIC CARBON AND NITROGEN IN COASTAL WATERS

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ABSTRACT

Dissolved organic matter (DOM) including carbon and nitrogen (DOC and DON) are important but poorly understood components of the marine biogeochemical cycle. In this study, the distribution and cycling of DOC and DON, and particulate organic carbon and nitrogen (POC and PON) were investigated in North Sea surface and bottom water during the stratified summer season in 2011 and 2012, along with other key biogeochemical parameters such as nutrients.
The summer DOC, DON, POC and PON ranged from 32.7-134.5, 2.8-13.7, 1.1-43.8 and 0.3-5.9 µM, respectively. The well-mixed water of the southern North Sea was also surveyed in the winter of 2011; measured concentration of DOC and DON were 56.2-224.8 and 3.7-12.3 µM. In summer, DOM and POM generally exhibited high levels in the southern well-mixed water (SM), whereas inorganic nutrient concentrations were higher in the northern bottom water (NB) due to nutrient regeneration and offshore water inflow. DOM in summer and inorganic nutrients in winter were also clearly influenced by riverine inputs. DON was the dominant nitrogen fraction of northern surface water and SM in summer, while in NB, TOxN (nitrate + nitrite) was the dominant fraction.

Analysis of SmartBuoy samples show phytoplankton provided a net source of DOM over the spring bloom period with net degradation in autumn and winter. Incubation experiments on water collected from two North Sea sites in autumn, winter 2013 and spring 2014 showed no nutrient (N and P) limitation on DOM degradation. The experiments yield mean bacterial decay rate constants (for three seasons) at the two sites of 4 ± 8 and 2 ± 3 $\%d^{-1}$ k_{DOC} and 3 ± 4 and 4 ± 4 $\%d^{-1}$ k_{DON}, under dark conditions. In comparison to the Redfield ratio, the bulk C:N molar ratio is enriched in carbon relative to nitrogen, while the slope C:N ratio is close to the Redfield ratio, but with a background of high C:N material.

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GLOSSARY OF TERMS

ANOVA	Analysis of variance
C	Carbon
CEFAS	Centre for the Environments, Fisheries and Aquaculture Sciences
CRM	Certified reference materials
CTD	Conductivity-temperature-depth
CV	Coefficient of variation
DIC	Dissolved inorganic carbon
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter (this study refers to DOC and DON)
DON	Dissolved organic nitrogen
DSR	Deep seawater reference
DS	Dowsing SmartBuoy site
FTU	Formazin Turbidity Unit
HCl	Hydrochloric acid
HMW	High molecular weight
HTC	High temperature combustion
HTCO	High temperature catalytic oxidation
k	Rate constant
KHP	Potassium hydrogen phthalate
KNO_3	Potassium nitrate
LCW	Low carbon water
LOD	Limit of detection
LMW	Low molecular weight
N	Nitrogen
N_2	Nitrogen gas
$NaHCO_3$	Sodium bicarbonate
$NaNO_3$	Sodium nitrate
NB	Northern bottom water
ND	Nitrogen detector
NDIR	Non-dispersive infrared
NH_4Cl	Ammonium chloride
NO	Nitric oxide
NPOC	Non-purgeable organic carbon
NS	Northern surface water
P	Phosphorus
PC	Polycarbonate
POC	Particulate organic carbon
POM	Particulate organic matter
PON	Particulate organic nitrogen
PP	Polypropylene
PSt	Prime station
Si	Silicon
SM	Southern well-mixed water
TDN	Total dissolved nitrogen
TOC	Total organic carbon
TOxN	Total oxidized inorganic nitrogen, the sum of nitrate and nitrite
WG	West Gabbard SmartBuoy site
WCO	Wet chemical oxidation

1 INTRODUCTION

In this first chapter, the general discussion of dissolved organic carbon (DOC) and nitrogen (DON) and their role in the biogeochemical cycling are first presented. Then, the processes concerning their source and sink and their behaviour in coastal waters are provided. Next, elemental stoichiometry and variations of DOM in seawater are presented. This is followed by a review of the general hydrography and nutrient cycling, focusing on both inorganic and organic nutrients, in the North Sea and surrounding regions which are the study area for the work presented here. Finally, the background of this present research is introduced along with the research objectives in the research overview section. The overall thesis structure is provided at the end of the chapter.

1.1 An overview of DOC and DON

The separation of dissolved and particulate forms of organic carbon and nitrogen compounds in waters is based on their filtration. Operationally, organic carbon and nitrogen which pass through the nominal pore size of a 0.7 µm glass fibre filter (or a pore size of 0.2 µm plastic (e.g. polycarbonate) filter, which is less frequently used) are defined as a dissolved form (DOC and DON), while material which does not pass the filter is the particulate form (POC and PON) (Carlson 2002, Hedges 2002, Carlson and Hansell 2015). Both DOC and DON are part of dissolved organic matter (DOM) in the aquatic ecosystems. Basically, the DOM includes both truly dissolved (solutes) and colloidal phases. Truly dissolved phases contain organic matter generally sized < 0.001 µm (1 nm) and colloids which have a size ~0.001 – 1 µm (Benner 2002, Hedges 2002). Colloidal particles are a major component of the marine dissolved material that affects the growth of phytoplankton (Wells 2002). DOM participates in nutrient cycling and has a close interaction with the microbial community (Nagata 2008, Sintes et al. 2010, Nelson and Wear 2014, Wear et al. 2015) occurring in rivers, estuaries, near shore, coastal seas and the open ocean. This study will concentrate on processes in the coastal water system, rather than the freshwater and open ocean.

In this present study, the ‘coastal zone’ is defined as the whole coastal seas/ shelf seas, including the areas of the estuarine plume, near shore and through the rest of the shelf sea to the shelf break, but does not include the open ocean. Therefore, the ‘coastal waters’ discussed cover all the waters in the shelf sea/ coastal seas and this present study will concentrate on the coastal zone rather than the open ocean. The shelf seas are the seas of continental shelf that connect the deep oceans (open oceans) and the continents, and generally contains shallow and flat seafloors extending to the shelf break at less than 500 meters water depth (Simpson and Sharples 2012).

As a boundary of two systems (terrestrial and open ocean), the coastal sea has distinct characteristics for nutrient cycling (discussed in section 1.2). This region generally has high primary productivity compared to the open ocean (Behrenfeld and Falkowski 1997, Simpson and Sharples 2012) because of significant nutrient inputs via rivers, groundwater, atmosphere and offshore water exchange (Jickells 1998) coinciding with light availability in the coastal sea. Therefore, over many past decades, researchers have studied inorganic nutrients, particularly nitrate and phosphate, as limiting factors on the productivity of phytoplankton and influences on coastal eutrophication (Riegman et al. 1990, Wollast 1998, Cantoni et al. 2003).

Although considerable research has been devoted to examine dissolved inorganic nitrogen (DIN) species and their importance for primary productivity and water quality, rather less attention has been paid to other fractions, including DON, because of difficulties in measuring them, and the underlying assumption that DON is biologically inert (Badr et al. 2003, Bronk et al. 2006). These omissions of DON studies may result in both an underestimation of the inputs of total nitrogen to coastal waters, and also the role of DON in the microbial loop (Bronk et al. 1994, Bronk et al. 2006, Bradley et al. 2010) which can impact on DOC concentration and phytoplankton productivity. This leads to the fact that we know a lot about inorganic nutrient cycling in coastal water, but much less about dissolved organic nutrients such as DOC and DON.

1.1.1 Composition

DOM is a complex mixture of organic substances, with diverse chemical composition, reactivity, and structure, which is not been entirely characterized (Aluwihare et al. 1997, Nagata 2008). Approximately 70-95 percent of marine DOM remains chemically uncharacterized (Benner 2002). However, this characterization is currently being improved, and DOM is known to broadly contain simple biological compounds (e.g. amino acids, fatty acid, sugars and vitamins), complex biopolymers (e.g. polysaccharides, protein and lignins), and more complex constituents of decayed products of partly characterised substances (e.g. humic substances and black carbon) (Repeta 2015).

The DON pool is known to include several compounds such as urea, amino acids (total hydrolysable amino acids (THAA) including dissolved free amino acids (DFAA) and dissolved combined amino acids (DCAA)), nucleic acid, humic and fulvic substances (Sipler and Bronk 2015). DON compounds in the form of urea contribute approximately 19% in coastal/ continental shelf, 7% in estuarine, 6% in riverine, 9% in oceanic surface, 10% in oceanic deep, and 8% in arctic waters of the total DON pool (Sipler and Bronk 2015). For DOC, the composition includes organic compounds such as carbohydrate, proteins (THAA), lipids (fatty acids, sterols, photosynthetic pigments), lignin, black carbon, and chromophoric DOC (CDOM: humic acid absorbing visible light) (Blough and Del Vecchio 2002, Bauer and Bianchi 2011).

1.1.2 Lability

The DOC pool in seawater can be broadly characterized into 5 fractions: a biologically labile (LDOC), a semi-labile (SLDOC), a semi-refractory (SRDOC), a refractory (RDOC) and an ultra-refractory (URDOC) fraction (Hansell 2013). Using remineralisation experiments, distribution patterns and radiocarbon ages to determine lifetimes (reactivity) indicate that these fractions have turnover times from hours-days, months-years, decades, thousands of years, and tens of thousands of years, respectively (Hansell et al. 2012, Hansell 2013, Nelson and Wear 2014). The last 4 fractions are defined together as recalcitrant DOC (RDOC) (Hansell 2013). Biologically labile DOM is mostly present in the surface ocean and rapidly

metabolized (Nelson and Wear 2014). The semi-labile fraction is largely in the upper ocean (< 500 meter depth) and declines at greater depths, while other fractions are largely present in the deeper ocean, but provide a background of DOM throughout the ocean (Ogawa and Tanoue 2003, Hansell et al. 2009). Even though labile DOM can be easily used by bacteria which rapidly consume it to support their growth (Church 2008), other fractions are resistant to fast degradation by bacteria and subsequently persist for a long time in the sea contributing to carbon and nutrient sequestration in the marine environment (Hedges 2002, Jiao et al. 2008, Jiao et al. 2014) as discussed further later in this chapter.

1.2 Dynamics of coastal zone influencing the DOM behaviour

The coastal zone is an important region in terms of a socio-economic benefit (Nobre 2011) and provides one of the most valuable and vulnerable habitats on earth (Jickells 1998). In comparison with the terrestrial and open ocean ecosystem, the coastal zone achieves higher economic value per unit area on the global scale (Costanza et al. 2014) and supports many activities e.g. fish catching, recreation areas, waste disposal and energy sources. However, coastal regions are currently under pressure because the population density in this area is approximately three times above the global averages with a rising trend (Small and Nicholls 2003, McGranahan et al. 2007) as well as a global increase of coastal cities (Barragán and de Andrés 2015). Other threats such as over fishing (Jackson et al. 2001), sea-level rise and global warming (Nicholls and Cazenave 2010, Neumann et al. 2015), eutrophication and harmful algal blooms (Oczkowski et al. 2014), and hypoxia (Diaz and Rosenberg 2008) are additional risks to coastal regions and affect the coastal ecosystem.

As a boundary of terrestrial areas and the open ocean, carbon and nutrient fluxes in coastal zones are influenced by inputs of both freshwater and high salinity deep ocean waters. Coastal zones have a role in the cycling and storage of nutrients coming from offshore waters, rivers, groundwater and the atmosphere (Jickells 1998). Thus, coastal nutrient cycling is a part of the support of marine ecosystem integrity. This region has distinct characteristics of nutrient processing, recognized as extremely dynamic, complex and unique (Simpson and Sharples 2012), including

sources at the primary fresh-salt water interface where strong physico-chemical gradients exist at the coast, and nutrients supplied from the shelf edge, air-sea interface, and remobilization from bottom sediment (Syvitski et al. 2005). Enhanced riverine nutrients in both organic and inorganic forms are transported and modified within the estuaries (Nedwell et al. 1999, Bauer and Bianchi 2011, Jickells and Weston 2011), and where high suspended particles may reduce light penetration and hence primary productivity (Voss et al. 2011, Liu et al. 2013). Estuaries have the capability of trapping nitrogen and phosphorous because of particle trapping, uptake of dissolved phosphate to suspended sediment and denitrification in sediment (Jickells et al. 2000)

The coastal zone is one of the most productive regions in the global ocean (Falkowski et al. 1998) with up to 20% contribution to organic matter production in the whole ocean, although the coastal water represents only 10% of the oceanic surface area (Wollast 1998). The contribution of this area to the cycling of DOM is therefore potentially significant to the global carbon budget (Cauwet 2002). In the open ocean, higher labile DOM levels generally occur in the surface water rather than the deep ocean and particularly in the euphotic zone (Hansell et al. 2009). Higher DOM concentrations are usually found in the surface water in coastal water as well (Hansell et al. 1993, Vlahos et al. 2002, Bradley et al. 2010, Engel et al. 2012). Light and nutrient available in surface waters as well as external nutrient sources contribute to coastal primary productivity (Jickells 2005). The primary productivity, together with microbial activity and physicochemical mechanisms consequently have the capability to control the presence of DOM in the coastal waters. As DOM cycling is strongly influenced by coastal processes, it can potentially be influenced by nutrient supply, light absorbance, and availability of microbes in the coastal system. Thus, coastal seas must be considered as an important pathway for processing of DOM, particularly DOM discharged from rivers, produced within the coastal waters and input from offshore (Cauwet 2002).

1.3 The role of DOM cycling in the global biogeochemical cycle

Carbon cycling is a central part of the biogeochemical cycle on Earth. This includes two forms, inorganic and organic carbon. Continuing increases in atmospheric CO_2 over recent years have the potential to affect the carbon cycle in sea surface water (Yoshimura et al. 2010). A recent study shows the large anthropogenic net carbon sinks over the last decade (2002–2011) with 2.5 ± 0.5 Pg C yr^{-1} taken up by the global ocean and 2.6 ± 0.8 Pg C yr^{-1} by the terrestrial ecosystem (Pg = Petagram = 10^{15}g) (Le Quéré 2013). However, over the past several decades, studies have concentrated on the inorganic form of carbon, and organic carbon is less well studied. Previous studies estimated a total marine DOC pool of 700 Pg C (Hansell and Carlson 1998, Ogawa and Tanoue 2003), comparable to approximately 750 Pg C of the atmospheric carbon stock as CO_2 and 600 Pg C of the terrestrial carbon stock (Hedges 1992). Among the estimated total stock of 700 Pg marine DOC, there is approximately 650 Pg of RDOC (Ogawa and Tanoue 2003) that contributes to the long term carbon sequestration in the marine environment. Thus, DOM in seawaters is one of the largest exchangeable pools of carbon on earth (Azam 2015). This seawater DOM includes the large bioreactive carbon pool as DOC (Hansell et al. 2009) alongside DIC (dissolved inorganic carbon), the largest marine carbon pool (38,100 Pg C) (Sarmiento and Gruber 2006). Consequently, the marine carbon pool is the earth's largest exchangeable carbon reservoir, larger than the carbon in other parts e.g. terrestrial biosphere (Ridgwell and Arndt 2015). The net uptake of CO_2 by the ocean is estimated to be 2 Pg C $year^{-1}$ (Takahashi et al. 2009). Hence oxidation of a small proportion of marine DOC, only one percent, is enough to create a CO_2 flux that is higher than the annual CO_2 produced by fossil fuel combustion (Hedges 2002). Therefore, small variations in DOC production and removal processes potentially could lead to an imbalance of CO_2 between ocean and atmosphere (Carlson and Hansell 2015), as well as the export of organic carbon (Hansell and Carlson 2001a).

DOM pools, including DOC and DON, are currently of substantial interest to marine biogeochemists who recognise their important role in biological and chemical oceanography (Hansell and Carlson 2001b, Hedges 2002, Ogawa and Tanoue 2003, Hansell et al. 2009, Repeta 2015), particularly their ecological significance. DOM is utilised by heterotrophic microbes in the ocean to support their growth (Kähler et al.

1997). Their utilization depends on the size class of DOM, the low molecular weight (LMW, <1 kDa) has been claimed to be generally less bioreactive compared to the high molecular weight (HMW, >1 kDa) DOM according to previous studies (Amon and Benner 1996, Carlson 2002). However, the relationship between size and lability of DOM also depends on time scale (Figure 1.1). Later studies have also proposed that DOM lability decreases with decreasing in molecular size when DOM is transformed from the semi-labile to refractory pool. However, the labile pool turns over much faster than the semi-labile pool and has DOM lability decreases with increasing molecular size (Nagata 2008). Therefore, there are two components of LMW DOM which are differently processed on different time scale including a short turn over time scale DOM with LMW which turns over faster than HMW as the chemical complexity of HMW DOM delays hydrolysis, and a long turn over time scale DOM with LMW which turns over more slowly than HMW because the unusual structures of the LMW produced during diagenesis of HMW and is less accessible for bacteria (Nagata 2008).

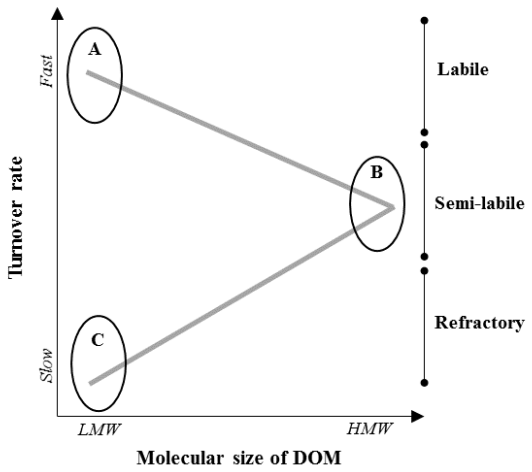


Figure 1.1 Diagram describing the "trend reversal" in relationship between size and lability of DOM depending on the time scale. Pool (B) turns over more slowly than pool (A) as the chemical complexity protects it from fast degradation, while Pool (C) turns over more slowly than pool (B) as chemical structures produced during diagenesis process are less accessible for bacteria (adapted from Nagata (2008)).

A recent study found that the bacterial abundance in the ocean was limited by availability of DOM, rather than inorganic nutrients (Pete et al. 2010). Not only heterotrophs consume DOM, but also autotrophs such as phytoplankton can utilise some DON compounds for their nutrition (Bronk et al. 2007, Bradley et al. 2010) as

well as DOC (Navarro et al. 2004). Remineralisation of DON to DIN by microbial activity (Maita and Yannada 1990, Vidal et al. 1999) is an important mechanism in the biogeochemical cycling of bioreactive forms of nitrogen. The inorganic nutrients mineralised from DOM, along with those regenerated from POM by bacterial processing (Simon et al. 2002) are important in the control of inorganic nutrient enrichment in the marine environment.

In addition, micro-heterotrophs and autotrophs can also produce DOC and DON (discussed in section 1.4.1.1). Bacteria can both use and release DOM (Nagata et al. 2000, Kujawinski 2011) and subsequently transform it to recalcitrant DOM by microbial processes (Ogawa et al. 2001, Jiao et al. 2010) with the new form resistant to decay by microbes over thousands of years and contributing to over 96% of marine DOM (Osterholz et al. 2015). This consequently leads to carbon sequestration in the ocean (Hedges 2002, Jiao et al. 2014). The microbial processes transform labile DOM (LDOM) to recalcitrant DOM (RDOM) via the mechanism called "Microbial carbon pump (MCP)" (Jiao et al. 2010, Jiao et al. 2011) contributing ~ 0.2 Pg C yr^{-1} to the world ocean (Legendre et al. 2015). Marine DOC and DON pools are therefore influenced by activities of both heterotrophic and autotrophic microbes in seawaters controlling their biogeochemical cycling. While the MCP contributes to carbon sequestration by producing RDOM, the organic or biological carbon pump (BCP) sequesters carbon via vertical transfer carbon to the deep ocean (Legendre et al. 2015). BCP is a process in which DIC is removed from the water column because of photosynthesis and is fixed as POC and DOC (Passow and Carlson 2012, Ridgwell and Arndt 2015). In addition to BCP, there are two other vertical carbon pumps which also sequester carbon from the atmosphere to the deep ocean i.e. solubility pump (SP), carbonate pump (CP). SP is a physicochemical process that transport DIC from the surface to ocean interior, mainly driven by CO_2 solubility (Jiao et al. 2010), whereas CP involves processes of biological precipitation of $CaCO_3$ (Ridgwell and Arndt 2015). This concept of oceanic carbon pumps (BCP, SP and CP) therefore refers to the “pumping” of carbon from the surface to depth (maintaining the vertical gradient of DIC), while another recent pump proposed by Jiao et al (2010), the MCP, plays a dominant role in “pumping” the labile carbon into relatively recalcitrant forms and connects with BCP in the

ocean carbon cycle (Jiao et al. 2010, Jiao and Azam 2011, Legendre et al. 2015, Ridgwell and Arndt 2015).

1.4 Sources and sinks in coastal waters

1.4.1 Sources of DOC and DON

The reservoir of DOM in the marine environment is thought to be mainly of marine origin, particularly in the open ocean (Opsahl and Benner 1997, Hansell et al. 2004, Carlson and Hansell 2015). Mechanisms related to DOM production in seawater are considerably influenced by in situ biological processes e.g. the extent of primary production (Carlson 2002, Carlson and Hansell 2015). However, external mechanisms also contribute to DOM sources entering seawater, particularly in the coastal region. Thus, sources of DOC and DON in coastal waters (as later summarised in Figure 1.5) generally include:

- the internal origin (autochthonous): DOM formed in the water mass itself, or produced within the marine environment, mainly from the decomposition and excreta of plankton and marine bacteria; and,
- the external origin (allochthonous): DOM produced by the decomposition of higher plants by microbes (bacteria and fungi) and leached from the soil of the drainage basin by rainwater and then delivered to coastal waters by river and groundwater via estuaries, from the atmosphere and from offshore waters.

1.4.1.1 Internal sources

1) Phytoplankton release

Phytoplankton produces DOM via exudation and extracellular release processes (Varela et al. 2005, López-Sandoval et al. 2013) contributing an important DOM source (Collos et al. 1992). In the past decades, DOM release by phytoplankton has been extensively studied (Sharp 1977, Bronk and Glibert 1991, Collos 1992, Bronk et al. 1994, Varela et al. 2005, López-Sandoval et al. 2013). The production rate is influenced by phytoplankton species, growth phase (Chen and

Wangersky 1993) and physiological stress on the phytoplankton (Bronk and Ward 1999), while DON release is also highly correlated with rates of nitrate uptake and phytoplankton growth (Hu and Smith 1998). In phytoplankton cultures, both DOC and DON are released from healthy cells during the mid-exponential growth phase (Suratman et al. 2008b). Phytoplankton extracellular release and their productivity shows a positive linear pattern in coastal waters (Baines and Pace 1991). Previous study in the North Sea suggests extracellular release from phytoplankton is a significant source of DOC during autumn and spring and the heterotrophic uptake of labile DOC leads to a lower DOC concentration in summer (Suratman et al. 2009). High percentage (~ 42%) of DON extracellular release relative to nitrate uptake were reported in one study (Varela et al. 2005), while the uptake of ammonium and urea produces lower DON release (~ 22 to 26%). Phytoplankton-derived DOC and DON are available to accumulate in coastal waters on the time scale of days to months (Williams 1995, Álvarez-Salgado et al. 2001, Hill and Wheeler 2002, Wetz and Wheeler 2004) and their persistence is influenced by the release and degradation balance (Thingstad et al. 1997).

2) Zooplankton grazing

The breakage of dead and decaying phytoplankton cells by grazing zooplankton is a major DOM source in seawater (Lampert 1978, Hygum et al. 1997). This process plays a role in controlling the population of phytoplankton and is a significant pathway of DOM to the bacterial community (Jumar et al. 1989, Daly and Smith 1993). Experimental studies show increasing DOC release in the presence of higher grazers population (Fouilland et al. 2014) and the grazers potentially influence the production of dissolved carbon from particulate forms via their consumption process and excretion (Carlson 2002). Not only DOC is released by the zooplankton grazing process (Møller 2005, Møller 2007, Puddu et al. 2000), but DON is also released from phytoplankton population via their cell breakage by "sloppy feeding" by zooplankton (Gilbert et al. 1991, Saba et al. 2011). Approximately 50-70% of carbon grazed is released as DOC by this process (Møller et al. 2003). In addition, zooplankton are also a predator of bacteria. Grazing of bacteria by bacteriovores releases DOM to water column (Kujawinski 2011). There are various size of bacteria grazers, and major bacteriovores include heterotrophic

nanoflagellates (HAF) (1-10 µm) and ciliates (10-100 µm) (Sherr et al. 2007, Jürgens and Massana 2008).

3) Bacterial release

Bacteria (e.g. heterotrophic bacterioplankton) can release DOM into the water column. They directly release DOM by excretion (Nagata et al. 2000, Kujawinski 2011). Bacteria also potentially transform DOM to recalcitrant forms by converting HMW to LMW DOM (Ogawa et al. 2001) via the process of the "Microbial carbon pump (MCP)" (Jiao et al. 2011). Furthermore, marine diazotrophs, N_2 fixing microorganisms that have the capability to utilise N_2 as a nutrient source (Mahaffey et al. 2005, Zehr and Paerl 2008), play an important role in providing a new nitrogen source to seawater (LaRoche and Breitbarth 2005, Zehr 2011). The diazotrophic cyanobacteria including *Trichodesmium* contribute to the DON pool by fixing atmospheric nitrogen gas and subsequently release DON and ammonium, particularly in the tropical and subtropical ocean (Glibert and Bronk 1994, Mulholland et al. 2004). A recent study in a unicellular diazotrophic cyanobacteria (e.g. *Cyanothece*) reveals that this marine nitrogen fixer can also release both DON and DOC to the water column (Benavides et al. 2013). In comparison to *Trichodesmium*, the unicellular cyanobacteria have higher nitrogen fixing rates and wider abundance in the ocean (Moisander et al. 2010, Luo et al. 2012). This suggests that the release of DOM by marine bacteria and diazotrophs can help support primary production in the ocean, particularly in oligotrophic waters.

4) Cell lysis

Viruses are abundant biological agents in seawater (Breitbart 2012). They generally result in bacterial infection and mortality (Fuhrman and Noble 1995, Kirchman 2013) and also influence the ecological and biogeochemical processes (e.g. control algal blooms, particle distribution and nutrient cycling) (Fuhrman 1999). The "viral shunt', is the process that moves nutrients from organisms into POM and DOM (Suttle 2007) fueling the microbial food web (Breitbart et al. 2008, Lønborg et al. 2013). The viral infection of bacteria releases viral lysate as DOM as DFAA and DCAA from infected cells (Middelboe and Jørgensen 2006). However, the importance of bacterial lysis in producing DOM remains unquantified (Carlson and Hansell 2015).

5) Solubilisation of sinking particles

Aggregation of particles provides an efficient substrate for bacteria (Simon et al. 2002). As bacteria can not directly consume the particles, they hydrolyse POM and other marine aggregates (e.g. colloidal substances, polymeric DOM and biopolymers) by releasing bacterial ectoenzymes (Christian and Karl 1995, Smith et al. 1992). These bacterial extracellular enzymes are delivered and mediate hydrolysis (solubilisation) of sinking particles, and subsequently produce DOM (Smith et al. 1992, Azam and Malfatti 2007, Hmelo et al. 2011). To date, DOM release during solubilisation of sinking particles has not been widely studied.

1.4.1.2 External sources

1) Riverine input

Sources of terrestrial organic matter in the marine environment are primarily transported via rivers to coastal zones (Lauerwald et al. 2012). Previous studies reported that on the global scale riverine runoff delivers ~ 0.21 – 0.25 Pg of DOC per year from the terrestrial to the marine system (Ludwig et al. 1996, Hedges et al. 1997, Cauwet 2002), consistent with recent estimates of 0.21 Pg $year^{-1}$ riverine DOC entering to the global coastal ocean (Dai et al. 2012). The Arctic rivers, glaciers and Antarctic ice sheets also contribute to the DOC released from the continents (Dittmar and Kattner 2003, Hood et al. 2015). For riverine DON, approximately 5 Tg N (0.005 Pg N) is transported to the global coastal ocean each year (Seitzinger and Harrison 2008).

The majority of fluvial DOC comes from sources external to the water body (Inamdar et al. 2004) such as stored in surface soil (Eswaran et al. 1993, Sickman et al. 2010), terrestrial biota and plant litter (Post 1993) and is mainly delivered from decayed organisms (Häder et al. 1998). Similarly, DON is derived from multiple sources to the riverine system, and high levels of DON concentration are also generated from the effluent of waste water treatment plants (Pehlivanoglu-Mantas and Sedlak 2006). Peatland catchments in the UK are a significant source of DON as well as DOC that is finally discharged to the peatland fluvial systems. DOM derived from the peatland catchment is mainly released as carbon rich material with high DOC:DON ratio (~23) (Edokpa et al. 2015).

There is evidence that DOC concentrations have increased during the last two decades in upland surface water of many areas, especially in the UK. One study found that DOC concentrations have increased by an average of 91% in 22 UK upland water (Evans et al. 2005). In term of the trend of DOC concentration in 198 sites across the UK, all sites showed a significant increase in its concentration (average annual increase was 0.17 mg C $l^{-1}year^{-1}$) (Worrall et al. 2004). Organic carbon transported by rivers through coastal waters is an important factor in the global carbon cycle (Ludwig et al. 1996).

2) Atmospheric input

Wet and dry deposition combine as an important source of atmospheric DOM input to surface seawater (Paerl 1997, Kieber et al. 2002, Avery et al. 2006, Jickells et al. 2013). The most important external source of DOC to seawater is wet deposition by rain, particularly in coastal surface water (Willey et al. 2000), and by dry deposition (Violaki et al. 2010). DON is also input to seawater by rain (Rendell et al. 1993, Cornell et al. 1995, Cornell et al. 2003) and can contribute to activate growth and productivity of phytoplankton and bacteria (Peierls and Paerl 1997, Seitzinger and Sanders 1999). Although atmospheric deposition is a relatively minor contribution for gross nitrogen input to the coastal sea, this pathway is suggested as an important source when there is nutrient limitation on primary production, particularly in the stratified area of the shelf sea (Rendell et al. 1993).

3) Groundwater discharge

Submarine groundwater discharge is a potential source supplying carbon and nutrients to coastal waters (Slomp and Van Cappellen 2004, Moore 2006). DOM discharged from groundwater has not been widely quantified and characterized as it is rarely recognized as an important pathway of delivery to the coast (Paerl 1997, Szymczycha et al. 2014). Most groundwater studies investigate anthropogenic nitrogen as nitrate, but groundwater actually also provides an important source of DON to the coastal zone and this DON may relate to anthropogenic activities (Kroeger et al. 2006, Kroeger et al. 2007). In addition, groundwater contains higher DOC concentration than surface seawater and releases DOC into the coastal zone (Stewart et al. 2015). To exemplify this, the annual mean DOC concentration in

groundwater around the Baltic Sea is 483 ± 75 µM and the DOC flux through this pathway into the Baltic Sea is ~ 25.5 ± 4.2 kt yr^{-1} (Szymczycha et al. 2014).

4) Sediment release

Diagenetic processes within bottom sediment releases DOM which can diffuse from sediment pore waters to the overlying water (Bauer et al. 1995, Burdige 2002, Lahajnar et al. 2005). This global benthic flux is ~ 0.1 Pg C yr^{-1} (Burdige et al. 1992), comparable to the riverine input. A previous study has demonstrated that the sediment pore water contains higher DOM concentrations than the overlying water (Bauer and Druffel 1998). Bioturbation and physical disturbance of bottom sediment by winter storms can induce sediment resuspension that leads to the DOM release from pore water to the overlying water (Burdige and Homstead 1994). These processes particularly bring old high molecular weight DOC to the water column (Guo and Santschi 2000). Since the organic matter in sediments is at least in part generated in the water column, most or all of this DOM cannot be considered "new" to the water column.

5) DOM input from offshore

Coastal regions receive DOM input from the open ocean as reported by a previous study in the North Sea (Thomas et al. 2005). It has been estimated that gross flux of organic carbon in the form of DOC and POC from the Atlantic Ocean to the North Sea is via the English Channel, Faire Island and Shetland Channel with a flux of 4.8 to 37.2 x 10^{12} g C yr^{-1} (Thomas et al. 2005). These organic carbon inputs are then partly transferred to the DIC pool (e.g. via remineralization process) within the North Sea and subsequently transported by the continental shelf pump to the North Atlantic Ocean (Thomas et al. 2004, Bozec et al. 2005, Thomas et al. 2005). Oceanic DOM input to the continental shelf water is also observed in other regions e.g. DOC inputs from the deep slope to the shelf estimated to be 1.9 ± 0.3 x 10^{12} g C yr^{-1} for the Mid-Atlantic Bight (Vlahos et al. 2002).

6) Release from other sources

Corals potentially release DOC to seawater. Cold water corals were found to release 47 ± 19 mg m^{-2} h^{-1} DOC to the water column (Wild et al. 2008). The warm water coral release rates are comparable to the cold water corals with the release rate

of ~ 41 to 46 mg m^{-2} h^{-1} (Tanaka et al. 2008). Recent studies report that hydrothermal vents also release DOM to the water column, but this process is only rather important in the deep ocean (Yang et al. 2012, Follett et al. 2014, Hawkes et al. 2015, Rossel et al. 2015).

1.4.2 Sinks for DOC and DON

While sources are defined by processes of DOC and DON production occurring within the water column or delivered from external origins, the sinks of DOC and DON are identified by the removal processes caused by biological activities and abiotic mechanisms within the water column.

1.4.2.1 Biological activities

1) Bacterial uptake

Traditionally, bacteria (e.g. heterotrophic bacterioplankton) are considered as organic matter decomposers, on account of changing DOM to inorganic nutrient or biomass (Azam et al. 1983). Therefore, DOM serves as a source of carbon and nutrients to heterotrophic bacteria, particularly DOC produced by photosynthesis (Cole et al. 1982) and providing their living substrate (DeLong et al. 1993). Heterotrophic bacteria generally prefer to assimilate DOC freshly produced by phytoplankton (Norrman et al. 1995), as it provides a more labile fraction containing compounds which are easily utilised by bacteria (Nagata 2008). A study in brackish waters reported that bacteria prefer to assimilate the non-humic fraction of DOC derived by photosynthesis (by phytoplankton) rather than the humic fraction (Kanuri et al. 2013). To take up HMW DOM, enzymes are released by bacteria to hydrolyse HMW to LMW DOM before assimilation by osmosis (Christian and Karl 1995, Arnosti 2011), as LMW DOM is directly able to be transported to their cell membranes (Carlson 2002). Many previous studies report that marine bacteria can uptake both DOC and DON (Kähler et al. 1997, Veuger et al. 2004, Lønborg and Søndergaard 2009, Bradley et al. 2010). Thus, bacterial uptake is the dominant sink for DOM and plays an important role in the removal of DOM from the water column.

2) Phytoplankton assimilation

As one of the bioavailable nitrogen sources, DON is also utilised by phytoplankton in order to support their growth (Bronk et al. 2006), particularly DON in the amino acid and urea form (Bradley et al. 2010). Phytoplankton cell surfaces generally have amine oxidases to assimilate amino acid (Bronk 2002). Additionally, DOC supports planktonic metabolism in oligotrophic waters (Navarro et al. 2004). Previous reports indicate that both DOC and DON are utilised by phytoplankton (Bronk and Glibert 1993, Navarro et al. 2004, Bradley et al. 2010, Van Engeland et al. 2013, Moneta et al. 2014) showing an important role for phytoplankton in removing DOM from seawater.

1.4.2.2 Abiotic mechanisms

1) Photoremineralisation

UV radiation to seawater influences the transformation of the DOM pool. It has been estimated that DOC is directly transformed to DIC by photochemical processes in the shelf waters at a rate of approximately 10 % $year^{-1}$ (Vodacek et al. 1997). The phototransformation results in marine DOC loss from the water column of ~ 12-16 Pg C $year^{-1}$ (Moran and Zepp 1997). In addition, whenever RDOC moves to the surface layer, this photooxidation process partly converts RDOC to CO_2 and CO (mostly CO_2) (Mopper and Kieber 2002, Stubbins et al. 2012). This is proposed as a dominant sink of RDOM (Riemer et al. 2000). The DOC photodegradation rate is approximately 20 nM $hour^{-1}$ (Mopper et al. 1991). Although photoremineralisation is a sink of DOM, this mechanism is limited to the photic zone of surface water.

2) Sorption and sinking

The influence of sorption and sinking mechanisms on DOC and DON is not widely studied (Druffel et al. 1998). However, these processes are expected to remove DOC at an approximate rate of 1-3 nmol C $kgPOC^{-1}$ $year^{-1}$ (Hansell et al. 2009) and act as a physical mechanism for DOM removal from the water column (Keil and Kirchman 1994, Druffel et al. 1996, Druffel et al. 1998, Hwang et al. 2006). In general, DOM can absorb onto the surface of sinking particles (e.g. POC) and subsequently accumulate in sediments (Hwang et al. 2006) where it may be

permanently buried or remineralised and redistributed back to the upper water column (Bauer et al. 1995, Santschi et al. 1999, Guo and Santschi 2000) and thereafter provide a source of DOM back to the water column.

3) Outflow of DOM in coastal waters to the open ocean

It has been proposed by a previous study that coastal seas act as a sink of organic carbon e.g. the North Sea (Thomas et al. 2005). Therefore, DOC persisting in coastal waters is potentially transported to the adjacent open ocean according to exchange of water across the shelf/slope front as reported in regional observations e.g. (Bauer et al. 2001, Vlahos et al. 2002, Hung et al. 2003, Munro et al. 2013). Approximate 45.6×10^{12} g C yr^{-1} of organic carbon (DOC and POC) outflows (gross flux) have been estimated from the North Sea to the North Atlantic Ocean via Norwegian Trench (Thomas et al. 2005). In the Mid-Atlantic Bight, gross DOC export across shelf is 18.7 to 19.6 MT C yr^{-1}, approximately four times POC export (Vlahos et al. 2002). Recent study on a global scale estimates that net DOC export from coastal waters to the open ocean is in the range 7.0 ± 5.8 to 29.0 ± 8.0 Pg C yr^{-1} (Barrón and Duarte 2015).

1.5 Elemental stoichiometry and variations of DOM in seawater

Biological, chemical and physical mechanisms control the chemical composition of seawater. The concept of the Redfield ratio refers to the relation between organism composition and aquatic chemistry that are both close to a C:N:P ratio of 106:16:1 (Redfield 1958). However, the C:N:P stoichiometry of phytoplankton is not a fixed value and deviations from the Redfield ratio have been noted in later reports (Geider and La Roche 2002, Arrigo 2005, Moore et al. 2013). Variability in C:N:P ratios that differ from the Redfield ratio provide understanding on nutrient limitation on primary production (Moore et al. 2013), phytoplankton physiology (Quigg et al. 2003) and capability of oceanic carbon sequestration (Sigman and Boyle 2000).

Recent studies observe that the C:N:P stoichiometry deviates from the Redfield ratio in both POM (Martiny et al. 2013) and DOM pool (Abell et al. 2000, Aminot and Kérouel 2004, Hopkinson and Vallino 2005, Ducklow et al. 2007, Pujo-

Pay et al. 2011, Letscher and Moore 2015). The different elemental balance of non-Redfield stoichiometry can potentially lead to different estimates of the current global carbon export and how this biological pump and the biogeochemical process may change with future climate change. A recent study using non-Redfield stoichiometry DOM estimated ~9 % greater global carbon export to the deep ocean than a previous estimate based on DOM cycling at the Redfield proportion (Letscher and Moore 2015).

Labile DOM is biologically significant as it is rapidly consumed within time periods of hours to days, whereas semi-labile and refractory forms have a longer turnover time from months-years and decades-tens of thousands of years, respectively (Hansell et al. 2012, Hansell 2013, Nelson and Wear 2014). The ratios of DOC:DON in labile DOM deviate from that in refractory DOM. Jiao et al. (2010) have suggested the labile pool has a C:N ratio ~ 10:1 and the refractory pool is ~17.4:1, both of which are much higher than the 6.6:1 of the Redfield ratio. This enrichment of carbon in more refractory DOM represents a potentially important process in the biological carbon pump as it effectively represents the more rapid recycling of nutrients relative to carbon i.e. more carbon can be fixed by a given amount of nitrogen than would be the case if everything was taken up and recycled at the Redfield ratio.

There are generally two ways to study C:N ratios of DOM. In addition to the C:N ratios derived from bulk molar DOC:DON ratios , the ratio can be derived from the slope of the best-fit linear regression computed from the DOC and DON concentrations (the plot of *y*-axis DOC versus *x*-axis DON). The slope can be determined as the stoichiometry of DOM (the C:N ratio), but this reflects alteration of DOM caused by relative variation in DOM composition which have been expressed by Hung et al. (2003) and Aminot and Kérouel (2004) as $\Delta DOC{:}\Delta DON$ (Figure 1.2b). This C:N ratio determined from the slope describes the stoichiometry of DOM net change due to decomposition and production (the stoichiometry of both DOM remineralization and production) which generally provides a C:N ratio slope ~ 10 (Hopkinson and Vallino 2005). The ratio from the slope (~ 10) was generally lower than the ratio of the bulk pools (~ > 14) but both higher than the Redfield ratio (~ 6.6) of recently produced DOM and POM pool in several studies (Hopkinson et

al. 1997, Hung et al. 2003, Hopkinson and Vallino 2005, Lønborg et al. 2010, Pujo-Pay et al. 2011, Singh et al. 2015).

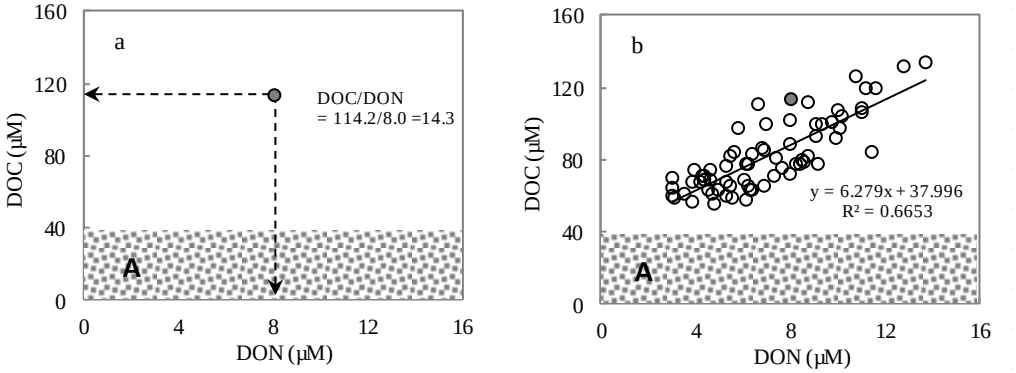


Figure 1.2 An example of DOC and DON ratios derived from (a) a DOC:DON ratio and (b) a slope of DOC:DON (ΔDOC:ΔDON) ratio. The filled circles in (a) and (b) are the same data point. The area A is a background pool of recalcitrant DOC (the *y*-intercept value) which in this illustration has a background level of DOC of ~38 µM which still persist when DON reaches zero. (a) Represents the bulk DOC:DON molar ratio of an individual data point included the area A providing the overall C:N molar ratio of 14.3. (b) Represents the slope of whole individual data plot (not included the area A) providing the slope C:N ratio of 6.3 (substantially lower than the average molar DOC:DON ratio of 12.6 ± 3.3 of the whole 70 data points). The presented data in (b) are from chapter 3 (DOC and DON concentrations in the whole bottom water, summer 2011 survey).

Therefore, in this study, these terms will be used to refer to the DOC to DON ratio derived from the two different methods.

- "DOC:DON ratio", "bulk C:N molar ratio" and "C:N molar ratio" refer to the 'bulk DOC:DON molar ratio' as described in Figure 1.2a.
- "Slope of the DOC:DON ratio" and "slope C:N ratio" refer to the 'regression slope of DOC and DON (ΔDOC:ΔDON)' as described in Figure 1.2b.

It has been suggested by Hopkinson and Vallino (2005) that the slope C:N ratio is most suitable to explain the stoichiometry of DOM at the global scale and a smaller scale studying along isopycnals, in both cases where depth can be considered as a proxy for time. Hopkinson and Vallino (2005) suggest that the slope C:N approach is inappropriate for other small scale studies because seasonal variation and surface water effects can break the depth-time relationships. However, my study considers processes along salinity gradient where all samples are effectively surface

samples (and so there is no depth/time effect), and salinity can be considered a proxy for distance from riverine/open ocean sources. Previous studies (Aminot and Kérouel 2004, Hopkinson and Vallino 2005, Lønborg et al. 2010) use the model II linear (Major Axis) regression to determine the slope ratio of DOM. Following investigation of the applicability of model I and model II regression analysis to the data in this thesis (Appendix 1.1), ordinary least squares (model I) regression was used in this study, as previously used in other studies to determine the slope C:N and slope N:P ratios (Krom et al. 1991, Fanning 1992, Sanders and Jickells 2000, Kress and Herut 2001, Hung et al. 2003, Schroeder et al. 2010, Pujo-Pay et al. 2011).

A high C:N ratio (both DOC:DON ratios and slope of DOC:DON ratios) reflects production of high C:N material or preferential remineralisation of N relative to C. In closed systems such as incubation bottles, the increase in the C:N ratio during DOM decomposition can be interpreted as preferential remineralisation of nitrogen relative to carbon in DOM (Hopkinson et al. 1997, Hopkinson et al. 2002). However, this is more complex in an open system such as the natural environment. In a seawater column, the preferential remineralisation of nitrogen is generally indicated by carbon rich DOM in deep waters (Loh and Bauer 2000, Church et al. 2002, Hopkinson and Vallino 2005). Hopkinson et al. (1997) suggests the factors controlling the C:N stoichiometry of oceanic DOM are still little known. In the coastal sea of shallow depth and more impacted by river discharge than the open ocean, riverine input creates high DOC (0.21 Pg C) and low DON (0.005 Pg N) materials entering to the global coastal ocean each year (Seitzinger and Harrison 2008, Dai et al. 2012). This potentially inputs high C:N stoichiometry of DOM to coastal waters. This terrestrial organic matter (TOM) input with high C:N ratio e.g. 30-60 leads to C:N ratio differences between the products of TOM decomposition and primary production in coastal water (close to the Redfield), and subsequently provides a condition with respiration (CO_2 production) exceeding primary production (CO_2 consumption) in coastal water (Bauer et al. 2013). To exemplify this, at least 30 moles of CO_2 are produced (for every one mole of production of inorganic nitrogen) during TOM remineralisation, and if all of this nitrogen is recycled and utilized by phytoplankton, there will only be 7 moles of this inorganic carbon taken up by phytoplankton according to C:N ratio close to the Redfield,

leading overall to more CO_2 production during TOM remineralisation than supply by primary production (Bauer et al. 2013).

In general, the C:N stoichiometry of DOM in seawater (particularly open ocean water) are reported based on DOC:DON molar ratios and their variations with depth. Table 1.1 presents reported values of DOC and DON concentration and their DOC:DON molar ratios in seawater. These data in the North Sea and its surrounding area are presented separately in the next section (section 1.6). In coastal oceans, DOM concentrations are generally greater inshore than offshore on a global scale (Barrón and Duarte 2015) and higher in surface than bottom waters as observed in the Mid-Atlantic Bight (Vlahos et al. 2002, Bauer et al. 2002) and shelf waters of the western Arctic Ocean (Wang et al. 2006). This suggest the influence of river input as a source of DOM on the coastal regions as well as, or instead of, higher production of DOM in coastal surface water because of high phytoplankton production. In comparison to the open ocean, the coastal region generally shows higher DOC and DON concentrations, as well as higher DOM C:N molar ratios. It has been proposed based on available data that average C:N molar ratio (± SD) of DOM in surface waters were relatively high in rivers (32.5 ± 16.3) compared to estuaries (16.4 ± 7.4), continental shelf waters (16.4 ± 7.0) and ocean surface waters (14.0 ± 2.9) (Sipler and Bronk 2015). This indicates a gradient of decreasing C:N molar ratios from freshwater to the marine environment, which may be due to materials transported from rivers to the global coastal ocean each year contain substantially higher DOC than DON and/or preferential nitrogen recycling from DOM.

The stoichiometric pattern of the DOC:DON ratio in ocean water generally varies with depth and time because the production and consumption of a labile DOM differs from Redfield stoichiometry (Hopkinson et al. 1997, Hopkinson and Vallino 2005). The molar ratio of C to N for the bulk DOM in the northeastern Atlantic Ocean shows higher ratios (15.4 ± 0.3) in the deep water at 1500-4000 meters than the surface layer at less than 200 meters (13.8 ± 0.4) (Aminot and Kérouel 2004). In regional seas and shelf seas this depth pattern is less clear. The Mediterranean Sea and Black Sea are considered here as regional seas because they are separated from the open ocean but much deeper than normal shelf sea systems. The higher C:N molar ratio in the Mediterranean (~15-17) does not show the same tendency with increasing depth (Aminot and Kérouel 2004). A later study presents a noticeable

Table 1.1 DOC and DON concentrations and their C:N molar ratios reported in the literature for coastal waters, regional sea waters and open ocean waters.

Area	Date	Sample depth (m)	DOC (μM)	DON (μM)	DOC:DON ratio	Reference
Coastal/ continental shelf waters[*]						
Georges Bank	Apr 1993	Surface 100-1500	75-82 50-55	-	-	Chen et al. 1996
South of Georges Bank, shelf slope	Apr 1993	Surface 200-1500	69-78 50-64	4.8-5.4 2.5-3.4	11.0-15.0 14.7-22.8	Hopkinson et al. 1997
South of Georges Bank to Cape Hatteras, the Mid-Atlantic Bight	Mar 1996 Aug 1996	Surface Deep slope Surface Deep slope	81-143 44 94-201 49	7.9-12.6 3.6 7.1-14.3 3.5	9.1-14.1 12.2 10.6-14.0 14.0	Hopkinson et al. 2002
Mid-Atlantic Bight	May 1993	2-100 400-800	67-90 47-50	-	-	Guo et al. 1995
Mid-Atlantic Bight	Apr 1994, Mar 1996, Aug 1996	0-20 200	60-165 42-56	-	-	Vlahos et al. 2002
Mid-Atlantic Bight	Apr-May 1994 Mar 1996 Jul-Aug 1996	5 300 1-7 ~300 5 ~300	77-115 46-53 58-126 42-50 69-121 36-43	-	-	Bauer et al. 2002
Mid-Atlantic Bight	Jul 2002	1 14	-	4.0-8.6 2.3-4.0	-	Bradley et al. 2010
Chesapeake Bay to Sargasso Sea	Sep-Oct 1996	Surface	125 ± 44.6	10.4 ± 4.4	12.4 ± 1.7	Bates and Hansell 1999
Northwestern Sargasso Sea	Aug 1997-2001	5-10 250	67.6-69.6 51.2-64.2	-	-	Carlson et al. 2004
Southern California Bight	Apr, Jul-Aug 1990	10-30 800-900	86-98 67 - 74	5-10 2-5	9-19 15-33	Hansell et al. 1993
Southern California Bight, nearshore station	Oct 1992	10	-	6.7 ± 0.1	-	Bronk and Ward 2005
Oregon continental shelf	Aug 2005 Sep 2005	Surface Surface	105.1 58.3	10.0 8.2	10.5 7.1	Wetz et al. 2008
West Florida shelf	Oct 2008	Surface	-	16.2 ± 0.3	-	Wawrik et al. 2009
Bay of Biscay, northeastern Atlantic Ocean	May-Jul 2006 May 2007	5-20 140-150	80-95 65-85	-	-	Engel et al. 2012
Northeastern shelf of the Gulf of Cádiz (Southwestern coast of Iberian Peninsula)	Jun 2006 Nov 2006 Feb 2007 May 2007	3 3 3 3	90.7 ± 21.9 83.7 ± 25.3 89.1 ± 26.4 106.2 ± 25.6	4.8 ± 1.5 6.2 ± 2.3 4.2 ± 2.8 8.6 ± 3.1	20 ± 8 13.0 ± 7.0 30.0 ± 26.0 14.0 ± 8.0	Ribas-Ribas et al. 2011
North Australian shelf	Nov 1999	Surface	-	5.8 ± 1.8	-	Knapp et al. 2012
Western Arctic Ocean	Sep 2002	5-10 > 100	69-81 46-72	-	-	Wang et al. 2006
Chukchi Sea shelf, Arctic Ocean	Jul-Aug 2002, Sep 2009 May-Jun 2002	0-30 0-30	- -	6.0-8.0 4.0 ± 0.7	- -	Letscher et al. 2013

Table 1.1 (Continued)

Area	Date	Sample depth (m)	DOC (μM)	DON (μM)	DOC:DON ratio	Reference
Gulf of Mexico	Jan 1993	2 100-400	70-86 47-71	-	-	Guo et al. 1995
Eastern Gulf of Mexico	Oct 2007	Surface	375 ± 18	13.6 ± 1.4	27.6	Sipler et al. 2013
East Japan Sea	May 2007	< 100	60-80	4-7	17.0 ± 3.0	Kim and Kim 2013
Northern South China Sea	Oct 2002, Jul 2003, Feb 2004	Surface Deep slope > 1000	70-85 43.0 ± 3.0	-	-	Hung et al. 2007
East China Sea	Jul 2011	5	54.4-143.7	3.9-26.9	4.9-25.1	Chen et al. 2016
Bohai Sea, northwest Pacific Ocean	Apr 2010	Surface	225.9 ± 75.4	-	-	Chen et al. 2013b
Hwasun Bay, Jeju Island, southern sea of Korea	Oct 2010 Jan 2011 Jun 2011	Surface	59 ± 5	25 ± 15	-	Kim et al. 2013
Regional sea waters						
Northwest shelf Shelf break of Western Black Sea	May-Jun 2001	Surface Surface	233-272 211-240	14.5-15.0 10.5-12.4	15.5-18.9 20.6-21.3	Ducklow et al. 2007
Northwestern Mediterranean Sea	Sep 1984	surface 200-600 800-1500	67-69 46-48 46	4.0-4.2 3.0 2.7	16.7-16.9 15.1-16.0 16.8-17.2	Aminot and Kérouel 2004
South east Levantine basin, eastern Mediterranean Sea	May 2002	Photic zone 500-1200	65-100 40-60	3-11 1-2	10-20 40-30	Krom et al. 2005
West Mediterranean Sea	Jun-Jul 2008	0-100 200-800 1000-2900	45.3-69.4 37.6-53.3 37.9-41.9	4.1-5.5 2.5-4.1 2.9-4.3	12.5 12.4 12.5	Pujo-Pay et al. 2011
East Mediterranean Sea	Jun-Jul 2008	0-100 200-800 1000-3000	49.4-72.4 37.5-54.1 38.4-43.9	3.5-6.3 2.1-5.4 2.1-4.0	13.0 12.4 12.1	Pujo-Pay et al. 2011
Northern Adriatic Sea	Sep 2009 Oct 2009 Nov 2009 Jan 2010	0-30 0-30 0-30 0-30	87-130 83-100 83-92 74-87	-	-	Marić et al. 2013
Southern Adriatic Sea	Sep 2007 Jan 2008	0-200 200-600 800-bottom 0-200 200-600 800-bottom	57-79 45-54 47-56 49-59 45-54 50-60	2.5-6.9 2.8-5.2 3.4-6.2 2.3-7.2 1.8-5.3 2.9-4.6	16 ± 3 13 ± 2 11 ± 2 14 ± 3 14 ± 4 15 ± 2	Santinelli et al. 2012
Marmara Sea North Aegean Sea	Aug 2008 Aug 2008	0-20 20-1200 0-20 20-1200	116-217 52-73 65-107 58-66	6.4-9.3 1.0-5.1 3.1-5.7 2.7-4.5	14-27 13-58 17-23 15-25	Zeri et al. 2014
Open ocean waters						
The Atlantic Ocean, off the Mid-Atlantic Bight	May 1993	0-100 1000-2500	58-75 46-48	-	-	Guo et al. 1995

Table 1.1 (Continued)

Area	Date	Sample depth (m)	DOC (μM)	DON (μM)	DOC:DON ratio	Reference
Northeastern Atlantic Ocean	Sep 1985	surface 200-600 800-1500	77-83 54 49	5.8-6.1 4.0 3.9	13.1-13.7 13.7 12.6	Aminot and Kérouel 2004
Northeastern Atlantic Ocean	Oct 1987	surface 200-600 800-1500 3000-4000	61-62 50-51 44-46 41-41	4.2-4.5 3.4-3.5 3.1-3.3 2.6-2.6	13.8-14.3 14.2-14.8 13.3-15.2 15.5-15.6	Aminot and Kérouel 2004
Northeastern Atlantic Ocean	Apr 2002	surface 200-600 800-1500 3000-4000	61 50-55 46 42-43	4.5 3.9-4.1 2.8-3.2 2.7-2.8	13.7 13.0-13.5 14.4-16.4 15.3-15.7	Aminot and Kérouel 2004
Atlantic Ocean	Apr-May 2000	0-250	-	3.0-6.5	-	Mahaffey et al. 2004
Atlantic Ocean	Aug 1998-Oct 2000	0-200	-	5.6-6.9	-	Varela et al. 2006
North Atlantic Ocean	Jun-Nov 2003	Surface Bottom	80 40	-	-	Carlson et al. 2010
North Atlantic subtropical Gyre	Apr-May 2001 Mar 2002	0-100	68.7-75.4		-	Kähler et al. 2010
Beaufort Gyre, East Siberian Sea, Arctic Ocean	Aug 2008 Sep 2009	0-30 0-30	- -	~ 4.0 6.0-7.0	- -	Letscher et al. 2013
Eastern North Pacific and Southern Ocean	Jun 1995	0-100 >1000	50-72 35-46	2.9-4.5 1.7-4.4	11-17 9-16	Loh and Bauer 2000
Southern Ocean	Nov 1994-Feb 1995	< 30 500-2500	45-55 40-46	4-8 2-4	5-16 11-22	Ogawa et al. 1999

Data in the table are obtained from tables, text or graph estimation in the references and is reported in term of the range and/or mean ± standard deviation (SD).

Data in the table does not include the North Sea and its surrounding areas (e.g. the Baltic Sea, English Channel, Celtic Sea and Irish Sea) which are presented separately in the next section (section 1.6).

* Data from literatures were classified in the coastal/ continental shelf waters region when the water column depth in the sampling area was less than 500 meter (Simpson and Sharples 2012), some areas (e.g. the Georges Bank) with a greater depth were included in this regions as sampling areas were extended to the shelf break.

stability of the C:N molar ratio (12-13) throughout the Mediterranean Sea (Pujo-Pay et al. 2011). No trends are observed in the vertical profiles (0-200 meters depth) of molar ratios of bulk DOC to DON concentration investigated in the Western Black Sea including the Northwest Shelf, Shelf-break and Southwestern Gyre (Ducklow et al. 2007). Similarly, the high C:N molar ratios (15.5 – 21.3) in surface water are not significantly different along the shelf-gyre transect in the Western Black Sea (Ducklow et al. 2007). The observed C:N molar ratios of the bulk DOM across the continental shelf, continental slope and central ocean gyre region exhibit lower C:N ratios when there are higher DOM concentration (Hopkinson and Vallino 2005).

The DOM production and removal processes within coastal regions (section 1.4) regulate the presence of DOM, its cycling within the water column and act as a sink or source of DOM exchange between coastal zones and the open ocean. In addition to being important as a sink of fixed nitrogen (Fennel 2010), a coastal region potentially exports DOC to the open ocean as reported on a regional (Bauer et al. 2001, Vlahos et al. 2002, Hung et al. 2003, Munro et al. 2013) and a global scale (Barrón and Duarte 2015). The observation in the Mid-Atlantic Bight estimates that recycled oceanic DOC (67%), DOC production on shelf (29%) and DOC supplied from rivers, rainwater and sediment (4%) contributes to coastal DOC exported to the adjacent open ocean (Vlahos et al. 2002). The balance of DOM production and decomposition influences shifts between CO_2 uptake and CO_2 release across the coastal water. The coastal zone is thought to be overall a net autotrophic system and thus a net sink for atmospheric CO_2 by previous observation (Cai et al. 2006, Laruelle et al. 2010, Kühn et al. 2010, Chen et al. 2013a) that is subsequently transported to the open ocean via the "continental shelf pump" firstly named by Tsunogai et al. (1999) and later investigation in the coastal region (Thomas et al. 2004, Thomas et al. 2005, Bozec et al. 2005, Kühn et al. 2010).

1.6 Distribution of nutrients in the North Sea

1.6.1 The North Sea topography and circulation

The North Sea (Figure 1.3) is characterized as a shelf sea. It is a semi-enclosed and relatively shallow shelf sea, which is approximately 1,000 km from north to south and 500 km from west to east (Howarth 2001, Thomas et al. 2010). There are three areas characterized by their topography including the shallow part from ~54°N to the south with depths of approximately < 40 m (include the shallow Dogger bank), a deeper part to the shelf edge in the north with various depth increasing from 40 to 200 m, and the deepest area in the north east, the Norwegian Trench (Howarth 2001). However, based on the water column stratification, the North Sea can be divided into two parts including: 1) the southern North Sea where the shallow water (< 50 m depth) is tidally well-mixed year round, with high primary

productivity (300 – 350 g C $m^{-2}year^{-1}$) and continental influence; and 2) the northern North Sea with greater water depth (> 50 m depth) seasonal stratification, more Atlantic water influence and lower primary productivity (50 – 100 g C $m^{-2}year^{-1}$). The boundary between these two areas is approximately 54°N (west side) and 57°N (east side) to the north and mostly covers the area north of the Dogger Bank (Ducrotoy et al. 2000, Emeis et al. 2015).

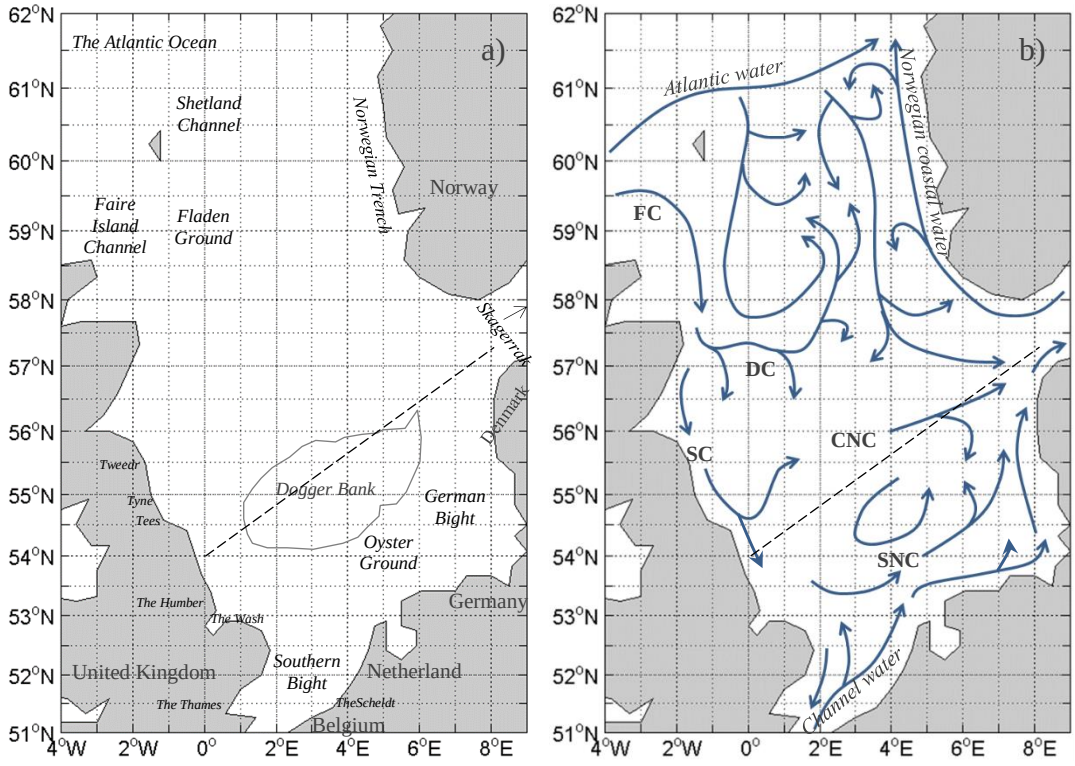


Figure 1.3 The North Sea topography and circulation. (a) Topography and the main areas mentioned in this thesis. (b) General circulation (adapted from Turrell et al. (1992) and Queste et al. (2013)). FC (Fair Isle current), SC (Scottish coastal current), DC (Dooley current), CNC (Central North Sea current), SNC (Southern North Sea current). The approximate boundary between the northern and southern North Sea is indicated by the broken line in (a) and (b).

The well-mixed zone in the south is considered as a high productivity area due partly to receiving nutrients from the continent, particularly the German Bight (Radach et al. 1990) and the Southern Bight area. Freshwater inputs to the sea include those from the Elbe and Ems (German coast), the Scheldt, the Rhine/ Meuse (the Netherlands and Belgium coast) as well as the riverine discharge from the eastern UK coast, particularly the Thames, Wash and Humber. In addition to the

riverine inputs, offshore water from the Atlantic and atmospheric input also add external nutrients into the regions (Jickells 1998). However, atmospheric deposition plays a less important role in this high productivity area (Spokes and Jickells 2005). Approximately 70 % of nitrogen flux through the German Bight is via the rivers, while atmospheric input contributes ~30% (Beddig et al. 1997). The river inputs also affect the salinity and density by introducing fresher less dense water. The Dogger Bank is a particular area in the North Sea with the shallow depth of 13 – 40 meters (Kröncke 2011). Clear water in this area supports light penetration and phytoplankton production which occurs throughout the year (Kröncke and Knust 1995).

The North Sea has a complex circulation (Figure 1.3b) but broadly Atlantic water enters from the north and via the English Channel and the circulation pattern leads to it exiting mainly along the Norwegian coast. The river inputs and input from the Baltic join the overall circulation pattern. A recent study shows the areas between the Dooley and Central North Sea currents and the area of the Oyster Ground, both have relatively low oxygen saturation (Queste et al. 2013). This is associated with remineralization of organic matter consuming oxygen, particularly during the summer stratification when oxygen transfer from surface water is blocked and an increase in temperature in summer decreases oxygen solubility (Greenwood et al. 2010). The well-mixed water in the southern North Sea is influenced by terrestrial inputs of carbon and nitrogen, but in the north, it is more strongly influenced by northeast Atlantic waters (Vermaat et al. 2008) and the seasonal stratification. As a shelf sea, the physical interaction processes in this area depend on the rate of water exchange and water chemistry which influences the pattern of nutrient transport (Jickells and Weston 2011).

On the global scale, the North Sea is one of the coastal regions surrounded by high basin runoff areas (Syvitski and Milliman 2007). Figure 1.4 demonstrates the North Sea suspended sediment transport from the satellite image showing most concentrated sediments around the river outlets and areas of high erosion in the southern North Sea. The highest suspended sediment level clearly are associated with the Thames plume which combines with the East Anglian plume flowing from UK coast eastward. As a shallow depth area (< 50 meters) (Emeis et al. 2015), the sediment can be resuspended from the sea bed, particularly in the storm season

during winter. In addition, high suspended particulate matter (SPM) is usually observed in the Thames plume and elsewhere during the winter months associated with high riverine discharge (Weston et al. 2008, Eleveld et al. 2008). The suspended load in the southern North Sea generally shows higher levels inshore than offshore with a winter maxima, whereas spring and summer show minimum levels (Sanders et al. 2001). By contrast, enhanced chlorophyll concentrations are exhibited in spring, while a low level is generally present throughout other seasons (Sanders et al. 2001, Moneta et al. 2014).

Figure 1.4 The satellite image of sediment in the southern North Sea acquired on 18 December 2004 (Schmaltz 2016) (credit: Jeff Schmaltz, MODIS Rapid Response Team, NASA/GSFC). The river outlet at the Thames on the southeastern coast of England has the most concentrated sediment load.

1.6.2 Seasonal cycle of nutrients in the North Sea

The North Sea, particularly the southern area is a high primary productivity area with 300 – 350 g C m^{-2} yr^{-1}, while the northern area has lower productivity (50 – 100 g C m^{-2} yr^{-1}) (Emeis et al. 2015) Riverine input of nutrients (e.g. nitrogen and phosphorous) play an important role in the southern North Sea, whereas atmospheric and offshore input are more important in the northern part (Rendell et al. 1993,

Jickells 2005). Therefore, when light is available, due to longer days and decreased vertical mixing, and inorganic nutrients are also available, phytoplankton usually bloom during the spring season, with highest values in the coastal area of the southern North Sea. The bloom generally does not dominate during winter as there is light limitation and higher riverine discharge of SPM to coastal surface waters over this period (Dyer and Moffat 1998, Neal et al. 2006) which reduces the light available to phytoplankton and suppresses primary productivity (Voss et al. 2011, Liu et al. 2013). However, phytoplankton still grow during the winter period of the North Sea, but at a low level (Weston et al. 2004).

Seasons influence biological cycles which strongly influence the seasonal cycle of nutrients in the North Sea (Weston et al. 2004). Availability of nutrients also conversely influences biological activities in the water column. Prior to the spring bloom, nutrients (mostly inorganic pools) are transported to the southern North Sea particularly (Brockmann et al. 1990), and the highest nitrate, phosphate and silicate levels are detected over the winter months of high river run off, net nutrients regeneration and least phytoplankton uptake (Van Bennekom and Wetsteijn 1990, Sanders et al. 1997a, Sanders et al. 1997b, Sanders et al. 2001, Nedwell et al. 2002, Weston et al. 2004). The elevated nutrient runoff with low biological activity during winter brings higher inputs to the region (Prandle et al. 1997, Gentilhomme and Lizon 1998) as well as the intense mixing up of deep nitrate to the surface water in winter in areas of seasonal stratification (Suratman et al. 2008a) and regeneration of nutrients within the water column and sediments. At the start of and during the spring bloom, high winter stocks of inorganic nutrients (particularly nitrate) are partly consumed by phytoplankton (De Galan et al. 2004, Suratman et al. 2008a), leading to a strong decline of nitrate coinciding with sharply elevated phytoplankton biomass (Weston et al. 2004, Johnson et al. 2013). This pattern continues during the bloom until it reaches a maximum chlorophyll *a* lasting for a few days, associated with reducing nutrient concentrations (Weston et al. 2004). Grazing and nutrient limitation then reduce phytoplankton levels and in the post spring bloom period, concentrations of nitrate, phosphate and silicate in surface water generally remain at a low level over the summer with a gradual rise in autumn to reach the highest level again in winter, prior to the spring bloom (De Galan et al. 2004, Suratman et al. 2008a). Ammonium in surface water shows the highest level in summer, but has a

low level in spring as for other inorganic nutrients, in response to phytoplankton utilisation (De Galan et al. 2004). This typical pattern of nutrients in the post spring bloom can be partly interrupted by small phytoplankton blooms in autumn.

Although organic nutrients in the North Sea are less well studied than the inorganic forms, previous reports at some specific areas typically show a distinctly different seasonal pattern from inorganic nutrients. The DON monitoring for three years (1997 – 2000) in the Belgian water indicates an absence of a seasonal pattern that may be the result of the low frequency of sampling, or due to there being no seasonal trend of DON in the studied region (De Galan et al. 2004). However, later studies in the central North Sea (north western Dogger Bank) reveals that DON and DOC exhibit low levels in summer, with high concentrations in the autumn and spring period correlated with high phytoplankton biomass, and the highest DON in winter driven by a source from bottom sediment (Suratman et al. 2008a, Suratman et al. 2009). In addition, DON variation over eight months at a single site shows the production of DON associated with the phytoplankton blooms (Johnson et al. 2013). High concentrations of DOC and DON are generally observed in nearshore rather than the offshore waters (Van Engeland et al. 2010) similar to the global pattern of Barrón and Duarte (2015). High concentrations of POC and PON in the spring bloom, as well as autumn and summer periods, correlate strongly with phytoplankton biomass (Weston et al. 2004, Suratman et al. 2008a, Suratman et al. 2009). The lowest POC and PON levels are in winter, consistent with low phytoplankton biomass (Suratman et al. 2008a, Suratman et al. 2009). Since some fraction of POC contain living (or recently dead) components e.g. phytoplankton, distribution of POC which is consistent with phytoplankton biomass is generally observed (Legendre and Michaud 1999).

1.6.3 Inorganic nutrients

Inorganic nutrients are generally taken up by phytoplankton to support their growth (Perry and Eppley 1981, Duhamel et al. 2006). Approximately 25 – 41 % of ammonium and nitrate taken up by phytoplankton is then released as DON (Bronk et al. 1994). Similar to phytoplankton, bacteria communities also take up inorganic nutrients to fuel their biomass production (Kirchman 1994, Kirchman and Wheeler

1998, Allen et al. 2002, Björkman et al. 2012). Heterotrophic bacteria prefer ammonium rather than nitrate as their nitrogen source (Kirchman 1994).

Considerable research has been devoted to the study of inorganic nutrients in the North Sea, Table 1.2 illustrates the available data on nutrient concentrations in the North Sea and nearby areas including the Baltic Sea and Channel waters. The data generally report nutrient concentrations in surface water. For inorganic nutrient reported in Table 1.2, TOxN is total oxidisable nitrogen (nitrate + nitrite) determination. Concentrations of ammonium, phosphate and silicate are also provided.

Table 1.2 Inorganic nutrient concentrations in the North Sea and its surrounding area.

Area	Season	Concentration (µM)				Ref.[b]
		TOxN [a]	Ammonium	Phosphate	Silicate	
The North Sea						
Central North Sea	Oct 2004	<0.1-4.5	<0.1-1.7	-	-	[1]
	Feb 2005	3.9-5.5	<0.1			
	Apr-May 2005	<0.1-7.2	<0.1-2.0			
	Aug 2005	<0.1-1.4	<0.1-1.3			
Thames plume and Southern North Sea (1996-1997)	April-May	0.1-27	-	<0.02-2.1	0.1-4	[2]
	July	<0.1-21		<0.02-2.7	0.2-2	
	Oct	2-32		0.2-3.4	2-10	
	Jan	8-33		0.5-2.5	5-13	
East Anglian plume and southern North Sea	Feb 2000	8.0-27.7	0.1-0.2	-	-	[3]
	Mar-May 2000	0.2-14.8	0.3-0.9			
	Jul-Aug 2000	0.1-2.6	0.1-1.9			
	Sep 2000	0.1-1.1	0.1-1.8			
Thames plume (Spring bloom on early Apr-mid May 2001, ~ 43 days)	Jan-Feb 2001	20-110	0-0.8	1.7-2.5	15-42.2	[4]
	Mar-May 2001	10-90	0-1.0	0.4-1.7	0.6-30.2	
Thames plume	Jun-Aug 2001	4-10	0-3.4	0.5-1.0	3.3	[4]
(Spring bloom on early Apr-mid May 2001, ~ 43 days)	Sep-Nov 2001	4-30	-	-	3.3-8.8	
	Dec 2001	20-30	0	1.0	6- 8.8	
Belgian area (1993-2000)	Spring	11.6±19.1	2.6±3.7	0.3±0.3	3.5±3.0	[5]
	Summer	10.5±10.2	3.9±3.0	0.8±0.6	6.3±5.8	
	Autumn	17.5±14.8	2.4±1.9	0.9±0.6	10.4±6.7	
	Winter	31.1±24.2	3.3±2.9	1.0±0.5	12.4±9.0	
Northern North Sea (North Dogger Bank to the Shetland Island)	Summer 1994 at 10 meters depth at 40 meters depth	 0.16±0.13 2.61±1.79	 0.17±0.05 1.40±0.90	 0.05±0.02 0.40±0.13	-	[6]
Southern North Sea	Aug1988 -Oct 1989	1-14	-	-	-	[7]
German Bight	Year round 1962-1984	1-32	2.5-15	0.25-1.50	1-16	[8]
Southern Bight	Sep 2002 -Dec 2003	0.5-92	0.5-12	0.1-1.9	0.5-49	[9]
Elbe river plume	Aug-Sep 2009	-	4	-	-	[10]
Inlet of the Wadden Sea (Marsdiep inlet)	Jan-May 1989	5-60	0.2-8	0.1-2	2-28	[11]

Table 1.2 (Continued)

Area	Season	Concentration (µM)				Ref.[b]
		TOxN [a]	Ammonium	Phosphate	Silicate	
Other surrounding areas						
Scheldt estuary, Belgium (salinity 0-32)	Winter 1996 Summer 1996	40-750 30-380	0-180 8-90	1-6.5 1-9	25-220 5-30	[12]
English Channel	Year round 1986-1988	0-16	-	0.8-1.2	5.5-7.5	[13]
Eastern English Channel	Year round 1994 coastal station offshore station	 0-20 0-8	 1-8 1-4	 -	 -	[14]
English Channel Year round 1974-1987	at 5 meters depth at 70 meters depth	0-11 -	-	0-0.8 0.05-1.0	-	[15]
Southampton estuarine water	Spring-Summer 2001	<0.1-96	<0.2-42	-	-	[16]
Bothnia Bay (Baltic Sea)	Aug-Sep 2009	0.8-2.1	-	-	-	[10]

Data in the table are obtained from tables, text or graph estimation in the references and is reported in term of the range and/or mean ± standard deviation (SD).

[a] TOxN is a total oxidisable nitrogen (nitrate + nitrite) concentration

[b] References:

[1] Suratman et al. 2008a
[2] Sanders et al. 2001
[3] Weston et al. 2004
[4] Weston et al. 2008
[5] De Galan et al. 2004
[6] Riegman and Noordeloos 1998
[7] Hydes et al. 1999
[8] Radach et al. 1990
[9] Van Der Zee and Chou 2005
[10] Korth et al. 2012
[11] Riegman et al. 1990
[12] CabeÇadas et al. 1999
[13] Laane et al. 1993
[14] Gentilhomme and Lizon 1998
[15] Jordan and Joint 1998
[16] Torres-Valdés and Purdie 2006

1.6.4 DOC and DON

In general, the study of dissolved nutrients in the North Sea has concentrated on the inorganic form (e.g. nitrate, ammonium, phosphate and silicate) as reported in previous studies (Table 1.2) since some of them (nitrate and phosphate) are known to be limiting nutrients for primary productivity (Riegman et al. 1990, Moore et al. 2013) and more easy to analyse than the organic form (Badr et al. 2003). Thus, there are limited data of DOC and DON concentrations in the North Sea region, compared to the inorganic nutrients and the importance and controls on DOC and DON are poorly understood. However, data from various studies in surface waters are summarised in Table 1.3. There is seasonal variability as discussed earlier in section 1.6.2. In general, DOC and DON concentrations in the North Sea agreed well with those measured for other surface waters in coastal sea (Table 1.1). There were only few published data sets for both DOC and DON together in the North Sea.

Therefore, few data are available for C:N molar ratios which are generally similar to the ratio in other coastal waters reported in Table 1.1.

Table 1.3 DOC and DON concentrations and their C:N molar ratios reported in the literature for the North Sea and its surrounding area.

Area	Season	Concentration (µM)		DOC:DON ratio	Ref.[b]
		DOC	DON		
The North Sea					
Central North Sea	Oct 2004 Feb 2005 Apr-May 2005 Aug 2005	72-130 85-112 156-318 68-146	4.1-11.2 7.4-9.7 2.6-11.2 1.9-6.5	14.3 11.1 36.9 22.5	[1],[2]
Southern North Sea Coast Open Sea	 Jan 1995-Dec 2004 Jan 1995-Dec 2004	 122±28 - 130±25 73±13 - 78±15	 11±3 - 12±3 5±1 - 6±2	 10.8 - 11.7 12.1 - 14.8	 [3]
Eastern North Sea	Aug-Sep 2009	-	10.1 ± 0.6	-	[4]
Southern North Sea (Dowsing SmartBuoy site) Pre-bloom Bloom/transition Post bloom	 Jan-Mar 2010 Apr 2010 May-Oct 2010	 -	 5.8 7.9 8.4	 -	 [5]
Western Wadden Sea and Marsdiep inlet	Year round 1978-1981	83-416	-	-	[6]
German Bight	June 1981	-	15-40	-	[7]
Fladen Ground, northern North Sea	May 1983	42-200	-	-	[8]
Belgian area (1997-2000)	Spring Summer Autumn Winter	-	21.7±11.2 15.6±7.7 19.4±7.6 20.4±10.4	-	[9]
Southern Bight [a]	Sep 2002-Dec 2003	80-260	1-40	-	[10]
Other surrounding areas					
Nine European estuaries	1996-1999	91-292	-	-	[11]
The English Channel	Year round 1969-1977	-	0.3-0.7	-	[12]
Horsens Fjord, east coast of Denmark	Aug 2001-Sep 2002	175-369	10.4-51.6	9-17	[13]
Horsens Fjord, east coast of Denmark	Sep 2004 - Jul 2005	172-394	12-35	11.4 ± 3.8	[14]
Darss Sill, Hjelm Bight, Baltic Sea	Sep 2004 - Jul 2005	186-324	17-36	10.6 ± 1.7	[14]
Bothnian Bay, central Baltic Sea	Aug-Sep 2009	-	15.9 ± 1.2 14.8 ± 3.0	-	[4]

Data in the table are obtained from tables, text or graph estimation in the references and is reported in term of the range and/or mean ± standard deviation (SD).

[a] The C:N molar ratio was not available because concentrations of DOC and DON were estimated from graphs and no mean concentrations reported in the text.

[b] References

[1] Suratman et al. 2009
[2] Suratman et al. 2008a
[3] Van Engeland et al. 2010
[4] Korth et al. 2012
[8] Cadée 1986
[9] De Galan et al. 2004
[10] Van Der Zee and Chou 2005
[11] Abril et al. 2002

[5] Johnson et al. 2013
[6] Cadée 1982
[7] Eberlein et al. 1985
[12] Butler et al. 1979
[13] Markager et al. 2011
[14] Lønborg and Søndergaard 2009

1.6.5 POC and PON

Phytoplankton biomass contributes to POC and PON production in the North Sea (Weston et al. 2004, Suratman et al. 2008a, Suratman et al. 2009). It has been estimated in the previous study that surface POC is generally produced (580 mg m^{-2} d^{-1}) during day time and mineralised (250 mg m^{-2} d^{-1}) at night in the upper 10 meters of the central North Sea water column (Postma and Rommets 1984). In addition, riverine particles and resuspended sediment also contribute to POC and PON concentration in this region (Weston et al. 2004, Van Der Zee and Chou 2005). It has been proposed that phytoplankton dominates as a POC source during spring in the North Sea (Tungaraza et al. 2003) and other continental shelf waters (Engel et al. 2012). A recent report suggests that only part of POC (~6 %) is phytoplankton e. g. Vetrov et al. (2015). Concentration of POC and PON investigated in the North Sea and surrounding area was summarised in Table 1.4. POM concentrations in the North Sea (Table 1.4) and other observations in continental shelf waters (Bauer et al. 2002, Hung et al. 2007, Wetz et al. 2008, Engel et al. 2012, Marić et al. 2013) were generally higher than estimated global ocean concentrations (POC < 4 to 20 µM and PON < 0.6 to 2.5 µM) in the upper 30 meters (Martiny et al. 2013).

Table 1.4 POC and PON concentrations and their C:N molar ratios reported in the literature for the North Sea and its surrounding area.

Area	Season	Concentration (µM)		POC:PON ratio	Ref.[a]
		POC	PON		
The North Sea					
Central North Sea	Oct 2004	9.5-36.3	0.3-4.4	15.4	[1],[2]
	Feb 2005	7.0-9.8	0.6-0.9	10.1	
	Apr-May 2005	1.9-38.4	0.7-5.6	7.2	
	Aug 2005	4.5-14.0	0.6-2.2	6.7	
East Anglian plume	Feb 2000	20.0-70.3	1.6-3.9	11.0-15.6	[3]
	Mar-May 2000	8.9-47.4	0.9-3.8	5.3-13.8	
	Jul-Aug 2000	15.8-39.2	1.7-5.5	4.2-10.7	
	Sep 2000	21.3-48.6	2.7-5.0	5.0-9.2	
Western Wadden Sea and Marsdiep inlet	Year round 1978-1981	42-500	-	-	[4]

Table 1.4 (Continued)

Area	Season	Concentration (µM)		POC:PON ratio	Ref.[a]
		POC	PON		
North Dogger Bank to the southern North Sea	May 1981	9.6-17.5	-	-	[5]
	Jul 1981	6.7-10			
	Sep 1981	12.1-19.1			
Fladen Ground, northern North Sea	May 1983				
	surface waters	17-42	-	-	[6]
	bottom waters	2.5-3.3			
Eastern North Sea	Aug-Sep 2009	-	3.6±6	-	[7]
Belgian coastal water	Spring 1996 and 1997	28.2-48.1	3.5-6.4	7.5-8.0	[8]
Southern Bight	Sep 2002-Dec 2003	8-458	-	-	[9]
Other surrounding areas					
Bothnian Bay, central Baltic Sea	Aug-Sep 2009	-	3.3±0.6	-	[7]
			3.0±0.6		

Data in the table are obtained from tables, text or graph estimation in the references and is reported in term of the range and/or mean ± standard deviation (SD).

[a] References

[1] Suratman et al. 2009
[2] Suratman et al. 2008a
[3] Weston et al. 2004
[4] Cadée 1982
[5] Postma and Rommets 1984
[6] Cadée 1986
[7] Korth et al 2012
[8] Tungaraza et al. 2003
[9] Van Der Zee and Chou 2005

1.7 Research overview

1.7.1 Background of the research

Recently, there has been growing interest in organic carbon and nitrogen in the aquatic system. While in the past, considerable research has been devoted to examining DIN species (nitrite, nitrate and ammonium) in terms of their importance to primary productivity and water quality, rather less attention has been paid to other fractions, including DON, because of difficulties in measuring and the underlying assumption that DON is biologically inert (Badr et al. 2003). However, there are increasing reports on DON being utilised by phytoplankton and heterotrophic bacteria as seen in previous studies suggesting it is not all biologically inert (Veuger et al. 2004, Lønborg and Søndergaard 2009, Bradley et al. 2010, Van Engeland et al. 2013, Moneta et al. 2014). Marine DOM is one of the largest global stores of exchangeable carbon (Hedges 2002, Amon and Benner 1994, Azam 2015) but its behaviour in the marine environment remains only partly understood (Ogawa and Tanoue 2003).

At present, the processes responsible for DOC and DON cycling are not entirely understood (Carlson and Hansell 2015), and their fate in the coastal zone is to date uncertain (De Galan et al. 2004, Hitchcock et al. 2010). It has been proposed that most of the organic matter in the ocean is from internal sources within the marine environment (Opsahl and Benner 1997, Ehrhardt and Koeve 1999, Carlson and Hansell 2015). In addition, external sources e.g. riverine input is also important as a source of DOM, particularly in the coastal sea (Cauwet 2002). The autochthonous DOM is generally thought to be more bioavailable than allochthonous material (especially DOC) (Repeta 2015) and its cycling is controlled by several biotic and abiotic processes. DOM is a complex mixture of organic substances, it can be subdivided into various components with different chemical composition (Benner 2002). Their compositional differences lead to different microbial utilization rates (Amon and Benner 1996). The process of microbes consuming DOM represents a major trophic pathway in the marine system (Azam 1998). A fraction of DON is assumed to be degraded into DIN by bacteria in surface seawater (Sipler and Bronk 2015).

When marine bacteria utilize some labile components of DOM, they may produce refractory DOM by altering its molecular structure (Ogawa et al. 2001, Jiao et al. 2010). The biologically refractory DOC is thought to be dominated by low molecular weight (< 1 kDa) compounds (Benner et al. 1992, Amon and Benner 1996) and the largest fraction (70 percent) of the bulk DOM in the ocean has a low molecular weight (Benner 2002). Recent reports suggest that molecular-level characterization of a low molecular weight DOM is needed to assess its bioavailability in different microbial processes; however, this DOM is still complex and difficult to characterise (Kujawinski 2011).

In experiments in productive coastal waters, DOM degradation by bacteria was estimated to remove 11% DOC and 28% DON of the initial quantities over 4 days (Lønborg et al. 2011). Similarly, in incubations of water samples from the coastal upwelling area, degradation removed 57% and 73% of the total bioavailable DOC and DON over long-term incubations (50 to 70 days) (Lønborg et al. 2010). This agreed with a short term incubation (3 days) of shelf waters that DOC was degraded approximately 41% (Wetz et al. 2008). Degradation generally follows the same pattern; a part of DOC and DON is rapidly degraded in the initial period of incubation suggesting lability of this part of the DOC and DON, while some of the rest is very old and slowly degraded (Hansell et al. 2012, Hansell 2013, Nelson and Wear 2014).

The DOM cycling (considered DOC and DON) in coastal seas is influenced by many processes as illustrated in Figure 1.5. High concentrations of DOM are generally observed at the inner shelf compared to offshore waters (Vlahos et al. 2002, Hopkinson et al. 2002, Van Engeland et al. 2010, Barrón and Duarte 2015). The coastal sea receives DOM inputs from various pathways including external and internal sources. The external sources are riverine transport, atmospheric deposition, groundwater discharge, sediment release, offshore and in some area release from other sources (corals and hydrothermal vents) as discussed in more detail in section 1.4.1.2. Among these, riverine discharge is thought to be the dominant terrestrial source with global total fluvial inputs of DOC ~ 0.21 Pg C $year^{-1}$ (Dai et al. 2012) and DON ~ 5 Tg N $year^{-1}$ (0.005 Pg N $year^{-1}$) (Seitzinger and Harrison 2008) delivered to the global coastal ocean. Although terrestrial DOM is partly considered as refractory, a relatively large fraction of this DOM is degraded and modified within

the coastal zone (Opsahl and Benner 1998, Cauwet 2002, Stubbins et al. 2010). In addition to riverine discharge, internal production contributes a large amount of DOM to coastal seas (Cauwet 2002). Therefore, DOM in the coastal sea is also thought to be produced by the internal sources such as phytoplankton and bacterial release, zooplankton grazing and cell lysis. DOM present in coastal seas and the inorganic substances produced during DOM cycling was then exchanged with open ocean waters.

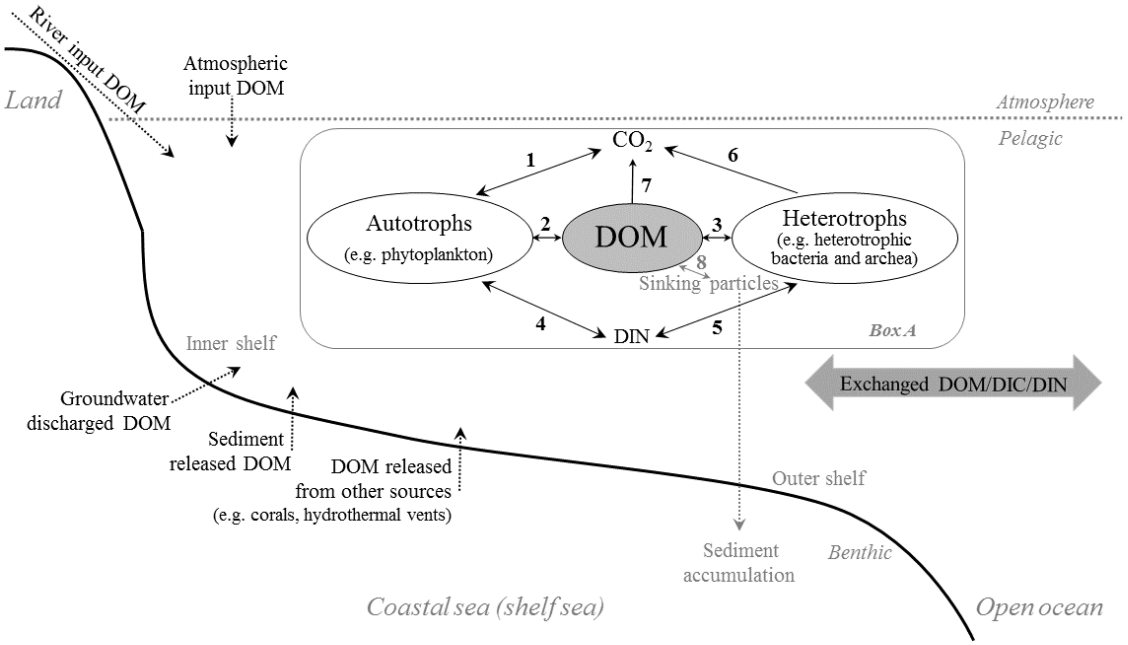


Figure 1.5 A conceptual model for DOM cycling in coastal seas. The processes illustrated here are also discussed in more detail in section 1.4 (sources and sinks in coastal waters). (1) phytoplankton production and respiration, (2) DOM assimilation and release by phytoplankton and DOM produced by cell lysis and zooplankton grazing of phytoplankton, (3) DOM uptake and release by bacteria and DOM produced by cell lysis and zooplankton grazing of bacteria, (4) DIN utilised and released by phytoplankton, (5) DIN utilisation and release by bacteria, (6) bacteria respiration, (7) photoremineralisation of DOM, (8) solubilisation and sorption of DOM on sinking particles. Nitrogen fixation (e.g. by cyanobacteria) does not generally dominate the nitrogen input to temperate coastal seas which are more influenced by nitrification and denitrification process plus inputs from the river, atmosphere and offshore for the nitrogen cycle (Herbert 1999). This figure is based on information from several sources (e.g. Collos 1998, Lomas et al. 2000, Brion et al. 2004, Thomas et al. 2004, Pätsch and Kühn 2008, Bauer et al. 2013, Repeta 2015, Carlson and Hansell 2015). Box A refers to internal cycling of DOM discussed in the text.

Box A in Figure 1.5 illustrates internal cycling of DOM within the coastal waters where DOM is autochthonously produced and removed by biological activities and abiotic mechanisms within the water column (more details are

discussed in section 1.4.1.1, 1.4.2.1 and 1.4.2.2 (not included outflow of DOM in coastal waters to the open ocean)). CO_2 is fixed by autotrophs (1) such as phytoplankton which can excrete DOC (2). Zooplankton grazing and cell lysis after viral infection of phytoplankton (2) and bacteria (3) can release additional DOM to be uptaken by heterotrophic bacteria (3) and assimilated by phytoplankton (2). In addition, bacteria can directly release DOM by excretion (3), as well as transform DOM to recalcitrant or inert forms. Both autotroph (1 and 4) and heterotroph (5 and 6) respiration processes release CO_2 and inorganic nutrients during DOM degradation. The released DIN can then be utilised by phytoplankton (4) and heterotrophic bacteria (5) during their growth. DOC is directly transformed to CO_2 by photoremineralisation (7). DOM can absorb onto the surface of sinking particles (POM) (8) and subsequently accumulate in sediment. Conversely, DOM releases during solubilisation of the sinking particles (8) can occur when bacteria hydrolyse POM from marine particles.

The coastal zone is generally more productive than open ocean waters (Jickells 1998, Simpson and Sharples 2012) and therefore may have a more rapid dissolved organic carbon and nitrogen (DOC and DON) turnover than in the open ocean because of faster production and degradation processes in the coastal regions. This may potentially impact on the global carbon and nitrogen cycles through the exchange processes between outer shelf waters and open ocean waters (Barrón and Duarte 2015). The coastal waters represent ~10% of the oceanic surface area but contributes ~20% of the production of organic matter in the whole ocean (Wollast 1998), and approximately 7.0 ± 5.8 to 29.0 ± 8.0 Pg C yr^{-1} of DOC in the coastal zones is estimated to be net exported to the open ocean on a global scale (Barrón and Duarte 2015). Thus, rates of DOM degradation in coastal regions are necessary to quantify (Wetz et al. 2008).

The North Sea is one of the most highly productive marine areas, particularly the southern part (300 – 350 g C $m^{-2}yr^{-1}$) (Emeis et al. 2015). Figure 1.6 illustrates inorganic carbon exchange in the North Sea. In the southern North Sea, respiration and production processes take place in the well mixed water, whereas in the seasonally stratified northern region, net respiration process principally occurs in the subsurface water masses where it is subject to exchange with the North Atlantic Ocean (Thomas et al. 2004). For the North Sea and other continental shelf waters,

inner shelf waters have been suggested to be sources of CO_2 to the atmosphere because of high rate of respiration of riverine discharged organic carbon. By contrast the outer shelf surface waters are a sink of CO_2 because seasonal stratification isolates surface primary productivity from net take up of CO_2 by net respiration/ remineralisation at depth (Jiang et al. 2008, Bauer et al. 2013, Emeis et al. 2015). This is consistent with other previous studies in the North Sea (Bozec et al. 2005). In summer, the well-mixed water in the southern part of the North Sea is heterotrophic (acts as a net source of CO_2 for the atmosphere), whereas in the stratified northern North Sea, the area is autotrophic (acts as a net sink of CO_2 from the atmosphere) in the surface layer as it is separated from the heterotrophic in subsurface layer (Bozec et al. 2005). There is estimated to be a weak net CO_2 source in the southern part of the North Sea (0.78 mol m^{-2} a^{-1}) as remineralisation process is comparable to primary production (except for high production during spring blooms) (Prowe et al. 2009). By contrast, high net CO_2 uptake (2.06 mol m^{-2} a^{-1}) is estimated in the surface layer of the stratified northern North Sea during the productive season and a semi-labile DOC released by overflow production (the formation of a C-rich and N-deplete DOM) is observed in summer (Prowe et al. 2009).

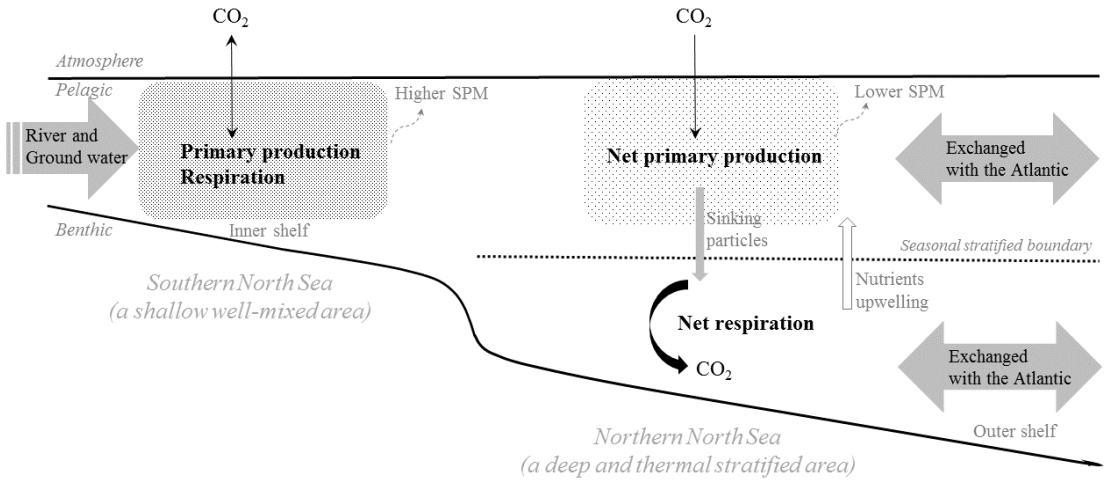


Figure 1.6 A conceptual model for inorganic carbon exchange in the North Sea. This figure is based on information from several sources (e.g. Thomas et al. 2004, Thomas et al. 2005, Bozec et al. 2005, Prowe et al. 2009, Jiang et al. 2008, Kühn et al. 2010, Bauer et al. 2013, Emeis et al. 2015).

It has been argued that this leads to the whole North Sea acting as a net sink of atmospheric CO_2 during late summer, but it still acts as a weak sink compared to the size of the sink estimated in the Baltic and the East China Sea at the same period of the year (Bozec et al. 2005). Kühn et al. (2010) also estimates that the North Sea is a net sink for atmospheric CO_2 with a rate of 0.98 mol C m^{-2} yr^{-1}. It has been proposed that the entire North Sea imports organic carbon and exports inorganic carbon across the outer shelf to the North Atlantic Ocean (Thomas et al. 2005, Kühn et al. 2010). Hence the North Sea has been characterised as an efficient continental shelf pump of CO_2 by previous reports (Thomas et al. 2004, Thomas et al. 2005, Bozec et al. 2005, Kühn et al. 2010) as ~ 90% of atmospheric CO_2 taken up in the North Sea is exported to the North Atlantic Ocean (Thomas et al. 2005).

Studies of nitrogen cycling in the North Sea suggest that coupled benthic nitrification/ denitrification is the main sink for nitrogen (Brion et al. 2004, Pätsch and Kühn 2008). The external input of organic nitrogen (riverine and atmospheric and imported across the northern boundary) through the North Sea is at least partly transformed to inorganic nitrogen. This inorganic N plus the inputs from atmosphere, rivers and offshore is partly denitrified and the rest of DIN exported to the North Atlantic waters (Pätsch and Kühn 2008). The North Sea have been characterised as an important sink for (total) nitrogen from the North Atlantic Ocean (Hydes et al. 1999, Pätsch and Kühn 2008) consistent with the investigation in other continental shelf waters (the Middle Atlantic Bight, Georges Bank, Gulf of Maine and the Scotian Shelf) of the Northwestern North Atlantic (Fennel 2010). In addition, recent research has suggested that the microbial communities and their ability to degrade organic compounds such as DOC and DON require further research to improve our understanding of DOC and DON cycling (Voss and Hietanen 2013, Nelson and Wear 2014).

To date, there have been few investigations of the standing stocks, distribution and cycling of DOC and DON in the North Sea (Suratman 2007, Suratman et al. 2008a, Suratman et al. 2009, Van Engeland et al. 2010, Johnson et al. 2013) where primary productivity is thought to be mostly controlled by internal cycling of nitrogen rather than external inputs. Thus there are many gaps in our knowledge on DOC and DON production and degradation processes and cycling in the North Sea. These gaps include the following:

- Lack of information on concentration of DOC and DON in bottom water of the North Sea and their C:N stoichiometry.
- DOC and DON overall distributions have only been investigated in specific area, particularly in the southern North Sea.
- Little information is available on processes that control DOC and DON distributions in the whole North Sea e.g. whether these are influenced by phytoplankton and bacterial biomass or external inputs.
- The degradation rate of DOC in the North Sea is currently not available.
- There is a lack of information on whether DON is coupled to DOC during DOM cycling (i.e. that the DOC and DON components are formed, degraded and released at the same rate and in constant proportion)

In this research, DOC and DON distribution data will be collected and used, along with other water column measurements and some laboratory incubations, to lead to a better understanding of the cycling of organic nitrogen and its relationship to the cycling of organic carbon in the North Sea.

1.7.2 Aim, objectives and hypotheses

The overall aim of the research is to investigate the biogeochemical cycling of DOC and DON in the North Sea. The specific objectives of this research are

1) To determine the concentration of DOC and DON in surface and bottom waters.
2) To investigate the spatial and temporal variation of DOC and DON concentrations.
3) To investigate the way bacteria and phytoplankton influence the DOC and DON concentration over time.
4) To use this information to improve understanding of the processes controlling DOC and DON cycling and distributions in the North Sea, including consideration of the C:N stoichiometry of the DOM pool.

The hypotheses of this research are

1) Surface water has higher DOC and DON concentrations than bottom water and lower C:N molar ratio.
2) The broad scale DOC and DON distribution is controlled by mixing between riverine and open ocean inputs of DOC and DON and thus a strong inverse relationship with salinity in DOM concentrations and C:N ratio is hypothesised.
3) Deviation from this broad scale mixing is hypothesised due to internal cycling of DOM which will for example modify C:N stoichiometry.
4) Preferential remineralisation of N compared to C will be seen in both field observations and incubation experiments.
5) Seasonal rate of DOC and DON net degradation will increase with initial supply concentration of DOC and DON, and with temperature.
6) Although there is evidence that phytoplankton and bacteria can both degrade and produce DOM, it is hypothesised that bacteria will dominate DOM degradation processes and phytoplankton dominate DOM production.
7) Both external inputs (i.e. river input) and internal processes (i.e. produced by phytoplankton and utilised by bacteria) are important factors regulating the cycling and distribution of DOC and DON in the North Sea.

Notes:

- Internal cycling (or internal processes) of DOM is defined here as DOM autochthonously produced and removed by biological activities and abiotic mechanisms within the coastal water column (more details are discussed in section 1.4.1.1, 1.4.2.1 and 1.4.2.2 (not included outflow of DOM in coastal waters to the open ocean)).
- External inputs of DOM are defined here as DOM delivered to coastal waters e.g. by river and groundwater via estuaries, from atmosphere and from offshore waters (more details are discussed in section 1.4.1.2).

1.8 Thesis structure

Chapter 1 (Introduction, the current chapter) contains a review of the current state of knowledge of marine DOC and DON on biogeochemical cycles, particularly in the coastal sea. A detailed description of the North Sea, which is the study area, and general nutrient research in the region are included. The background of this research, aim and objectives are presented in the research overview section. Chapter 2 (Methodology and analytical assessments) describes the sampling sites, sample collection and storage and the procedure for setting up degradation experiments. Details of analytical methods and their optimization are also presented. Chapter 3 (Spatial and temporal distribution pattern) presents results of cruise survey samples in summer 2011, winter 2011, and summer 2012 and their spatial and temporal distribution. Results of the analysis of SmartBuoy samples collected from West Gabbard and Dowsing sites in autumn 2013, winter 2013 and spring 2014 (same sites as incubated water samples) are presented and used to discuss the seasonal cycle of DOC and DON. Results and discussion of the degradation experiments are given in chapter 4 (Incubation experiment). Chapter 5 (Conclusion) summarises the main findings of the thesis and considerations for further research.

The first and second objectives explained in section 1.7.2 will be addressed in chapter 3, while the third objective will be addressed in chapter 4. The fourth objective will be addressed in chapter 5. The link between objectives, hypotheses and results is illustrated in Table 1.5 and also will be referred to in the conclusion chapter (chapter 5).

Table 1.5 The link between objectives, hypotheses and results in this research.

Objective	Hypothesis	Result
1	1	chapter 3
2	2 and 3	chapter 3
	4	chapter 3 and chapter 4
3	5 and 6	chapter 4
4	7	chapter 5

2 METHODOLOGY AND ANALYTICAL ASSESSMENTS

This chapter describes the methodology applied in the research. The first subtopic presents all study sites in the North Sea where seawater was collected to conduct the incubation experiments and investigate spatial and temporal distribution of nutrients. Next, the main field sample collection, preservation and overall analytical techniques are presented followed by details of setting up the DOM degradation experiments. Then, a detailed description of analytical methods used to determine chlorophyll *a*, particulate organic nutrients (POC and PON), dissolved inorganic nutrients (TOxN, ammonium, phosphate and silicate) are presented. Finally, the analytical assessment and optimisation of the method to determine dissolved organic nutrients (DOC and TDN) are presented in rather more detail since they required more method development as part of this thesis work.

2.1 Study sites

Water samples are collected from the North Sea during a series of cruises in 2011-2014 during different seasons. A transect of sites in the North Sea was sampled on CEFAS Endeavour cruises (International Bottom Trawl Survey (IBTS) cruise and SmartBuoy cruise). Generally, samples for conducting incubation experiments and studying SmartBuoy time series were collected on SmartBuoy cruises. While, samples for studying spatial and temporal distribution were collected on IBTS cruises. The sampling sites are constrained by the CEFAS sampling schedule in each cruise and the sites for collecting water for incubation experiments were chosen because of the suitable distance and time for sample transportation back to laboratories based at UEA. Figure 2.1 shows all sampling areas in the North Sea during 2011-2014. All sampling cruises in the North Sea are summarised in Table 2.1. SmartBuoy deployments used in this study are presented in Table 2.2 including the West Gabbard (WG) and Dowsing (DS) SmartBuoy sites located in the southern North Sea.

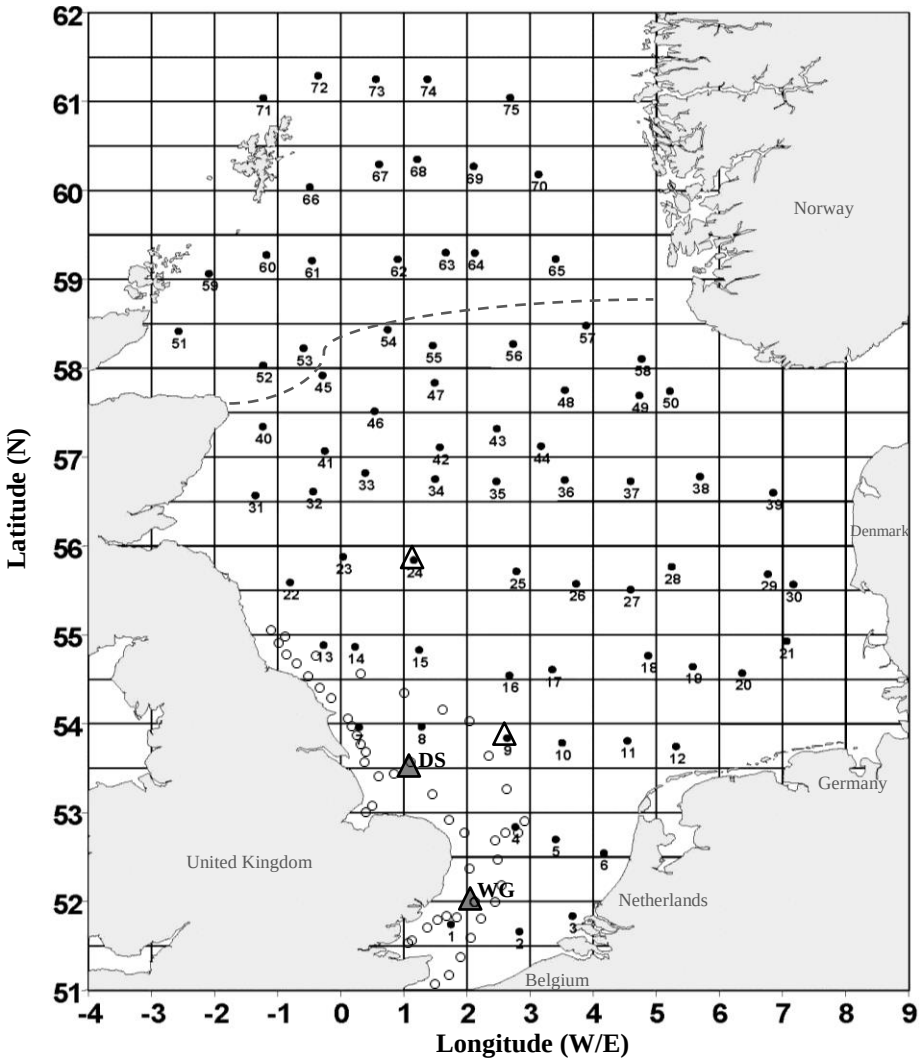


Figure 2.1 Sampling sites in the North Sea (modified from IBTS cruise track, CEFAS) including summer 2011 survey (74 stations in the whole North Sea, filled dot), winter 2011 survey (52 stations in the western North Sea, blank dot), summer 2012 survey (53 stations in the whole North Sea, filled dots but not including the area above the broken line), summer 2012 incubation experiment (3 stations, blank triangle and filled triangle (WG)), autumn 2013, winter 2013 and spring 2014 incubation experiments (2 stations in each season, filled triangle (WG and DS)), and SmartBuoy sites (filled triangle (WG and DS)).

Table 2.1 Summaries of sampling cruise in the North Sea and description.

Cruises		Dates	Season	Number of station	Sampling description
1	CEND 14/11	8 Aug – 7 Sep 2011	Summer 2011	74	Distribution pattern [a]
2	CEND 02/12	20 Jan – 31 Jan 2012	Winter 2011	52	Distribution pattern [b]
3	CEND 12/12	2 Aug – 8 Aug 2012	Summer 2012	1	Incubation experiment [c]
4	CEND 13/12	9 Aug – 23 Aug 2012	Summer 2012	53	Distribution pattern [a] and incubation experiment [d]
5	CEND 19/13	6 Oct – 8 Oct 2013	Autumn 2013	2	Incubation experiment [e]
6	CEND 03/14	30 Jan – 4 Feb 2014	Winter 2013	2	Incubation experiment [e]
7	CEND 08/14	11 May – 14 May 2014	Spring 2014	2	Incubation experiment [e]

[a] collected surface and bottom waters, whole North Sea
[b] collected surface and bottom waters, western North Sea
[c] collected surface water, West Gabbard site
[d] collected surface water, southern and northern North Sea sites
[e] collected surface water, West Gabbard and Dowsing sites

Table 2.2 Summary of SmartBuoy deployments in the North Sea used in the study.

Identification		Smartbuoy sites	Time water in	Time water out	Number of bag samples analysed
1	WG 94	West Gabbard	6 Sep 2013 15:55	6 Oct 2013 12:15	8
2	WG 96	West Gabbard	2 Feb 2014 16:45	13 May 2014 19:15	23
3	DS 33	Dowsing	29 Jul 2013 08:25	8 Oct 2013 07:45	18
4	DS 34	Dowsing	8 Oct 2013 08:15	22 Jan 2014 08:15	29
5	DS 35	Dowsing	30 Jan 2014 17:25	13 May 2014 06:45	22

2.2 Sample collection, preservation and analytical techniques

One of the important procedures to assure the quality of analytical data is the appropriate treatment of samples prior to analysis, for example, cleaning containers, proper sample preparation and storage. Therefore, before fieldwork sampling, plasticware and glassware were cleaned by soaking in decon®90 solution (5% v/v, Analar grade, England) for 24 hours, rinsing with de-ionised water (Milli-Q water) (18.2 MΩ.cm, Purelab Ultra, ELGA Process Water, England) 2 times and followed by soaking in Milli-Q water for 24 hours. Then, these containers were soaked in HCl (10% v/v, Analar grade, Sigma-Aldrich, England) for 24 hours, rinsed with Milli-Q water 2 times, and followed by soaking in Milli-Q water for 24 hours. Glassware was then combusted at 550 °C for 5 hours to remove any remaining organic residues. After combustion, glassware was rinsed with Milli-Q water and water samples before use. All plasticware and glassware used in this study, whether in the fieldwork or laboratory based at UEA were cleaned by the same procedure.

During seawater sampling and handling on a cruise, Milli-Q water was used for thorough rinsing between each sample step. Sampling procedures are presented in the Figure 2.2. The position of sampling stations occupied on the CEFAS Endeavour cruise track in the North Sea are shown in Figure 2.1. Standard measurements of temperature, salinity and depth were conducted at each site at the time of sampling.

Generally, 10 liter Niskin bottles attached on a CTD rosette were used for seawater sampling. Surface and bottom water samples were collected from well-mixed and stratified water columns at 2-4 meters below the surface and 5-6 meters

above the seabed. For the summer 2012 cruise, surface waters were collected by the ship's continuous flow system, because for more than half of the cruise track during the summer 2012, the CTD rosette was broken. The continuous flow system also supplies the on ship ferry box system and has an intake at a depth of 2 meters. Therefore, the ship's continuous flow water system and single 30 liter Niskin bottle deployed on a wire have been used instead for surface and bottom water collection, respectively.

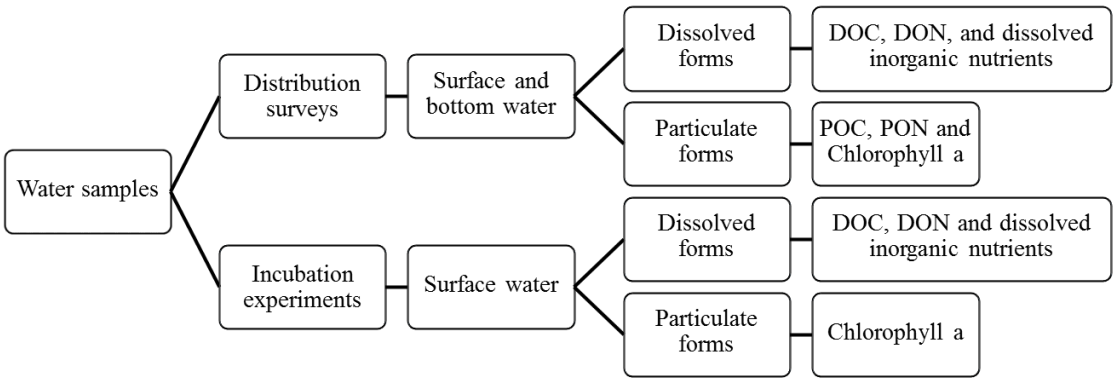


Figure 2.2 Field sampling process.

The separation of particulate material (POC, PON, chlorophyll *a*) from dissolved material (DOC, DON) was done by filtering water samples. Sample-collection protocols for these materials are designed to minimize changes in sample composition resulting from contamination, sorption onto container walls, physico-chemical flocculation processes and biological activities. In order to minimise the influences of these, samples were filtered immediately upon collection with suitable containers and procedures.

Filtration (gentle vacuum ~5 kPa) was undertaken through pre-combusted (450 °C, 5 hours) glass fibre filters (Satorius Stedim Biotech GF/F, England), 47 mm diameter of nominal pore size 0.7 μm with an ashed (550 °C, 5 hours) glass filtration unit. Filters and most of the filtration unit were combusted in a muffle furnace to ensure any remaining organic residues were removed (Kaplan 1992, Sharp et al. 1993). Filtrates were then collected in PP (polypropylene) sample tubes for DOC,

TDN and inorganic nutrients analysis. PP tubes are suitable for use as a sample container, and details of the PP test to confirm this are presented in section 2.8.1. Filters were wrapped in aluminium foil and placed in a plastic bag for POC and PON analysis, and the water volume recorded. Samples for chlorophyll *a* were collected from a separate water sub-sample on the same type of GF/F glass fibre filters (without combustion, gentle vacuum filtration ~10 kPa) and the water volume recorded. All samples were immediately frozen at -20 °C after filtration on board (-60 °C for chlorophyll *a* samples) until further analysis in the laboratory in order to reduce biological processes.

For the incubation experiment to study DOM degradation rate, surface water samples were collected at 2-4 m depth and treated as described in section 2.3.2 for the first onboard experiment in summer 2012 and section 2.3.3 for the later three laboratory based experiments in autumn and winter 2013 and spring 2014, respectively. Generally, sample analysis was conducted at UEA. However, some parameters were analysed at CEFAS (Lowestoft). The person analysing each parameter is presented in the Table 2.3. Details of collection and preservation of Smartbuoy samples are described separately in chapter 3 (section 3.7 SmartBuoy time series).

Table 2.3 Summaries of selected parameters and analytical techniques.

Cruises	Parameters	Analytical techniques	Personal
CEND 14/11	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	P. Nelson[b]
CEND 02/12	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	P. Nelson[b]
	Chlorophyll *a*	Acetone extraction and fluorometry	P. Nelson[b]
CEND 12/12	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	S. Chaichana[a]
	Chlorophyll *a*	Acetone extraction and fluorometry	S. Chaichana[a]

Table 2.3 (Continued).

Cruises	Parameters	Analytical techniques	Personal
CEND 13/12	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Particulate organic carbon	Acid extraction and CHN analyser	S. Chaichana[a], J. Hunter[a] and S. Wexler[a]
	Particulate organic nitrogen	Acid extraction and CHN analyser	S. Chaichana[a], J. Hunter[a] and S. Wexler[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	S. Chaichana[a]
	Chlorophyll *a*	Acetone extraction and fluorometry	S. Chaichana[a]
CEND 19/13 CEND 03/14 CEND 08/14	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	S. Chaichana[a]
	Chlorophyll *a*	Acetone extraction and fluorometry	S. Chaichana[a]
SmartBuoy time series	Dissolved organic carbon	High temperature combustion	S. Chaichana[a]
	Dissolved organic nitrogen	High temperature combustion	S. Chaichana[a]
	Micromolar TOxN, Ammonium, Phosphate, Silicate	Nutrient autoanalyser	S. Chaichana[a]
	In situ monitoring of temperature, salinity, chlorophyll florescence, oxygen concentration, oxygen saturation, wave height, and turbidity.	In situ sensors	T. Hull[b]

[a] University of East Anglia

[b] CEFAS Laboratory (Lowestoft)

2.3 DOM degradation experiment method

2.3.1 Review of methods in degradation experiments

There are limited studies on the microbial degradation of DOM in seawater. The challenge is how the sampling treatment processes (e.g. filtration or inoculum approach) affect the microbial population (particularly bacteria) in each treatment batch. Processes in the ocean, particularly phytoplankton are controlled in part by nutrient limitation (Hansell 2002, Moore et al. 2013). However, not only

phytoplankton respond to nutrient depletion, the bacteria are also affected (Zweifel 1993, Puddu et al. 2000, Church 2008). Generally, nutrients (i.e. nitrate and phosphate) are added to the incubation bottle in studies of the degradation rate of DOM by bacteria. If the system shows nutrient limitation, cell numbers of bacteria are increased (higher growth rate) after external nutrient addition (Thingstad et al. 1998, Lønborg et al. 2011) and then respond by consuming the DOM faster. This leads to a higher degradation rate of DOM in the system. Different methods were used in recently published studies to study of the DOM degradation rate, details in Table 2.4 using the inoculum and filtration without inoculum methods. This inoculum approach generally adds bacteria to filtered seawater (Lønborg and Søndergaard 2009), while the filtration approach without inoculum keeps a more natural microbial community (Wetz et al. 2008).

Table 2.4 An example of typical methods used in degradation experiment.

Order	Experimental design	References
1	- Filter seawater in 2 parts: 1st part: filter through a dual stage (0.8 µm and 0.2 µm) filter cartridge, pre-washed with 10 L of Milli-Q water to remove bacteria. 2nd part: filter through GF/C filters to establish a microbial inoculum culture. - water was kept in the dark condition until arrival in the base laboratory, within 2 h of collection. - transfer water to a 20 L carboy and the microbial inoculum was added to the 0.2 µm filtrate corresponding to 10% of the total volume. - Kept in the dark at 15 °C, 53 days (70 days for summer)	(Lønborg et al. 2010)
2	- Filter seawater through GF/F filter, transfer to 1 L glass bottles. - Establish a microbial culture by adding an inoculum of GF/C filtered sample water to GF/F filtrate, 5% of total volume (5% bacteria inoculum), with headspace (~200 ml) still left in the incubation flask. Two experimental conditions including: I: only the inoculum-control bottles (2 bottles) II: the inoculum + 3.33 µmol L^{-1}glucose $C_6H_{12}O_6$ + 2 µmol L^{-1} phosphate KH_2PO_4 (2 bottles) - Kept in the dark at room temperature (18-20 °C), 150 days	(Lønborg and Søndergaard 2009)
3	- Filter seawater through GF/F filter (0.7 µm), transfer to 2 L amber glass bottles. - Establish a microbial culture by adding an inoculum of GF/C (~1.2 µm) filtered sample water to GF/F filtrate, 5% of total volume, with headspace (~400 ml) still left in the incubation flask. Three experimental condition including: I: only the inoculum-control bottles (2 bottles) II: the inoculum + carbon 60 µmolL^{-1}, $C_6H_{12}O_6$ + nitrate 10 µmolL^{-1}, KNO_3^- (2 bottles) III: the inoculum + carbon 60 µmolL^{-1}, $C_6H_{12}O_6$ + phosphate 1 µmolL^{-1}, KH_2PO_4 (2 bottles) - Kept in the dark at 14°C, 150 days	(Lønborg et al. 2009)
4	- Following the degradation by the natural population after seawater filtration through 0.7 µm filter in 2 or 3 L polycarbonate bottles - Kept in the dark at room temperature (20 °C) for 129 and 299 days	(Hopkinson et al. 1997)

Table 2.4 (Continued)

Order	Experimental design	References
5	- Following the degradation by the natural population after seawater filtration through 0.7 µm filter in 1 L polycarbonate bottles - Kept in the dark at in situ temperatures for 28 days	(Raymond and Bauer 2000)
6	- Following the degradation by the natural population after seawater filtration through 208 µm filter in 50-ml flame-sealed glass ampoules - Kept in the dark at room temperature (19-20 °C) for 180 days	(Hopkinson et al. 2002)
7	- Following the degradation by the natural population after seawater filtration through 0.8 and 3 µm filter (without and with bacterivores respectively) in 3-10 L high density polyethylene (HDPE) cubitainers - 11-16 $\mu molL^{-1}$ NH_4Cl and 3-5 $\mu molL^{-1}$ KH_2PO_4 were added to filtrates for nutrient addition treatments. $HgCl_2$ was added to filtrate for a control treatment. - Kept in the dark at 12 °C for 3 days	(Wetz et al. 2008)

In this present study, two main degradation experiments were performed and designed to use a procedure keeping a more natural microbial community than the inoculum method used in other studies. Incubation experiments were performed in order to determine rates of DOC and DON degradation by natural microbial communities and whether inorganic nutrients (nitrogen and phosphorus) limit the bacterial capacity for degradation of DOC and DON. Thus the experiments involved measuring the loss of DOC and DON over time in the whole water samples after various additions. The first set of incubation experiments in summer 2012 was conducted onboard until the end of incubation time as explained in subsection 2.3.2. While, in another set in autumn and winter 2013 and spring 2014, the incubation experiments were started onboard and continued in the UEA laboratory, details in subsection 2.3.3

2.3.2 Incubation experiment onboard

Onboard incubations were performed on the CEFAS Endeavour cruise in summer 2012. Experimental waters were exposed to six treatments (Table 2.5) in each batch designed to estimate the degradation rates of DOC and DON, any inorganic nutrient limitation on the degradation, and to test whether antibiotics could be used to stop microbial activity. There appear to be no published studies on using antibiotics on DOC and DON degradation experiment. To do this, waters from Niskin bottles at three chosen stations were immediately filtered through 200 µm mesh to remove large zooplankton and hence reduced grazers. The filtrate is then

divided into twelve 2 liter polycarbonate (PC) bottles (2 replicate bottles × 6 treatments) at each sampling station, West Gabbard (WG), station 9 and station 24. (Figure 2.3 and Figure 2.4).

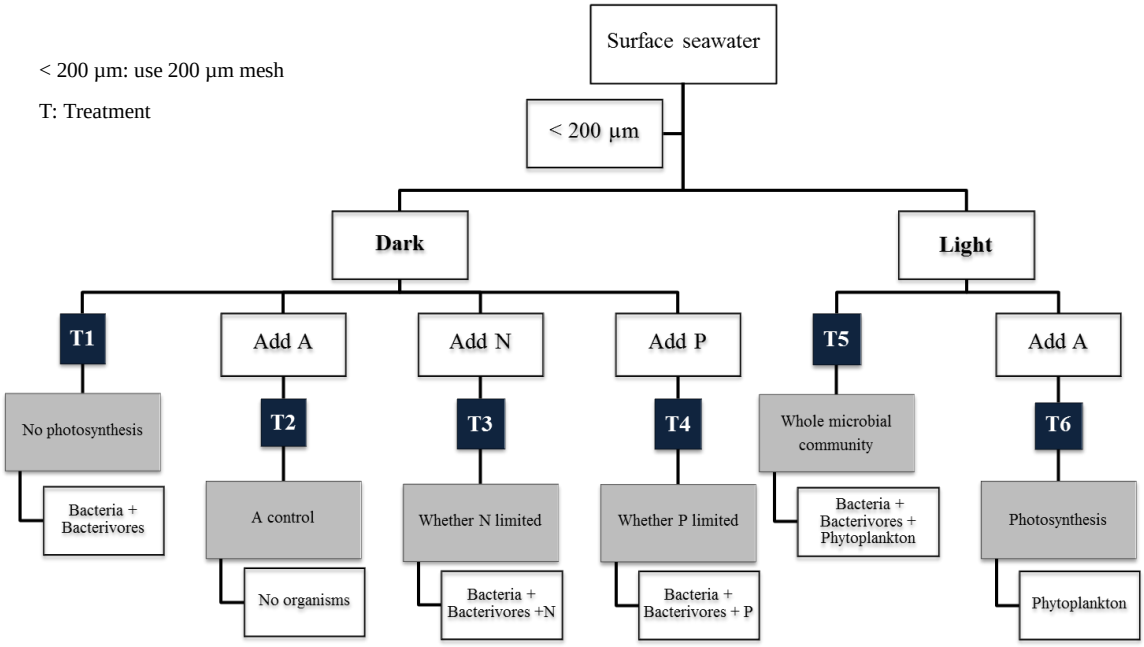
The bottles were kept in either the dark or natural light condition on the cruise, at ambient seawater temperature controlled by the continuous flow of the online supply water. The temperature was 16-19 °C at each station. Water samples were incubated for 5 days (extended to 20 days in the first set of the first station only). All incubations were conducted on deck until the end of incubation time. During this period sub-samples were collected four times, one each on day 0, 2, 4 and 5, except for the first set from the first station where sub-samples were collected eight times, one each on day 0, 2, 4, 5, 7, 10, 15 and 20. Additionally, sub-samples were collected in triplicate on day 2, 5, 10, 15 and 20. The timescale was chosen according to high degradation rate generally observed within the first 5 days (Lønborg et al. 2009).

Table 2.5 Experimental treatments on summer 2012.

Condition	Treatment [a]		Description
Dark	T1	No addition	No photosynthesis
	T2	Add antibiotics	Reduced microbial decomposition
	T3	Add 1 ml of 10 mM NH_4Cl (final concentration 5.0 µM N)	To test for N limited degradation
	T4	Add 1 ml of 1 mM Na_2HPO_4 (final concentration 0.5 µM P)	To test for P limited degradation
Light	T5	No addition	Whole microbial community
	T6	Add antibiotics	Phytoplankton community with reduced microbial decomposition

[a] Water samples were filtered through 200 µm mesh

DOM and inorganic nutrients samples are collected in 50 ml PP tubes and immediately frozen at – 20 °C until laboratory analysis. For chlorophyll *a* samples, 600 – 1,000 ml of sample waters were collected before and after filtration through 200 µm mesh in each station at the start of the experiment, and immediately frozen at – 60 °C after filtration onboard. Additional samples were collected at the end of each batch of incubation for chlorophyll *a* analysis.



Remarks:

- N = Ammonium chloride (1 ml of 10 mM NH_4Cl, final concentration 5.0 µM N) and
  P = Sodium monohydrogen phosphate (1 ml of 1 mM Na_2HPO_4, final concentration 0.5 µM P) were added to final volume of 2 L of seawater samples in each bottle.
- A =Antibiotics, 5.57 ml of a cocktail of antibiotics (Jaeckisch et al. 2011) including:
  2.22 ml of 45 mg/ml Ampicillin (final concentration 50 µg/ml),
  0.44 ml of 15 mg/ml Gentamycin (final concentration 3.3 µg/ml),
  1.11 ml of 45 mg/ml Streptomycin (final concentration 25 µg/ml),
  0.80 ml of 2.5 mg/ml Chloramphenical (final concentration 1 µg/ml), and
  1.00 ml of 20 mg/ml Ciprofloxacin (final concentration 10 µg/ml) was added to final volume of 2 L of seawater samples in each bottle.

Figure 2.3 Filtration processes and experimental treatments on summer 2012.

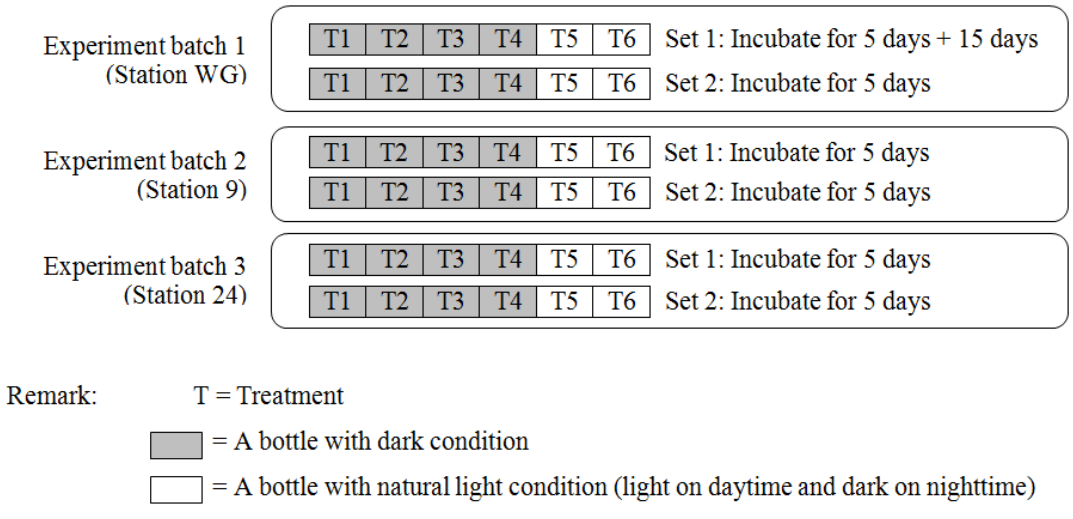


Figure 2.4 Incubation bottles at 3 stations on summer 2012, temperature controlled by natural ambient seawater.

2.3.3 Laboratory based incubation experiment

There were many valuable points learned from results of the preliminary experiment on board during summer 2012 cruise, especially that antibiotics are not a suitable treatment for removing bacterial activity in the experiments and that darkness only slowly kills a phytoplankton population (details are presented in chapter 4). Therefore, new methods to control bacteria and phytoplankton based on filtration method were applied with later experiments in autumn and winter 2013 and spring 2014. To do this, experimental treatments have been reconsidered and modified from the former onboard experiments. In this laboratory based experiment, the filtration method was used to separate phytoplankton and bacteria in water samples based on filter sizes (Table 2.6 and Figure 2.5). Details of filters used in the experiment are presented in section 2.8.2. The sampling sites were West Gabbard (WG) and Dowsing (DS) in each season (Figure 2.1 and Figure 2.6)

In this study, all treatments in Table 2.6 represent net change process with different communities. The dark condition reflects a consumption process, whereas the light condition reflects primary production and consumption of DOM. T7 contains whole community with size less than 200 µm, and hence large grazers (i.e. zooplankton) are reduced. T1, T3, T4 and T5 contains bacteria and small phytoplankton, whose size is less than 1.0 µm, whereas T2 and T6 (< 0.1 µm) may contain small bacteria (more discussion on bacteria passed through 0.1 µm filter in section 4.2.4 (chapter 4)). In the dark condition, bacteria not only degrade DOM, but also can release DOM as well, while there is no light to support phytoplankton photosynthesing. The 1.0 µm filtrate was also light incubated (T5) because the filtrate may contain photoheterotrophic bacteria which need light to support their utilization of organic compound (Koblížek 2011). Additionally, picophytoplankton, whose size is less than 2 or 3 µm (Sieburth et al. 1978, Raven 1998, Vaulot et al. 2008) and may pass through a 1.0 µm filters, need light to support their growth. Thus, all treatments in the dark are considered to be measuring net degradation process. For light treatments, they are considered to be measuring net production or degradation process, except for T6 in which no primary production is expected in the < 0.1 µm filtrate. Only in T5 and T7 was phytoplankton biomass detectable (as measurable chlorophyll *a*) at the end of the incubation on day 20 (details are presented in section 4.2.2, Figure 4.10).

Table 2.6 Experimental treatments in autumn and winter 2013 and spring 2014.

Condition [a]	Treatment [b]	
Dark	T1	< 1.0 µm
	T2	< 0.1 µm
	T3	< 1.0 µm + Add 1 ml of 10 mM NH_4Cl, final concentration 5.0 µM N
	T4	< 1.0 µm + Add 1 ml of 1 mM Na_2HPO_4, final concentration 0.5 µM P
Light	T5	< 1.0 µm
	T6	< 0.1 µm
	T7	< 200 µm

[a] In bottles in the dark, it is assumed there is no phytoplankton photosynthesing, while this still takes place in the light. The addition of N and P in T3 and T4 was designed to test for N and P limitation of DOC and DON degradation. In T5, T6 and T7 filtration was used to separate the bacterial and phytoplankton community.

[b] Filtration based on general size structure scale (Sieburth et al. 1978, Lalli and Parsons 2006) and available filter size; < 200 µm: expect reduced zooplankton, < 1.0 µm: expect reduced zooplankton, phytoplankton and bacterivores, and < 0.1 µm: expect reduced zooplankton, phytoplankton, bacterivores and bacteria.

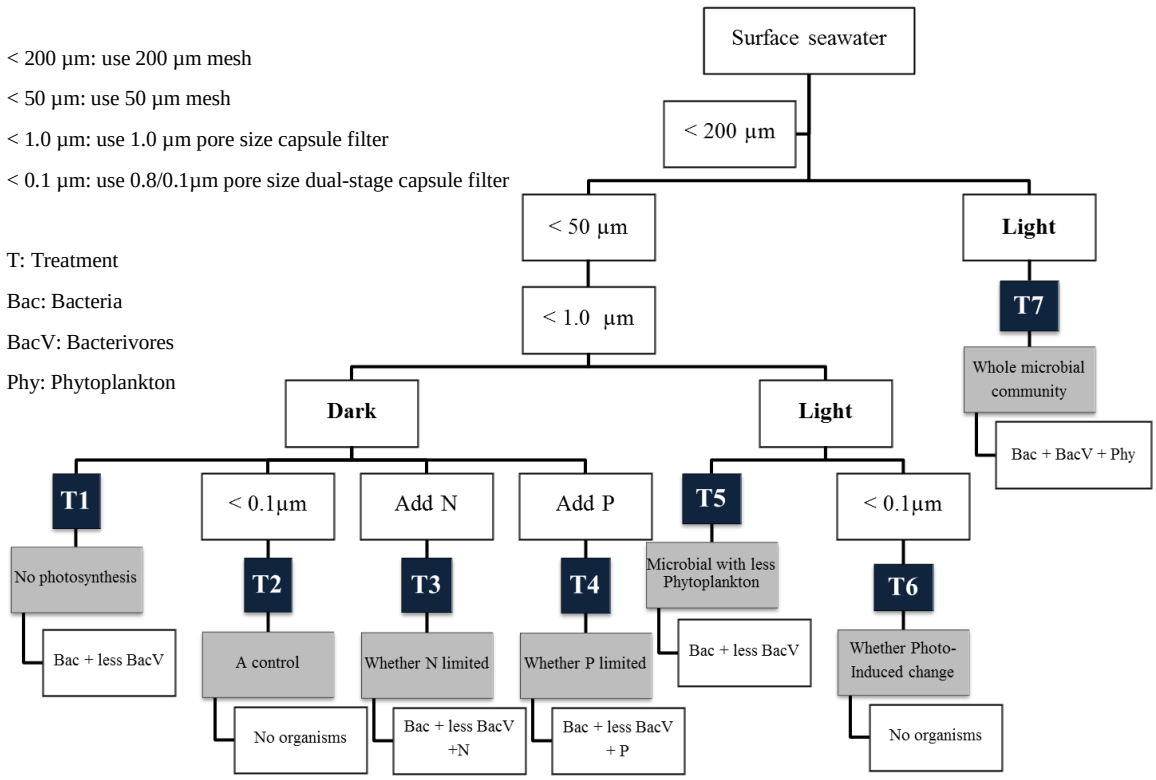


Figure 2.5 Filtration processes and experimental treatments on autumn and winter 2013 and spring 2014.

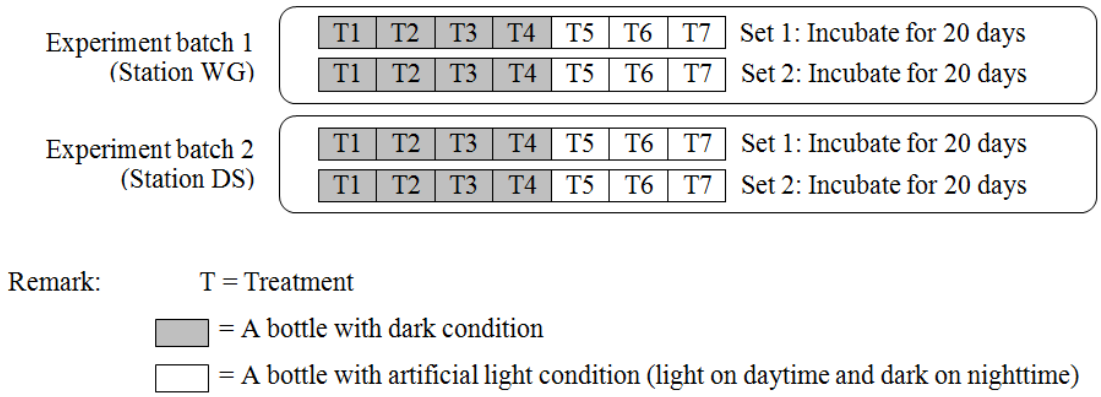


Figure 2.6 Incubation bottles at 2 stations on autumn and winter 2013 and spring 2014, temperature controlled by incubator. Spring 2014 was extended to 70 days.

General description of experiments.

Surface seawater samples were collected at 2 stations (from West Gabbard (WG) and Dowsing (DS) station in the coastal area of the North Sea (Figure 2.1)) with duplicate experiments at each station. These samples were collected on short cruises of only a few days, so incubations could be set up on board but not run to completion and so samples were returned to UEA for the incubation. Generally, water samples were treated in the same way as in subsection 2.3.2 experiments, however, there are modification in some steps. Details of the experimental process are as follows (T1 to T7 refer to treatments in Table 2.6):

1) Prior to starting the incubation, surface waters (2 meters depth) from Niskin bottles attached on a CTD rosette were immediately filtered through 200 µm mesh to remove most of the large zooplankton.

2) The water was collected for T7 (< 200 µm) and then filtered in the next step by 50 µm mesh before filtering through a 1.0 µm capsule filter (Polycap™ 75TC series (Whatman™), collected for T1 and T3-T5) and then a 0.8/0.1 µm dual-stage capsule filter (Polycap™ 150TC series (Whatman™) effective final pore size 0.1 µm, collected for T2 and T6), respectively, depending on the treatment (Table 2.6 and Figure 2.5). The 0.1 µm filtration was assumed to remove most bacteria and the 1.0 µm filter to remove most phytoplankton (Sieburth et al. 1978, Lalli and Parsons 2006).

3) After final filtration in each treatment, the filtrate was divided into fourteen 2 liter PC bottles (2 duplicate bottles × 7 treatments) at each station. Experimental waters were exposed to seven treatments in dark or light conditions (constant temperature at 15°C, 7°C and 11°C in autumn 2013, winter 2013 and spring 2014, respectively, based on CEFAS data for the site) designed to test the degradation rates and any inorganic nutrient limitation at two chosen stations in each season.

4) Water samples were incubated for 20 days (extended to 70 days in spring 2014). During this period, sub-samples (75 ml) for DOC, TDN, inorganic nutrients analysis were collected on 8 occasions on day 0, 2, 4, 5, 7, 10, 15 and 20 from each PC bottle. Sub-samples are collected in triplicate at day 2, 5, 10, 15 and 20. On every sub-sample collecting day, these sub-samples were each taken from the same two duplicate 2 liter PC bottles

5) Sub-samples (day 0) were immediately collected by filtration, through combusted (450 °C, 5 hours) glass fibre filters (Satorius Stedim Biotech GF/F, England) of nominal pore size 0.7 µm, 47 mm diameter with an ashed glass filtration unit (filter 100 ml and 50 ml Milli-Q water and 25 ml sub-sample, then discarded before filtering the actual sub-sample). Filtrates were then collected in PP sample tubes for DOC, TDN and nutrients (TOxN, ammonium, phosphate, silicate) for analysis.

   All sub-samples of day 0 were immediately frozen at – 20 °C after filtration and kept frozen until arrival in the base laboratory, in order to arrest biological processes.

6) All incubated bottles (twenty eight 2 liters PC bottles in each season) were kept in dark or light condition in a controlled temperature room on board, in cold boxes during transport to base laboratory within one hour and finally kept in the incubator to control the condition until the end of the incubation time at the UEA base laboratory.

7) Chlorophyll *a* sample was collected before and after filtering through 200 µm mesh, after filtering through 1.0 µm capsule filter, and after the finish of the incubation. The samples were immediately frozen at – 20 °C on board and continued at – 80 °C when returned to the base laboratory until analysis.

2.4 Determination of chlorophyll *a*

After filtration (600 – 1000 ml of water samples) and frozen storage, each batch of chlorophyll *a* filter was analysed by acetone extraction and the spectrofluorometric method (Holm-Hansen et al. 1965, Parsons et al. 1985). To extract chlorophyll *a* from filters, the filter was placed in an 15 ml amber screw top vial, (Supelco, USA) and extracted using 10 ml of 90% acetone overnight (12 h) in the dark at 4 °C, then analysed next day by spectrofluorometer (Perkin Elmer LS45, USA, 680 nm emission and 440 nm excitation wavelengths) with suitable calibration using approximately 2 mgL^{-1} chlorophyll *a* stock standard (*Anacystis nidulans* algae, Sigma-Aldrich, USA). The standard was checked to obtain the actual concentration by R. Utting (UEA) before dilution by me to the working standard on the analytical day. The detection limit of the measurement is 0.1 µg/L.

Figure 2.7 shows an example of calibration curves used for determination of chlorophyll *a*. In order to determine the chlorophyll in the actual seawater, the value was divided by the volume of seawater (l) and multiplied by the total volume of acetone extract (ml). For the sample batches extracted and analysed at CEFAS laboratory (Lowestoft) by P. Nelson (Table 2.3), chlorophyll *a* was analysed by Turner 10AU-005CE fluorometer after acetone extraction. The detection limit of the measurement is 0.02 µg/L.

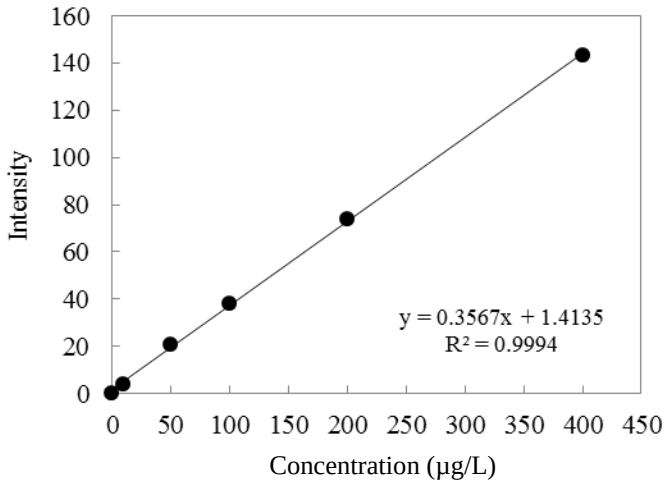


Figure 2.7 Examples of calibration curve for chlorophyll *a* analysis.

2.5 Determination of particulate organic nutrients

In order to analyse particulate forms of organic carbon and nitrogen (POC and PON), after filtration by a glass fibre filter of typically 0.7 µm pore size under low vacuum (< 100 mm Hg), residues collected on the filter can be analysed by two methods to determine particulate forms of carbon and nitrogen: wet and dry oxidation.

In the wet oxidation method, organic carbon and nitrogen are digested using persulfate (Raimbault et al. 1999) or chromic acid at temperature higher than 100 °C. In dry combustion, high temperature (> 800 °C) is used to oxidize organic carbon and nitrogen. All residues on filters are fumed in acid to remove inorganic forms of carbon and dried overnight before this oxidation process which typically uses CHN Elemental analyzer. The organic carbon and nitrogen are converted to CO_2 and NO, respectively. Then, the nitrogen oxides are subsequently reduced to N_2 gas. Finally, both CO_2 and N_2 are measured by thermal conductivity (Ehrhardt and Koeve 1999)

In this study, POC and PON were measured by the dry oxidation method using the Exeter Analytical CE440 Elemental analyser (Exeter analytical Ltd.,UK). The sample was oxidized in a high temperature furnace using pure oxygen gas under static conditions at 975 °C. POC and PON were combusted and converted to CO_2 and N_2 gases, respectively in a subsequent reduction column. The gases entered a mixing chamber to ensure a homogeneous mixture and were finally detected by a series of thermal conductivity detectors, each containing a pair of thermal conductivity cells. Helium was used as a carrier gas through the analytical system. POC and PON concentrations were obtained by proportional comparison with high purity acetanilide (C_8H_9NO (71.09% C, 10.36% N, 6.71% H, 11.84% O), Exeter analytical Ltd, UK).

Prior to analysis, all frozen POC and PON on the filters were allowed to defrost and a subsample cut from each filter (1 cm diameter size) by stainless steel plunger. Three replicate samples were taken from each filter and placed together in a glass petri dish. Then, filter samples were placed overnight (12 hours) in a desiccator saturated with concentrated hydrochloric acid (HCl, 36% w/v) fumes to remove inorganic carbon (carbonate). Thereafter, the filters were dried for 24 hours at 60 °C and ready to pack for analyzing by CHN elemental analyzer.

In the packing process, tin capsules and nickel sleeves were used for standard and sample containers. The standard (acetanilide) was weighed directly into tin capsules using a microelectrobalance (about 1600 – 2000 µg). Then, the tin capsule was cold welded shut using an Exeter Analytical capsule sealer and placed in a nickel sleeve. A blank for standards was obtained by placing an empty tin capsule in a nickel sleeve. Filter samples were folded and placed directly into nickel sleeves by stainless steel tweezers. Blank filters (i.e. GF/F glass fibre filter only, fumed with HCl and dried) were used as a blank for POC and PON filter samples in each batch. Then, all nickel sleeves were placed into a shallow cavity in a clean Plexiglass (Perspex) filter transport box in a sample sequence (maximum 64 rack positions per box). After the acidification and packing step, samples were then measured at UEA by J. Hunter and S. Wexler.

As all samples were analysed in triplicate, the mean concentration of each subsample was calculated after blank correction. The limit of detection (LOD) of the instruments has been calculated based on the analyte concentration that gave a signal equal to the blank signal plus three times the standard deviation of the blank (Miller and Miller 2010). The limit of detection for POC and PON was 0.20 µmole C and 0.05 µmole N. The precision as the coefficient of variation (CV) was about 1% and 4% for C and N. In order to calculate POC and PON concentrations for the whole area of the filter sample, the ratio between the area of the analysed subsamples and the actual filter was calculated, and finally converted to µM from the volume filtered.

2.6 Determination of dissolved inorganic nutrients

Dissolved inorganic nutrients including TOxN (nitrate + nitrite), ammonium, phosphate and silicate were analysed at CEFAS (Lowestoft) and UEA based on the sampling cruise (Table 2.3). At CEFAS, low nutrient seawater supplied by OSIL (Ocean Scientific International Ltd.) was used to prepare the standard working solutions and blanks, whereas ~ 25 g l^{-1}sodium chloride (baked at 450 °C, 5 hours) solution was used as the matrix at UEA to avoid optical matrix effects. For sample analysis at both UEA and CEFAS, calibration curves and sample data were obtained by measuring the peak heights by the software of the Skalar San^{++} autoanalyser

(segmented flow analysis and colourmetric chemistry, Skalar analytical, Netherlands).

Figure 2.8 shows typical calibration curves obtained at UEA. Sodium nitrate, ammonium chloride, potassium di-hydrogen ortho-phosphate and sodium meta-silicate was used to prepare mixed standard solutions for TOxN, ammonium, phosphate and silicate, respectively. The standard solution set was prepared in a range of 0.3 – 8.0 µM N, 0.5 – 10.0 µM N, 0.1 – 1.6 µM P and 0.5 – 9.0 µM Si for TOxN, ammonium, phosphate and silicate, respectively.

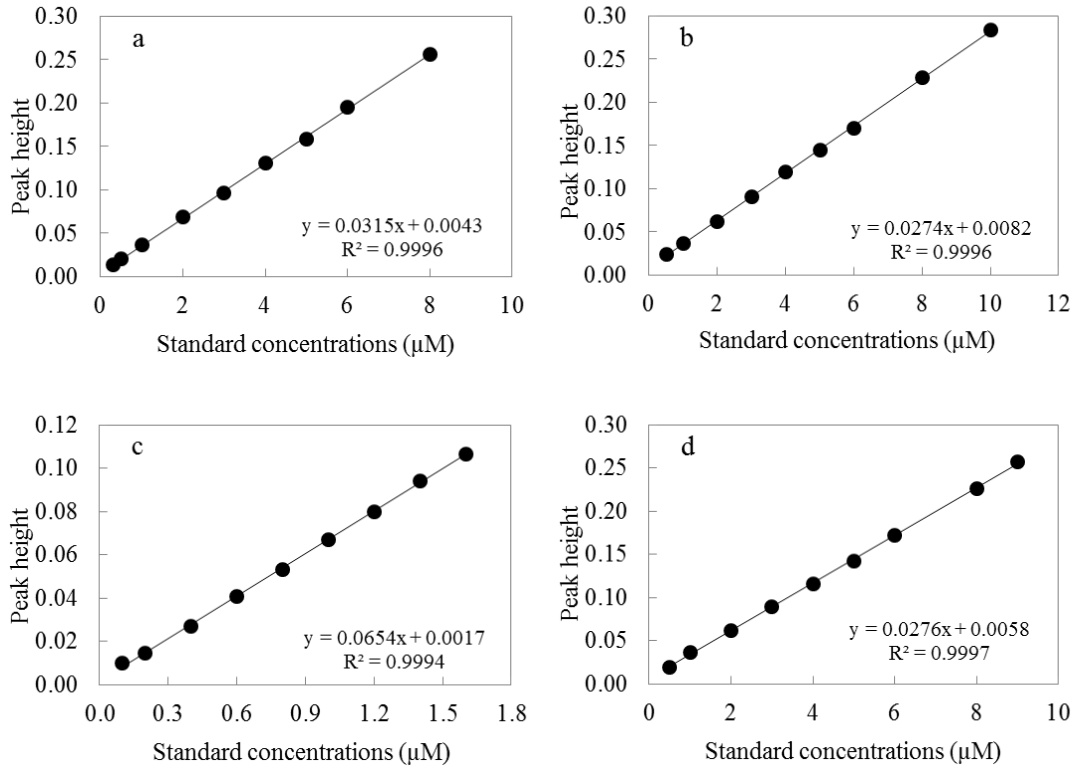


Figure 2.8 Examples of calibration curves for TOxN (a), ammonium (b), phosphate (c) and silicate (d) analysis.

To calculate sample concentration values out of peak high values, an equation was produced from a linear regression line as following:

$$y = mx + c \qquad \text{……..Equation 1}$$

where y = peak height

m = slope of the calibration curve

x = standard (or unknown sample) concentration

c = intercept at y axis (i.e. an estimation of the blank)

For quality control during analysis, a medium concentration sample of standard working solution was also analysed in each batch as an unknown. The recovery of the standard (n = 11) was about 95 – 103% (101 ± 3%), 99 – 113% (108 ± 5%), 94 – 100% (98 ± 2%), and 101 – 106% (103 ± 2%) for TOxN, ammonium, phosphate and silicate, respectively. The coefficient of variation (CV) of replicate samples were about 3%, 4%, 2%, and 1% for TOxN, ammonium, phosphate and silicate, respectively. The certified reference materials (CRM) from Environment Canada (Canada) were also used during analysis. The concentration of CRM during sample analysis is presented in Table 2.7. These reference materials yielded mean concentrations in good accord with the consensus values of CRM. The limit of detection for TOxN, ammonium, phosphate and silicate were 0.1, 0.2, 0.1 and 0.1 µM, respectively (P. Nelson (CEFAS), personal communication); and 0.2 ± 0.0, 0.4 ± 0.1, 0.1 ± 0.1, and 0.2 ± 0.1 (n = 18) µM, respectively (UEA).

Table 2.7 Results of CRM measurement in dissolved inorganic nutrients analysis.

Dates	Concentration (Mean ± SD, µM)				n
	TOxN	Ammonium	Phosphate	Silicate	
January 2013	2.1 ± 0.2	4.3 ± 0.2	1.0 ± 0.0	7.5 ± 0.3	16
February 2013	2.1 ± 0.0	4.5 ± 0.1	1.0 ± 0.0	7.5 ± 0.1	4
March 2013	2.2 ± 0.1	4.5 ± 0.1	1.1 ± 0.1	7.4 ± 0.3	19
Summary [a]	**2.1 ± 0.1**	**4.4 ± 0.2**	**1.0 ± 0.1**	**7.4 ± 0.3**	**39**
Consensus values	**2.1**	**4.6**	**1.0**	**7.7**	
April 2014	3.2 ± 0.1	2.7 ± 0.2	1.0 ± 0.1	3.7 ± 0.2	14
May 2014	3.2 ± 0.1	2.6 ± 0.2	1.1 ± 0.0	4.1 ± 0.4	35
June 2014	3.1 ± 0.1	2.6 ± 0.2	1.1 ± 0.0	4.2 ± 0.2	41
October 2014	3.1 ± 0.2	2.6 ± 0.2	1.1 ± 0.1	4.1 ± 0.1	9
Summary [b]	**3.1 ± 0.1**	**2.6 ± 0.2**	**1.1 ± 0.1**	**4.1 ± 0.3**	**99**
Consensus values	**3.0**	**2.4**	**1.0**	**4.0**	

[a] Summary of CRM 13 (nitrate +nitrite, ammonium and silicate) and CRM 8 (phosphate) results

[b] Summary of CRM 16 (nitrate +nitrite, ammonium and phosphate) and CRM 34 (silicate) results

2.7 Determination of dissolved organic nutrients

2.7.1 Background of methods in DOC and DON analysis

The dissolved form of organic carbon and nitrogen is defined here as materials which pass through the nominal pore size of a 0.7 μm glass fibre filter (Carlson 2002, Hedges 2002, Carlson and Hansell 2015) and hence includes colloidal material. This filtrate can be analysed by different oxidation methods to estimate DOC and TDN.

All methods used for determination of dissolved forms of organic carbon and nitrogen as DOC and DON are based on the total oxidation of organic matter by chemical oxidation, or UV oxidation (wet oxidation method), or high-temperature combustion (HTC) (dry oxidation or dry combustion method) (Cauwet 1999). In DON determination in the wet oxidation method, all TDN is converted to NO_3^- with a complete oxidation, with DIN ($NO_3^- + NO_2^- + NH_4$) measured separately and subtracted to give DON. In the HTC method, all TDN is converted to nitric oxide (NO) by pyrolysis. For DOC determination, carbon compounds are oxidized to CO_2 (Sharp 2002) , which are directly measured as DOC or indirectly measured as TC and DIC (results of subtraction is DOC), depending on the type of the instrument.

Recently, HTC methods with catalysts such as metals or metal oxides (high-temperature catalytic oxidation (HTCO)) has been most widely used (Suzuki et al. 1992, Benner and Strom 1993, Hansell 1993, Miller et al. 1993, Álvarez-Salgado and Miller 1998b, Spyres et al. 2000, Badr et al. 2003, Peterson et al. 2003, Pan et al. 2005, Spencer et al. 2007, Suratman et al. 2008a, Suratman et al. 2009, Johnson et al. 2013, Santinelli et al. 2013). This technique was asserted as more efficient, easier, faster, more readily automated, giving more consistent results and using much smaller sample volumes than wet oxidation (Bronk et al. 2000, Sharp 2002). Its potential for simultaneous DOC and TDN analysis also made further exploration of HTCO method desirable.

There are four ways of quality assurance in the HTCO analysis affecting the reliability of the data from this method (Badr et al. 2003).

1) careful blank determination

2) a systematic evaluation of the oxidation efficiency of a variety of organic compounds (including less easily oxidised compounds)

3) accurate and precise instrumental calibration using easily oxidised standard compounds

4) testing analytical accuracy with consensus reference material (CRM)

Despite the increasing interest in DON determination in many media such as soil solution, ground water, freshwater, brackish water and seawater; the analytical method still faces difficulties and serious limitation. This is because concentration cannot be quantified directly, but must be calculated by subtracting dissolved inorganic nitrogen (DIN) concentration (the sum of nitrogen in the form of nitrite, nitrate and ammonium) from the total dissolved nitrogen (TDN) concentration:

$$[DON] = [TDN] – [DIN]$$

This leads to some challenges when determining DON concentration in aqueous samples with high DIN concentration. Especially in freshwater (e.g. soil solution and ground water) or where the DIN/TDN ratios exceed 0.85, and the presence of high nitrate in the samples may lead to an error propagation problem in the measurement (Kähler and Koeve 2001, Vandenbruwane et al. 2007).

2.7.2 DOC and DON analysis in this study

In this study, DOC and TDN were measured by the high temperature catalytic oxidation (HTCO) method coupled with nitrogen chemiluminescence detector system. Hereafter, the term HTCO-TOC-ND system is used to describe these coupled systems. DON content is calculated by subtracting dissolved inorganic nitrogen (DIN) concentration (the sum of nitrogen in the form of nitrite, nitrate and ammonium) from the total dissolved nitrogen (TDN) concentration.

HTCO-TOC-ND measurements of DOC and TDN were performed using a Skalar Formacs^{HT} combustion TOC/TN analyser (Skalar analytical, Netherlands) coupled with a Skalar nitrogen chemiluminescence detector (ND20, Skalar analytical, Netherlands). Carbon-free, high purity air (Zero grade air, BOC gases, England) was applied as carrier gas. The catalyst column consisted of a quartz glass column filled with two layers of (1) cobalt-chromium (CoCr, ~15 g on the bottom (on the quartz

wool to prevent the catalyst from running out)) and (2) cerium oxide (CeO_2, ~2.5 g on the top) Cleaning of a new catalyst column was performed with ~30 injection of 200 µl Milli-Q water onto a hot column. Optimum gas flow rate when starting analysis is 240 ml/min, lower flow rates indicated higher salt accumulation in the mixed catalyst reactor. During analysis this rate was constant or has only minor changes (± 2 ml/min). To decrease salt accumulation in the reactor, the catalyst was reactivated by rinsing with 1 liter Milli-Q water after each run and baked at 105 °C overnight (12 hours). The catalyst can be reactivated several times before it has to be replaced. However, the catalyst column was typically changed after running 200 seawater samples to prevent the quartz glass column breaking because of the salt effect.

The non-purgeable organic carbon (NPOC) mode was set during the analysis. Therefore, automatic acidification was applied in which 100 µl of 10% hydrochloric acid was added to 6 ml of sample to analyse DOC. This was followed by sparging and stirring samples in order to drive off the inorganic carbon before sample take-up by syringe to the catalyst reactor. For both CRM (DSR and LCW) analysis, the NPOC mode was not applied because the CRM already has added acid from the manufacturer. DSR is only stirred before the sample is taken. The syringe was flushed with sample 2 times (each 200 µl) before the actual sampling for all samples. During the measurements, 2 - 4 injections of 200 µl samples were performed. The best 2 injections were chosen automatically with a maximum extra 2 sample injections in order to achieve the coefficient of variation (CV) better than 2 %. Thus, the peak area of these 2 best injections was used to calculate the average peak area. Conditions used for the analysis are presented in Table 2.8.

Table 2.8 Instrument condition for DOC and TDN analysis.

Analyser setting	conditions
Combustion temperature	750 °C
Carrier gas flow rate	240 ml/min
Flush count (rinsed with samples)	2 times
Flush volume	200 µl
Rinse time	28 s
Acid to sample cup volume	100 µl
Sample volume injection	200 µl
Sample sparging time	240 s
Sample stir time	180 s
Number of injection	2 - 4
CV maximum	2.00 %

The concentration of DOC and TDN were determined in a similar way to dissolved inorganic nutrients using equation 1 in subsection 2.6. However, peak area was used instead of peak height in dissolved inorganic nutrients and the c intercept in the equation was zero because the area for all standards has been blank corrected. Therefore, in this case, the concentrations were calculated by subtracting a Milli-Q blank (system blank) and dividing by the slope of a daily standard curve made from potassium hydrogen phthalate (DOC analysis) and a mixture of ammonium sulphate and potassium nitrate (TDN analysis). In each analytical day, the injection order included a system blank, CRM, standard solutions and 15-20 samples, CRM and system blank. The run was repeated with samples, CRM and system blank until it finished and at the end of the run with standard solutions run as unknown, CRM and system blank. Urea was used to determine the oxidation efficiency of the measurement.

Figure 2.9 presents a schematic diagram of HTCO-TOC-ND system with Skalar Formacs^{HT} combustion TOC/TN analyser coupled with a Skalar ND20 nitrogen chemiluminescence detector. Samples were acidified and sparged with pure air for 240 s and then stirred for 180 s to remove inorganic carbon. The syringe then was rinsed with samples (200 µl) two times before the actual sample (200 µl) was injected through the sample injection port into the combustion column (TC/TN reactor). Meanwhile, the carrier gas entered the CO_2 scrubber which traps CO_2 and moisture and then passes through a valve and a flow regulator where the flow was adjusted to 240 ml/min and then a restrictor. The carrier gas then entered the combustion TC/TN reactor (750 °C) and joined the evaporated sample when the sample was injected through the sample injection port. The gas then passed through a teflon cooling coil and condensation trap. The gas was then cooled to ~2 °C by the peltier cooler where any liquid was removed by a second condensation trap and passed a halogen scrubber to remove any halogens and a dust filter. The gas stream entered the infrared detector where the formed CO_2 was measured. The gas then passed the flow meter (the gas flow was checked, a drop in the gas flow was showed on the computer screen and usually indicate the column needed to be changed). The gas stream was led to the ND20 nitrogen chemiluminescence detector and analysed as NO. Within the nitrogen detector, NO reacts with ozone in the instrument to

produce the excited nitrogen dioxide (NO_2). During return to the ground state, this emits the photon detected by the detector.

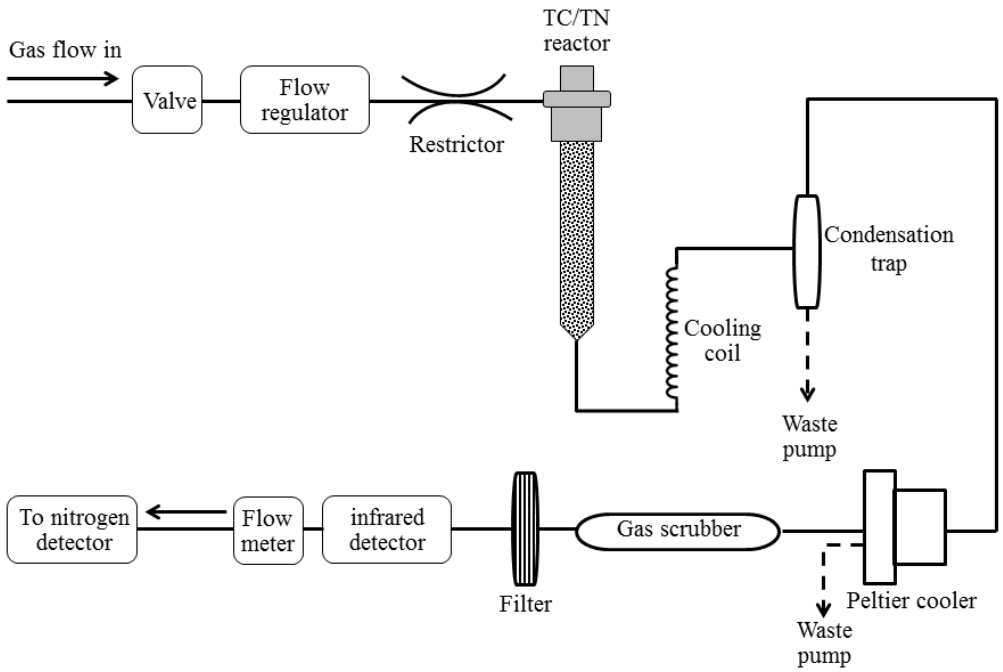


Figure 2.9 a schematic diagram of HTCO-TOC-ND system with Skalar Formacs^{HT} combustion TOC/TN analyser coupled with a Skalar ND20 nitrogen chemiluminescent detector.

Before DOC was determined by the HTCO-TOC-ND system with NPOC mode (direct DOC measurement) described above, the DOC concentrations of preliminary samples had been measured by the indirect measurement. This was obtained by separately measured dissolved total carbon (TC) and inorganic carbon (IC) concentration and DOC then estimated as the difference in their concentration.

$$[DOC] = [TC] – [IC]$$

This measurement gave results with high value of the system blank, LCW and DSR (Table 2.9), which did not agree with the consensus values of CRM. This method suggests the DOC concentrations contain the integrated errors of the independent measurements of TC and IC. Generally, the IC concentration is higher than 50% of the TC concentration, and two large amounts must be subtracted. This can lead to an unreliable result. A small error in TC or IC measurements can

generate a large error in the estimate of DOC, particularly when the DOC has low concentration compared to fractions of TC and IC. Therefore, hereafter, the samples were analysed by the HTCO-TOC-NCD system with NPOC mode, direct DOC analysis. LCW and DSR are standards discussed in more detail in subsection 2.7.3.

Table 2.9 Result of blank and CRM measurement on DOC preliminary analysis using "indirect DOC" approach [a].

Measurement	Concentration (µM)	
	Range	Average (mean ± SD)
System blank[b]	128.4 – 330.3	195.0 ± 60.8 (n = 10)
LCW	3.0-44.9	16.8 ± 13.6 (n = 10)
DSR	54.8 – 170.8	96.3 ± 35.3 (n = 10)

[a] indirect DOC approach is DOC concentrations obtained by separately measured dissolved total carbon (TC) and inorganic carbon (IC) concentration and DOC estimated as the difference in their concentration.

[b] Milli-Q water injection, DOC system blank = TC system blank – IC systemblank
n: number of analytical day (10 analytical days run on July 2012 – November 2012)
Consensus values: 1 µM for LCW and 41-44 µM for DSR

2.7.3 Optimisation of DOC analysis

After recognizing the problems with the "indirect DOC" approach the instrumentation and method was subsequently optimized using the "direct method". Potassium hydrogen phthalate, KHP (Analar Grade, Sigma-Aldrich, USA) was used for calibration. Preparation of stock and standard solution details are in Appendix 2.1. An example of the six point calibration curve after system blank correction for DOC determination is presented in Figure 2.10. Generally, the standard concentration was prepared in the range of 0-300 µM (i.e., 0, 25, 50, 100, 200, and 300 µM).

The key issue of importance for high-quality DOC and TDN data is the correct procedure for determination of the instrument or system blank (Badr et al. 2003). Therefore, the source and magnitude of the analytical blank of instruments need to be evaluated in order to accurately determine DOC and TDN concentration. The system blank was estimated by using acidified and sparged Milli-Q blank injection which was 22.3 – 38.5 µM (29.2 ± 4.2 µM, n = 78). In other studies 15 – 30 µM (24 ± 6 µM) (Suzuki et al. 1992), ~ 6 – 50 µM (Benner and Strom 1993), ~ 80 µM (Cauwet 1994), ~ 10 µM (Spyres et al. 2000) and 51 ± 4 µM (Suratman 2007) blanks for DOC analysis have been reported. The limit of detection for DOC analysis, estimated as the analyte concentration giving a signal equal to the blank signal plus

three standard deviations of the blank (Miller and Miller 2010) was ~ 6 µM. The oxidation efficiency of KHP during sample analysis was investigated by comparison with urea. The results were in the range of 93-105% (100 ± 3%, n=50) for 50 µM and 97 – 108% (100 ± 2, n=20) for 200 µM, and agreed with previous finding, which showed the result ~100% for 200 µM KHP-glycine standard compared to urea (Watanabe et al. 2007).

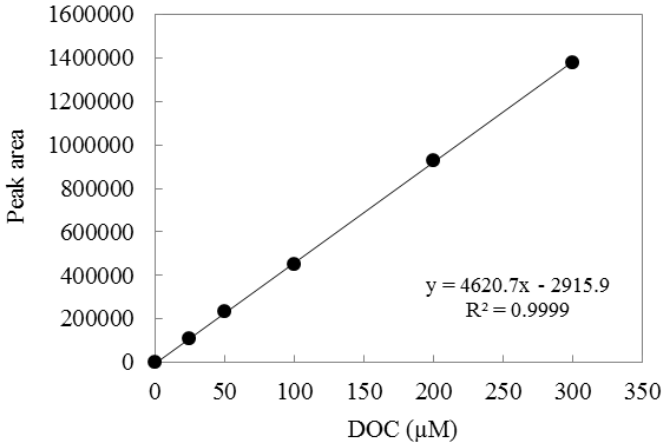


Figure 2.10 Example of calibration curve for DOC analysis.

Precision is usually expressed as a coefficient of variation (CV), standard deviation (SD) or relative standard deviation (RSD), and it can be obtained by replicate measurement of the same sample (Miller and Miller 2010). In this study, the precision was measured by running 40 standards with the same concentration (100 µM) over ~ 10 hours. The result showed a CV value of 2% (Appendix 2.3). Additionally, the CV was typically better than 2% for DOC analysis with 2 – 4 replicate sample injections. Some of the frozen samples were reanalysed after storaged more than 17 months and there were no significant differences between the duplicate samples ($P > 0.05$), ANOVA test (Appendix 2.4).

To evaluate analytical accuracy, two types of consensus reference materials (CRM) (low carbon water (LCW) and deep seawater reference water (DSR)) provided by the Hansell laboratory, the University of Miami (Hansell 2005) are used to verify the measurement. The CRM was supplied acidified with hydrochloric acid to 0.1% by volume and preserved in 10 ml glass ampoules, they are stable for at least two years if stored in the dark at room temperature (Chen 2011). The rate of CRM usage was 2 – 3 LCW and 2 – 3 DSR per analytical day, depending on amount of

analysed samples. A consensus value of DOC for LCW is 1 µM. The analysis of LCW here yielded a negative value of DOC concentration as the DOC value for LCW is lower than the system blank value, therefore, sample concentrations was not corrected by the LCW value.

Consensus values of DOC for DSR vary in each batch. In this study, DSR from three different batches were used; these include Batch 10 Lot # 05-10 (consensus values 41 – 44 µM) collected from a depth of 700 m in the Florida Strait, Batch 13 Lot # 02-13 (consensus values 41 – 44 µM) collected from a depth of 800 m in the Florida Strait and Batch 14 Lot # 01-14 (consensus values 42 – 45 µM) collected from a depth of 750 m in the Florida Strait. The analysis of these DSR yielded mean concentration of 42.6 ± 2.9 µM (n = 98) and 42.4 ± 2.6 µM (n = 66) (Table 2.10), which were in good accord with the consensus values of 41 – 44 µM and 42 – 45 µM. Therefore, the quantitative recovery of DSR relative to the consensus values is (100 ± 7%, n = 98) and (98 ± 6%, n = 66) in which 42.5 µM and 43.5 µM as a median was used for calculation and no recovery correction was necessary.

Table 2.10 Results of DSR measurement in DOC analysis.

Dates	Concentration[a] (µM)	Recovery[a] (%)	n[d]
June 2013	38.3 - 49.2 (43.1 ± 3.0)	90 - 116 (101 ± 7)	15
July 2013	39.6 - 46.1 (44.2 ± 3.1)	93 - 108 (104 ± 7)	4
October 2013	43.1 - 44.8 (44.0 ± 1.1)	102 - 105 (103 ± 3)	2
November 2013	39.1 - 48.2 (43.0 ± 2.7)	92 - 114 (101 ± 6)	17
December 2013	45.2 - 47.4 (46.4 ± 1.1)	106 - 111 (109 ± 3)	3
January 2014	37.2 - 47.8 (42.0 ± 3.2)	88 - 112 (99 ± 8)	17
February 2014	37.5 - 45.7 (42.2 ± 2.5)	88 - 108 (99 ± 6)	21
March 2014	39.3 - 45.5 (41.5 ± 2.4)	92 - 107 (98 ± 6)	7
April 2014	36.8 - 45.4 (40.5 ± 3.2)	87 - 107 (95 ± 8)	5
May 2014	37.9 - 46.2 (43.0 ± 2.9)	89 - 109 (101 ± 7)	7
Summary [b]	**36.8 - 49.2 (42.6 ± 2.9)**	**87 - 116 (100 ± 7)**	**98**
May 2014	37.4 - 44.5 (41.5 ± 2.5)	86 - 102 (95 ± 6)	8
June 2014	39.3 - 46.9 (42.7 ± 3.1)	90 - 108 (98 ± 7)	6
July 2014	42.3 - 47.3 (44.1 ± 1.6)	97 - 109 (101 ± 4)	9
August 2014	38.3 - 46.9 (42.2 ± 2.8)	88 - 108 (97 ± 6)	22
September 2014	39.2 - 45.4 (42.1 ± 1.7)	90 - 104 (97 ± 4)	10
October 2014	39.1 - 46.5 (43.1 ± 2.7)	90 - 107 (99 ± 6)	9
November 2014	38.3 - 39.0 (38.6 ± 0.5)	88 - 90 (89 ± 1)	2
Summary [c]	**37.4 - 47.3 (42.4 ± 2.6)**	**86 - 109 (98 ± 6)**	**66**

[a] Range (mean ± SD) [b] Batch 10 Lot # 05-10 and Batch 13 Lot # 02-13 (consensus values 41 – 44 µM)
[c] Batch 14 Lot # 01-14 (consensus values 42 – 45 µM) [d] Number of DSR

2.7.4 Optimisation of TDN analysis

A mixture of ammonium sulphate and potassium nitrate (Sigma-Aldrich, USA) dissolved in Milli-Q water (Millipore Inc, England) was used for calibration. Details of the preparation of stock and standard solution are in Appendix 2.2, all chemicals used are analytical grade. Figure 2.11 presents an example of a standard solution curve for TDN determinations. Generally, the standard set was prepared in a range of 0 – 50 µM (i.e., 0, 5, 10, 20, 30, and 50 µM). The system blank estimated from injecting Milli-Q blank (acidified and sparged) was generally below the limit of detection, the value in the range of 0.0 – 2.1 µM (0.6 ± 0.6 µM, n = 79). The 0.0 µM value means there was no peak area detected during analyses. The value agreed with the system blank in other studies which were 1 ± 0.1 µM (near the LOD of 1 µM (Badr et al. 2003)), 1 – 3 µM (Hopkinson et al. 1993), 2.37 µM (Koike and Tupas 1993), and < 0.3 – 0.6 µM (Álvarez-Salgado and Miller 1998b).

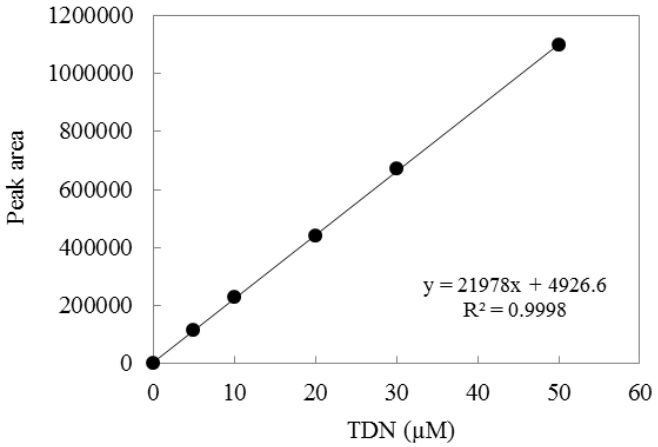


Figure 2.11 Example of calibration curve for TDN analysis.

The limit of detection for TDN analysis, calculated based on the analyte concentration giving a signal equal to the blank signal plus three standard deviations of the blank (Miller and Miller 2010) was ~ 1 µM. The oxidation efficiency of the mixed standard relative to urea was 92 – 106 (98 ± 4, n = 52) and 94 – 105 (99 ± 3, n = 32) for 10 µM and 50 µM, respectively. The analytical precision (Appendix 2.5), CV was about 4% for a continuous run of 40 standards (10 µM) in the same batch as described for DOC. Generally, the CV was better than 2% for TDN analysis with 2 – 4 replicate sample injections. The frozen samples stored more than 17 months were

reanalyzed and the results showed no significant differences between the duplicate samples ($P > 0.05$), ANOVA test (Appendix 2.4).

Two types of CRM were used to evaluate analytical accuracy as used in DOC analysis. The analysis of LCW yielded a concentration 0 µM (no peak areas were detected during TDN analysis), which was in good agreement with the consensus values of 0 µM. In this study, DSR from three different batches were used. The consensus values of TDN for DSR in all batches was 31 – 33 µM. The analysis of these DSR yielded a mean concentration of 32.8 ± 1.7 µM (n = 176) (Table 2.11), which was in good agreement with the consensus value. The quantitative recovery of DSR relative to the consensus values is 102 ± 5% (n = 176) with 32 µM as a median concentration which was used for the calculation. Therefore, no blank or recovery correction was required

Table 2.11 Results of DSR measurement in TDN analysis.

Dates	Concentration[a] (µM)	Recovery[a] (%)	n[d]
June 2013	29.5 - 37.7 (32.5 ± 2.4)	92 - 118 (102 ± 7)	15
July 2013	31.8 - 34.8 (33.1 ± 0.9)	99 - 109 (103 ± 3)	8
August 2013	31.6 - 33.8 (32.7 ± 0.7)	99 - 106 (102 ± 2)	12
October 2013	33.2 - 37.2 (35.7 ± 1.3)	104 - 116 (112 ± 4)	7
November 2013	33.1 - 35.8 (34.6 ± 0.8)	103 - 112 (108 ± 3)	8
December 2013	34.2 - 35.3 (35 ± 0.6)	107 - 110 (109 ± 2)	3
January 2014	30.7 - 34.2 (32.8 ± 0.9)	96 - 107 (103 ± 3)	17
February 2014	29.4 - 36.9 (32.8 ± 1.8)	92 - 115 (102 ± 6)	21
March 2014	30.1 - 36.0 (33.0 ± 1.9)	94 - 113 (103 ± 6)	7
April 2014	34.4 - 35.4 (34.9 ± 0.4)	108 - 111 (109 ± 1)	5
May 2014	29.3 - 33.7 (31.7 ± 1.3)	92 - 105 (99 ± 4)	15
June 2014	30.8 - 33.1 (31.8 ± 0.8)	96 - 103 (99 ± 3)	6
July 2014	33.0 - 35.0 (34.1 ± 0.7)	103 - 109 (107 ± 2)	9
August 2014	29.9 - 33.8 (31.9 ± 1.1)	94 - 106 (100 ± 3)	22
September 2014	31.1 - 32.7 (32.1 ± 0.6)	97 - 102 (100 ± 2)	10
October 2014	30.2 - 32.6 (31.2 ± 0.8)	94 - 102 (97 ± 2)	9
November 2014	30.9 - 31.5 (31.2 ± 0.4)	96 - 98 (97 ± 1)	2
Summary [b]	**29.3 - 37.7 (32.8 ± 1.7)**	**92 - 118 (102 ± 5)**	**176**

[a] Range (mean ± SD)

[b] Batch 10 Lot # 05-10, Batch 13 Lot # 02-13 and Batch 14 Lot # 01-14 (consensus values 31 – 33 µM)

[d] Number of DSR

2.8 Other blank determination

Potential contamination during each sample treatment process has been investigated. There are PP tubes used for sample container and capsule filters applied in the incubation experiment.

2.8.1 Polypropylene tubes

To determine possible contamination of DOC and DON (as TDN) from polypropylene (PP) tubes during frozen storage, the Milli-Q water kept in the same tube was measured for DOC and TDN concentration over time on 21 June 2013, 24 January 2014 and 28 November 2014. The DOC concentrations in all tubes were lower than the LOD of DOC analysis and there was no peak areas detected during TDN analysis. With the results, therefore, there is no detectable amount of DOC and TDN, and this suggests no net leaching over time. Previous studies also found a similar result (Tupas et al. 1994, Yoro et al. 1999, Suratman 2007). Therefore, the DOC and TDN concentration of the PP tube were not corrected for sample storage in PP tubes.

2.8.2 Capsule filters

All capsule filters used in the incubation experiment are the Polycap™ TC series (Whatman™, Whatman International Ltd., Maidstone, UK). The TC series are made by hydrophilic polyethersulfone membrane which is suitable for sample types including aqueous solutions, salt solutions, tissue culture media, nutrients, biologicals, buffers, enzymes, reagents and virus suspensions, according to the manufacturer. The possibility of DOC and DON contamination during the filtration process had been tested in duplicate for each type of capsule filters (1.0 µm 75TC capsule filter and 0.8/0.1 µm 150TC capsule filter). The 0.8/0.1 µm 150TC capsule filter is a dual-stage capsule filter with effective final pore size 0.1 µm (A 0.1 µm pore size capsule filter with a 0.8 µm pre-filter).

Two types of capsule filter had been pre-washed with Milli-Q water and the filtrate was collected (first 50 ml (0.05 L) for initial concentration, then after 1, 2, 4,

6, 8, 10, 15 and 20 L washing, respectively). The result (Figure 2.12) shows that filter media contains DOC and DON. However, this can be reduced by a pre-wash with Milli-Q water. Percentage of DOC and DON removal by Milli-Q water in 1.0 µm 75TC capsule filter and 0.8/0.1 µm 150TC capsule filter are shown in Table 2.12.

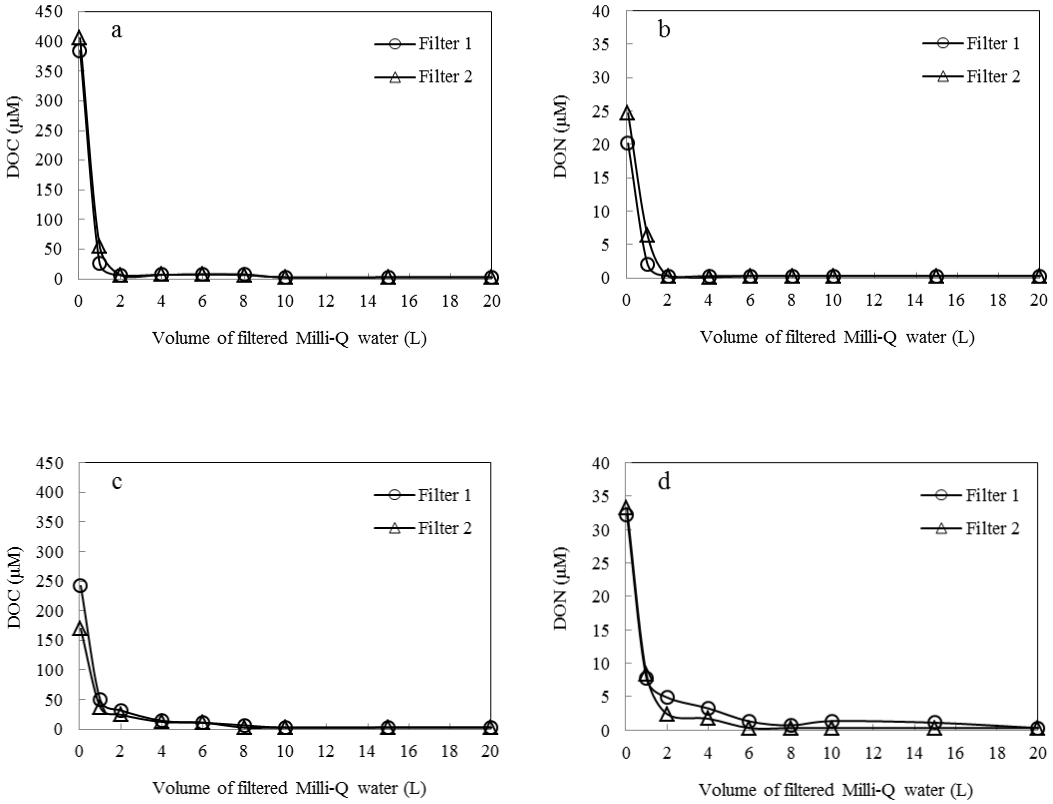


Figure 2.12 DOC and DON concentrations of Milli-Q water filtered through two types of capsule filters (1.0 µM pore size 75TC capsule filter (a, b) and 0.8/0.1 µM pore size 150TC capsule filter (c,d)).

In filter set one (filter1), the initial concentrations are 385.0 µM DOC and 20.2 µM DON in 1.0 µm 75TC capsule filter, and 242.2 µM DOC and 32.2 µM DON in 0.8/0.1 µm 150TC capsule filter, and for a duplicate filter set two (filter 2), the initial concentrations are 406.2 µM DOC and 24.7 µM DON in 1.0 µm 75TC capsule filter, and 169.8 µM DOC and 33.3 µM DON in 0.8/0.1 µm 150TC capsule filter. Final DOC and DON concentration of filter 1 and filter 2 in both types of the capsule filter were lower than the limit of detection (DON concentration was lower than the limit of detection as both TDN, and DIN concentration were lower than the limit of

detection). Generally, most of the filter DOC and DON blank are efficiently removed after pre-washing with 10 L Milli-Q water, after which concentrations were at the detection limit. The only exception was the DON concentration in filter 1 of 0.8/0.1 µm 150TC capsule filter, where the concentration was lower than the limit of detection when pre-washed with 20 L Milli-Q water.

Table 2.12 Percentage of DOC and DON removal compared to initial concentrations by Milli-Q water filtered through two types of capsule filters.

Milli-Q water filtered volume (L)	% Removal							
	1.0 µM pore size (75TC capsule filter)				0.8/0.1 µM pore size (150TC capsule filter)			
	DOC		DON		DOC		DON	
	Filter 1	Filter 2	Filter 1	Filter 2	Filter 1	Filter 2	Filter 1	Filter 2
1	93.3	86.5	90.0	74.4	79.6	78.1	76.0	74.9
2	98.2	98.3	98.5	98.8	86.8	85.5	84.8	92.8
4	98.1	98.3	98.5	99.5	94.1	92.7	89.9	94.9
6	97.9	98.1	98.5	98.8	95.4	93.5	96.0	99.1
8	97.9	98.3	98.5	98.8	97.2	98.3	97.8	99.1
10	99.3	99.3	98.5	98.8	98.8	98.3	95.8	99.1
15	99.3	99.3	98.5	98.8	98.8	98.3	96.6	99.1
20	99.3	99.3	98.5	98.8	98.8	98.3	99.1	99.1

Therefore, all new capsule filters used in this research have been pre-washed with at least 20 L Milli-Q water and followed by rinsing with 1 L seawater samples prior to use, to make sure that the filtration processes do not affect the DOC and DON concentrations of water samples.

3 SPATIAL AND TEMPORAL DISTRIBUTION PATTERNS

This chapter presents results and discussion of the field surveys. Details include a general summary of all surveys, followed by the surface and bottom water distribution in each season. The main summer surveys in the North Sea were performed to take water samples on the CEFAS Endeavour research cruise on 8 August 2011 – 7 September 2011 (CEND 14/11 cruise) and 9 – 23 August 2012 (CEND 13/12 cruises). The goal of the sampling was mapping the DOC and DON distribution in the North Sea in relation to other variables in summer when the water columns are generally stratified in the north and well mixed in the south region. For the summer 2011 survey, there were 144 samples including surface and bottom samples for DOC and DON determination at UEA, the inorganic nutrients were done at the CEFAS laboratory. All samples were analysed at UEA for summer 2012 survey with 318 samples including 106 surface and bottom water samples for DOC, DON and inorganic nutrients determination and 212 particulate samples for POC, PON and chlorophyll *a* determination. In addition, analyses were performed on previously collected samples from winter 2011 (CEND 02/12, 20 – 31 January 2012, 60 samples of surface and bottom waters) to compare DOC, DON and inorganic nutrient patterns with the fieldwork surveys in summer 2011 and 2012.

In this present study, all sampling sites are based on CEFAS sampling programme. Thus, the sampling sites covered the whole area of the North Sea during the summer 2011 cruise. Many fewer sampling sites were visited during the winter cruise, sampling only covered the coastal area in the western North Sea, approximately from the Tyne through the Thames river plume, because the cruise was mainly servicing equipment in other areas (the English Channel and the Celtic Sea) and the bottom water sampling was limited by the weather conditions. Nevertheless, winter sampling sites are more frequent and closer to the shore than the summer sites, providing an opportunity to investigate river influence during the winter time. In each section the data are first described and then interpreted in the final part of the section and then synthesized together in section 3.5 and 3.6

The last part of this chapter focuses on nutrient variations in the high frequency measurements over time in autumn 2013, winter 2013 and spring 2014 collected at each single site of the West Gabbard and Dowsing SmartBuoy in the southern North Sea. The overall discussions of cruise surveys and individual SmartBuoy site are provided at the end of the chapter.

3.1 General distribution of surveyed samples in water column

The results of survey samples in the North Sea collected by three cruises are presented in Appendix 3.1 – Appendix 3.6 for surface and bottom waters of summer 2011, winter 2011 and summer 2012, respectively. The general distribution of nutrients and chlorophyll *a* in surface and bottom water is summaried in Table 3.1.

In general, the water column was stratified in summer with the temperature, lower in the bottom water in the northern North Sea (Figure 3.2 (a-b) and Figure 3.17 (a-b)). In contrast, there were minor temperature differences in winter for surface and bottom water. Overall temperature ranged between 5.7 °C and 18.5 °C with the lowest temperature in the winter bottom water and the highest in surface water in summer 2012. The maximum temperature was similar in summer surface and bottom water with 17.8 °C in 2011 and 18.5 °C in 2012. In general, mean temperature was higher in the surface water in both summer and winter seasons. Although winter sampling was close to the shore, the mean salinity was ~ 34 in all surveys with a higher salinity range in the surface than bottom water over the summer period.

The chlorophyll *a* data was not available for the summer 2011 cruise. Measurements during winter 2011 (Figure 3.10) and summer 2012 (Figure 3.19) cruises showed the range of chlorophyll *a* concentration < LOD (< 0.1) – 7.8 µg/L with both minimum and maximum concentrations recorded in the bottom water in summer. Lower mean concentration was recorded in winter bottom water (0.5 ± 0.3 µg/L), with average concentration three times higher in summer bottom water (1.4 ± 1.8 µg/L).

The minimum concentration of TOxN as a total oxidisable nitrogen compound (nitrate + nitrite) was observed in both surface and bottom waters of the

Table 3.1 Summary of temperature (°C), salinity, chlorophyll *a* (µg/L) and nutrients (µM) for three survey cruises during summer 2011, winter 2011 and summer 2012.

Parameter	Season	Number of Samples		Concentrations	
				Range	Mean [a] ± SD
Temperature	Summer 2011	Surface	72	12.2 – 17.8	14.8 ± 1.3
		Bottom	70	6.7 – 17.8	10.4 ± 3.5
	Winter 2011	Surface	12	5.8 – 8.7	7.4 ± 1.0
		Bottom	8	5.7 – 7.9	6.8 ± 0.7
	Summer 2012	Surface	53	13.2 – 18.5	16.6 ± 0.9
		Bottom	53	7.5 – 18.5	11.7 ± 3.6
Salinity	Summer 2011	Surface	74	31.8 – 35.4	34.3 ± 0.9
		Bottom	70	33.0 – 35.4	34.9 ± 0.5
	Winter 2011	Surface	52	33.3 – 35.4	34.9 ± 0.4
		Bottom	8	34.1 – 35.1	34.7 ± 0.4
	Summer 2012	Surface	53	30.9 – 35.2	34.4 ± 0.8
		Bottom	53	33.5 – 35.4	34.8 ± 0.4
Chlorophyll *a*	Winter 2011	Surface	52	0.3 – 1.7	0.6 ± 0.3
		Bottom	8	0.3 – 1.1	0.5 ± 0.3
	Summer 2012	Surface	53	0.2 – 7.0	0.8 ± 1.2
		Bottom	53	< LOD – 7.8	1.4 ± 1.8
TOxN	Summer 2011	Surface	74	0.1 – 4.6	0.5 ± 0.8
		Bottom	70	0.1 – 14.4	5.7 ± 5.4
	Winter 2011	Surface	52	4.9 – 22.9	8.5 ± 3.2
		Bottom	8	5.5 – 14.5	8.3 ± 3.7
	Summer 2012	Surface	53	0.2 – 1.1	0.2 ± 0.2
		Bottom	53	0.2 – 10.7	2.4 ± 2.9
Ammonium	Summer 2011	Surface	74	< LOD – 3.9	0.3 ± 0.6
		Bottom	70	0.3 – 4.6	1.8 ± 1.0
	Winter 2011	Surface	52	< LOD – 0.7	0.3 ± 0.1
		Bottom	8	< LOD – 0.8	0.3 ± 0.2
	Summer 2012	Surface	53	< LOD – 8.1	0.5 ± 1.1
		Bottom	53	< LOD – 4.0	1.1 ± 1.2
Phosphate	Summer 2011	Surface	74	0.1 – 0.5	0.2 ± 0.1
		Bottom	70	0.1 – 1.1	0.6 ± 0.3
	Winter 2011	Surface	52	0.4 – 0.9	0.6 ± 0.1
		Bottom	8	0.5 – 0.8	0.6 ± 0.1
	Summer 2012	Surface	53	< LOD – 0.4	0.1 ± 0.1
		Bottom	53	0.1 – 0.9	0.4 ± 0.3
Silicate	Summer 2011	Surface	74	0.4 – 6.6	1.5 ± 0.9
		Bottom	70	0.3 – 7.7	3.9 ± 1.9
	Winter 2011	Surface	52	4.1 – 8.9	5.4 ± 1.0
		Bottom	8	4.3 – 6.7	5.3 ± 0.9
	Summer 2012	Surface	53	0.1 – 2.7	1.0 ± 0.6
		Bottom	53	0.3 – 5.2	2.6 ± 1.2
DOC	Summer 2011	Surface	74	51.2 – 118.0	80.3 ± 14.4
		Bottom	70	55.3 – 134.5	82.1 ± 19.9
	Winter 2011	Surface	52	56.2 – 224.8	108.0 ± 31.3
		Bottom	8	85.7 – 118.5	104.3 ± 14.3
	Summer 2012	Surface	53	32.7 – 124.4	63.7 ± 15.7
		Bottom	53	36.3 – 98.4	54.1 ± 13.5
DON	Summer 2011	Surface	74	4.8 – 11.5	7.2 ± 1.5
		Bottom	70	3.0 – 13.7	7.0 ± 2.6
	Winter 2011	Surface	52	3.7 – 12.3	6.6 ± 2.0
		Bottom	8	5.8 – 11.0	7.3 ± 1.7
	Summer 2012	Surface	53	3.0 – 9.8	5.3 ± 1.2
		Bottom	53	2.8 – 8.2	5.2 ± 1.1
POC	Summer 2012	Surface	53	2.7 – 43.8	11.8 ± 6.8
		Bottom	53	1.1 – 39.3	12.2 ± 8.7
PON	Summer 2012	Surface	53	0.6 – 5.9	1.9 ± 1.0
		Bottom	53	0.3 – 5.6	1.9 ± 1.0

Surface = surface water samples for the whole area were collected from water columns at 2-4 meters below the surface.
Bottom = bottom water samples for the whole area were collected from water columns at 5-6 meters above the seabed.

[a] Mean is the averaged quantity of each parameter for each season in the whole surface or the whole bottom water. For instance, mean temperature in summer 2011 for the whole surface water (72 water samples were collected in surface water) was 14.8 ± 1.3 (mean ± SD). SD = standard deviation.

LOD = Limit of detection at UEA as 0.1 µg/L for chlorophyll *a*, 0.4 µM for ammonium and 0.1 µM for phosphate in summer 2012 samples; Limit of detection at CEFAS as 0.2 µM for ammonium in summer 2011 and winter 2011 samples. For parameters presented < LOD, the half of detection limit was used to calculate the mean value.

summer 2011 cruise with a concentration of 0.1 µM (Figure 3.4(a-b)), while the maximum level of 22.9 µM was in winter surface water (Figure 3.11a) where the maximum mean concentration (8.5 ± 3.2 µM for whole surface water in winter) was also found. The minimum mean concentration was measured in surface water of summer 2012 (0.2 ± 0.2 µM).

The lowest concentration of the most reduced nitrogen form, ammonium, in all surveys was below the detection limit, except the bottom water in summer 2011 where the minimum ammonium level was 0.3 µM (Figure 3.4d). The highest level was in the surface water of summer 2012 with 8.1 µM (Figure 3.20c), whereas, the highest mean concentration was found in bottom water of summer 2011 (1.8 ± 1.0 µM) and the lowest in winter surface water (0.3 ± 0.1 µM).

Phosphate concentrations ranged between below the detection limit (< 0.1 µM in surface water, summer 2012 (Figure 3.20g)) to 1.1 µM (bottom water, summer 2011 (Figure 3.4h) with the minimum mean concentration in the surface water of summer 2012 (0.1 ± 1.1 µM) and the maximum mean concentration in summer 2011, bottom water (0.6 ± 0.3 µM). In winter, both surface and bottom waters recorded mean concentrations in the same range with 0.6 ± 0.1 µM. For silicate, the concentration ranged from 0.1 µM during summer surface water in 2012 (Figure 3.20i) to 8.9 µM in winter surface water (Figure 3.11i). Lower mean level was also measured in surface water of summer 2012 with a concentration of 1.0 ± 0.6 µM, but higher in winter surface water with a mean of 5.4 ± 1.0 µM.

For DOM, the DOC concentration was measured between 32.7 and 224.8 µM, the lowest in surface water of summer 2012 (Figure 3.21a) and the highest in winter surface water (Figure 3.13a). The minimum of mean DOC concentration was 54.1 ± 13.5 µM during summer 2012 in bottom water, while the maximum mean concentration was recorded in winter surface water with 108.0 ± 31.3 µM. The lowest DON concentration was also found in summer 2012, as recorded for DOC, but in the bottom water with a concentration of 2.8 µM. The highest DON concentration was observed in bottom water of summer 2011 (Figure 3.5d) with 13.7 µM. Similar to DOC, the minimum mean concentration of DON (5.2 ± 1.1 µM) was measured in bottom water of summer 2012 but the maximum (7.3 ± 1.7 µM) in winter bottom water.

POM was only available in summer 2012 cruise (Figure 3.23). POC concentrations ranged from 1.1 µM in the bottom to 43.8 µM in surface water with lower mean concentration in the surface (11.8 ± 6.8 µM) and slightly higher in bottom water (12.2 ± 8.7 µM). The minimum level for the PON was also observed in bottom water (0.3 µM) and the maximum in the surface (5.9 µM). The mean concentration for PON in surface and bottom water were similar, 1.9 ± 1.0 µM.

To investigate distribution patterns of surface and bottom waters for general hydrography, chlorophyll *a* and nutrients during each survey cruise in this study, all data are initially presented as contour map plots (MatLab version 2012a X64). Wherever possible, the same parameter was displayed in the same scale in all three surveys. In addition, for related parameters such as TOxN, ammonium, DIN and DON, the same scale was also used for visible comparison. The summer 2011 survey is the first presented, followed by winter 2011 survey and then the cruise surveys for the summer 2012 cruise. The individual results and discussion is provided within the section of each survey cruise and the overall discussion of all survey cruises minimum then discussed in later sections.

As both summer survey cruises in 2011 and 2012 were based on the same IBTS cruise track, the "prime station number" (identified and used by CEFAS, hereafter called PSt.) was used in later results and discussions in order to clarify the sample locations. Each PSt. was previously shown in Figure 2.1 in chapter 2 and are repeated here in Figure 3.1 (both figures show PSt. in the filled dots) for all summer sampling sites in the North Sea. Both summer surveys were performed during the stratification period in the North Sea; the end of stratification period in the north of Dogger Bank was in early November (Greenwood et al. 2010). In addition, to simplify the discussion related to the spatial distribution, the area located approximately from the north of the Dogger bank (approximately from 55.5° N) was defined here as 'the stratified northern water or the north' and the other in the south was 'the southern North Sea, the well-mixed southern water or the south' (Figure 3.1). The surface and bottom temperature ratios separated the stratified northern water and the well mixed southern water during the sampling period over summer 2011 and summer 2012 (Figure 3.2e and Figure 3.17e). The winter cruise in 2011 was not based on the IBTS cruise track used for the summer cruises, but serviced the

SmartBuoy sites and all sampling sites during winter were located in the south western North Sea. Winter sampling stations were presented in open circles (Figure 3.1)

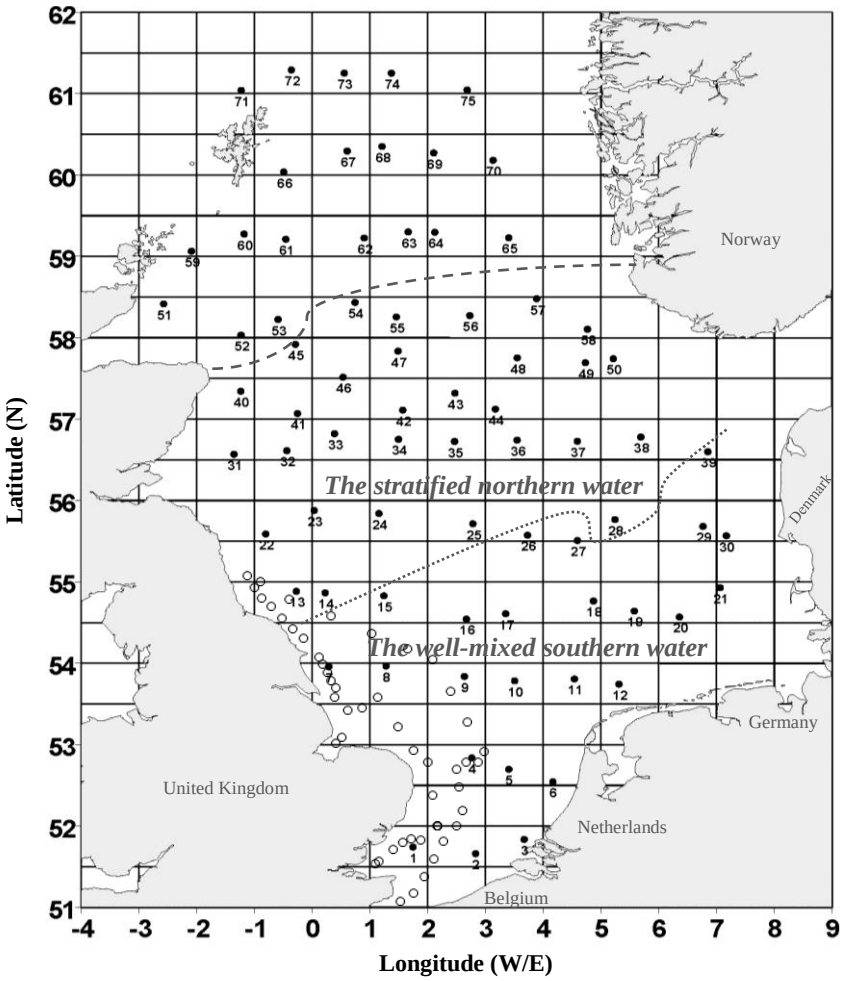


Figure 3.1 The summer and winter sampling sites in the North Sea (modified from IBTS cruise track, CEFAS) for summer 2011 (74 stations in the whole North Sea, filled dots), summer 2012 survey (53 stations in the whole North Sea, filled dots but not including the area above the broken line) and winter 2011 survey (52 stations in the south western North Sea covering the East Anglian Plume, open circles). The boundary of the stratified northern and well-mixed southern North Sea is indicated by a dotted line.

3.2 Summer 2011 survey

3.2.1 General hydrography

The sampling of the whole of the North Sea in summer 2011 survey was carried out between 8 August – 7 September 2011 (CEND 14/11). The general hydrography investigated during the cruise track is shown in Figure 3.2. Higher temperature was observed in the surface water (12.2 – 17.8 °C, mean 14.8 ± 1.3 °C) and lower in the bottom (6.7 – 17.8 °C, mean 10.4 ± 3.5 °C). The warmest water was found near the Scheldt mouth (PSt. 3) in both surface and bottom water. The coldest was recorded in the bottom water of the northern North Sea (PSt. 62) as well as surrounding the north of Dogger Bank (PSt. 34, 35 and 42). There was a significant difference ($P < 0.05$) in mean temperature between the whole surface and bottom water. In general, the water column was well mixed in the southern North Sea, whereas it obviously exhibited thermal stratification in the north (Figure 3.2e). The water column depth ranged between 18 and 205 meters with mean depth 84 ± 44 meters (Figure 3.2f). The greatest depth (approximately > 150 meters) was generally recorded off the coastal area of Norway. Higher salinity was observed at the deeper water column, the bottom salinity had a significant positive correlation with the water column depth ($R^2 = 0.58$, $P< 0.05$, $n = 70$). Lower salinity was recorded in the surface water with mean salinity of 34.3 ± 0.9 (31.8 – 35.4), compared to a bottom mean salinity of 34.9 ± 0.5 (33.0 – 35.4).

Lower surface salinity generally occurred at near shore stations suggesting an impact of river discharge on surface water during the sampling period although the survey design did not allow waters with particularly low salinity to be sampled. The evidence showed more influence of freshwater near the coast of Norway surrounding the Norwegian Trench and the Skagerrak as lower surface salinity is obviously more pronounced in this area than other regions (Figure 3.2c), probably reflecting outflow from the Baltic. In addition, the temperature and salinity plot in Figure 3.3 provides evidence of water masses separated in three main types including: 1) the northern surface water (NS) with high range of salinity; 2) northern bottom water (NB) with high salinity and low temperature (most of NB was located in the area B); and 3) southern mixed water (mixed surface and bottom waters). The area A within the

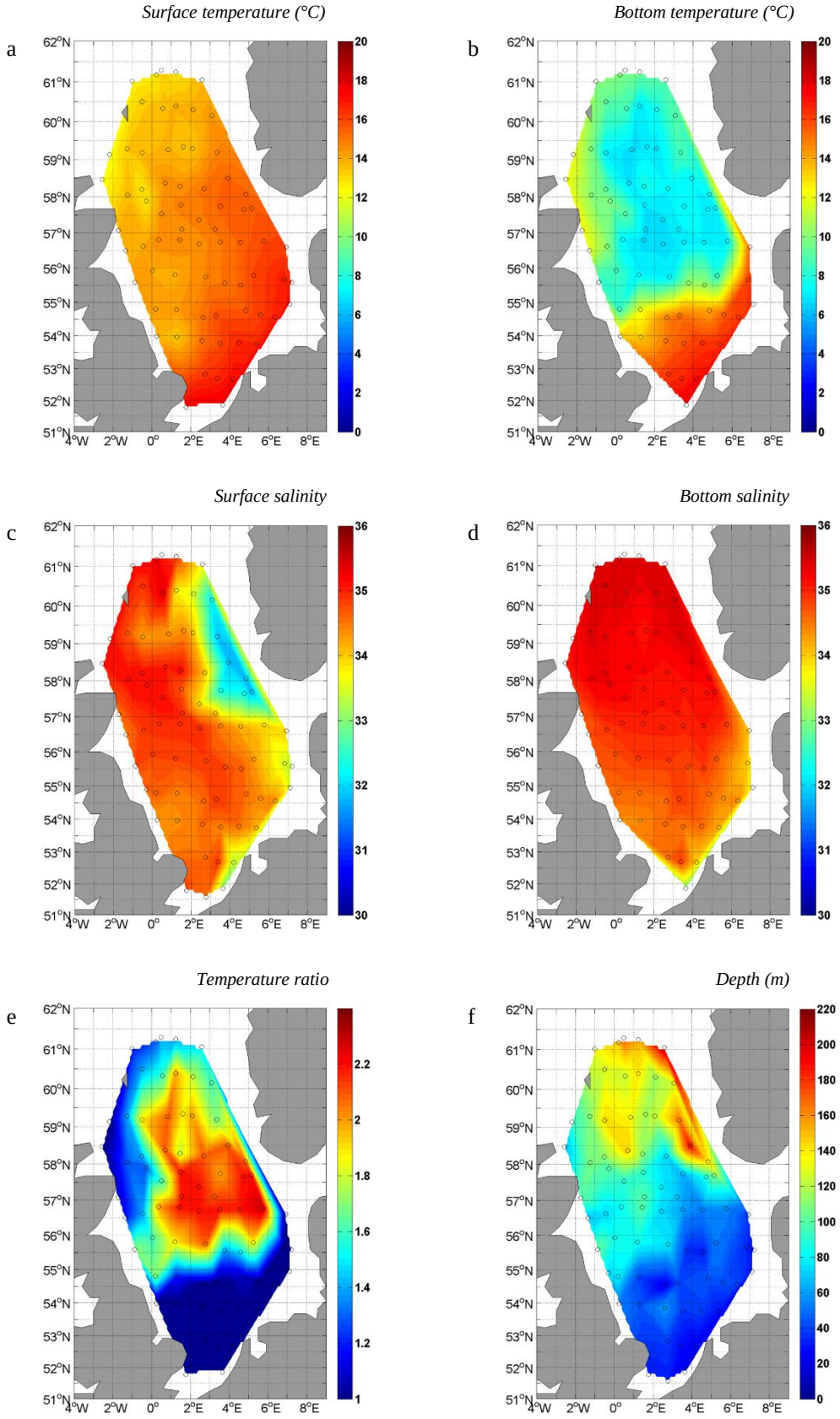


Figure 3.2 General hydrography in summer 2011. Distribution of temperature (°C) and salinity for surface and bottom (a-b) temperature and (c-d) salinity; (e) surface and bottom temperature ratio and (f) water column depth (meter).

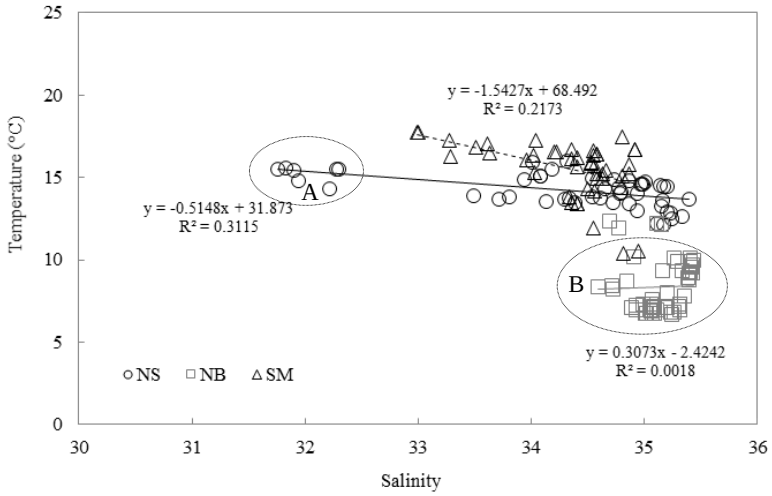


Figure 3.3 Characteristics of three water masses in the North Sea during summer 2011: northern surface water (NS), northern bottom water (NB) and southern well-mixed water (SM). The line for each water mass was fitted by linear regression analysis. The area A represents a low salinity with high temperature water mass, whereas the area B is high salinity with low temperature water mass (discussed in the text).

stratified northern surface water representing a low salinity (31.8 – 32.3) with high temperature (14.4 – 15.6°C) water mass near the coast of Norway along the Norwegian Trench is dominated by a water mass from the Skagerrak and is separated from water masses in other areas (salinity 33.5 – 35.4 and temperature 12.2 – 16.0°C) within northern surface water. All bottom water in the stratified north generally fall within the high salinity (34.6 – 35.4) with low temperature (6.7 – 12.4 °C) water mass (area B in Figure 3.3). The salinities of well mixed southern water ranged from 33.0 – 34.9 and the temperature was between 10.4 and 17.8 °C.

Therefore in this present study for the summer season, most of the area in the north of Dogger Bank was generally stratified and identified here as the seasonal stratified northern water, whereas, the water south of the Dogger Bank is identified here as the well mixed southern water. Even though, some areas in the south of Dogger Bank (i.e. oyster ground) have been reported as thermally stratified water this appears to be for a much shorter period than north of the Dogger Bank (Greenwood et al. 2010). Additionally, the shallow depth area surrounding Dogger Bank was considered as less stratified water compared with the northern part (Vested et al. 1996, Ducrotoy et al. 2000).

3.2.2 Dissolved inorganic nutrients

The surface and bottom distributions of inorganic nutrients are shown in Figure 3.4. The range of nutrient concentrations was 0.1 – 4.6, < LOD – 3.9, 0.2 – 4.7, 0.1 – 0.5 and 0.4 – 6.6 µM for TOxN, ammonium, DIN (nitrate + nitrite + ammonium), phosphate and silicate in surface water, respectively. In the bottom water, nutrients were generally higher concentration than in the surface layer. Deep water nutrients were recorded in the range 0.1 – 14.4, 0.3 – 4.6, 0.5 – 16.2, 0.1 – 1.1 and 0.3 – 7.7 µM for TOxN, ammonium, DIN, phosphate and silicate, respectively. Considering the whole North Sea, all inorganic nutrients presented significantly (t-test, $P < 0.05$) higher concentration in the bottom waters than the surface during summer 2011.

TOxN was the dominant form of DIN in the northern water as the DIN distribution in both northern surface and bottom waters clearly shows the same general pattern as TOxN, particularly the high concentration area in the northern bottom water where high concentrations of phosphate and silicate were also determined. While most of the high bottom concentration TOxN were recorded in the north for inorganic nutrients, ammonium showed a slightly different pattern. The highest bottom ammonium concentration (3.1 – 4.6 µM) was found to the north of Dogger Bank (area I – III in Figure 3.4d) suggesting a link to the lowest oxygen condition of bottom water in this region since strong thermal stratification and low dissolved oxygen were also found in a previous study during summer 2010 (Queste et al. 2013). In addition to high bottom concentration found in the north, highest silicate concentration was also recorded at the same site in the southern North Sea for both surface (6.6 µM) and bottom waters (7.7 µM) (Figure 3.4i - Figure 3.4j) suggesting the land based source arriving via the German Bight.

In consideration of the three water masses, there was little evidence of riverine inputs of dissolved inorganic nutrients within the study period (note a narrow salinity range (31.8 – 35.4)) as no significant negative relationship between dissolved inorganic nutrient and salinity was observed, except bottom ammonium in the north where the significant negative correlation with salinity was found ($R^2 = 0.21$, $P < 0.05$, $n = 49$). By contrast, most bottom nutrients in the northern water demonstrated statistically significant positive correlations ($P < 0.05$, $n = 49$) with salinity: TOxN ($R^2 = 0.56$), DIN ($R^2 = 0.51$), phosphate ($R^2 = 0.27$), and silicate

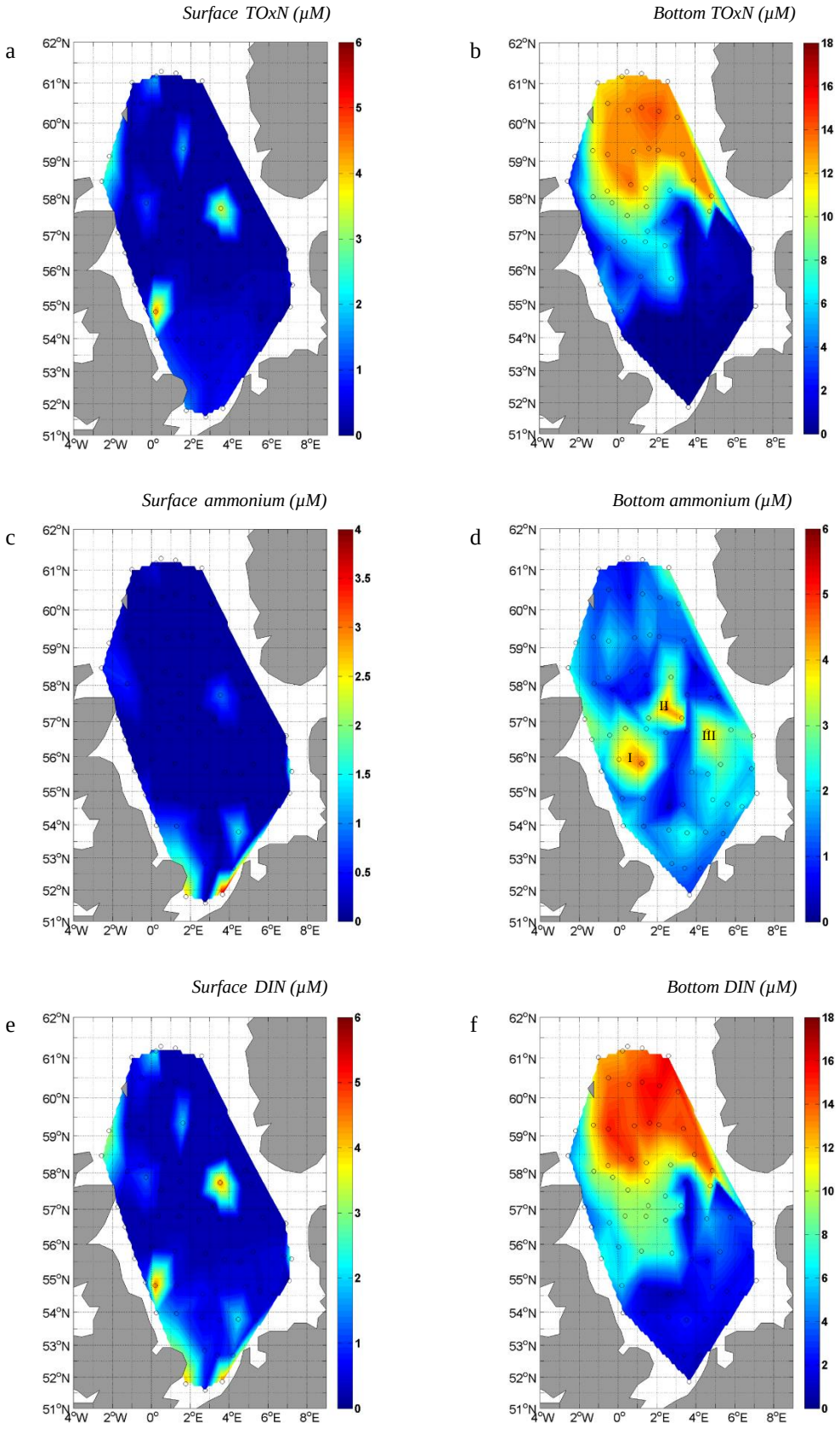


Figure 3.4 Distribution of dissolved inorganic nutrients in summer 2011 for surface and bottom (a-b) TOxN, (c-d) ammonium, (e-f) DIN, (g-h) phosphate and (i-j) silicate. Note different scales in surface and bottom concentrations.

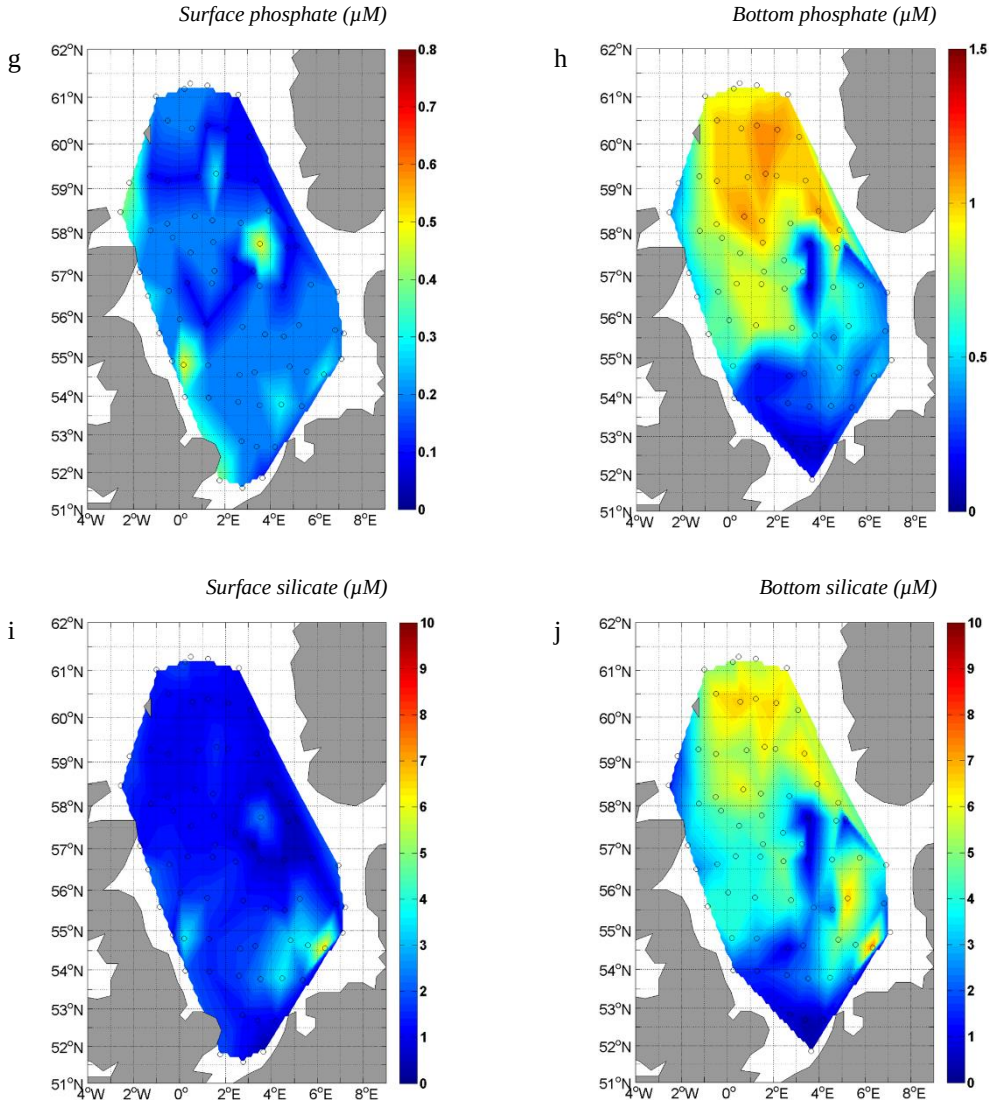


Figure 3.4 (Continued).

(R^2 = 0.17). In addition, only surface silicate in the north had a significant positive relationship with salinity (R^2 = 0.09, P < 0.05, n = 50), while other nutrients in both northern surface water and well-mixed southern waters were not significantly correlated with salinity (R^2 < 0.09, P > 0.05, northern surface water (n = 50) and well-mixed southern water (n = 49)).

In this study, the bottom water samples were collected at 5 – 6 meters above the seabed. There was the northward increase in water column depth (Figure 3.2f). Therefore, the positive correlation between inorganic nutrients and water column depth in the northern bottom water may reflect the inorganic nutrient input partly by the outer shelf water exchanged with the North Atlantic water since these nutrient

concentrations increase with depth (Pilson 2013). Statistically significant positive correlations were observed between inorganic nutrient concentrations and water column depth in the northern bottom water (Appendix 3.7). The positive correlation found for TOxN ($R^2 = 0.64$, $P < 0.05$, $n = 49$), DIN ($R^2 = 0.61$, $P < 0.05$, $n = 49$), phosphate ($R^2 = 0.41$, $P < 0.05$, $n = 49$) and silicate ($R^2 = 0.34$, $P < 0.05$, $n = 49$).

3.2.3 DOC and DON

The surface and bottom distributions of DOC and DON are presented in Figure 3.5. Surface DOC concentrations ranged from 51.2 – 118.0 µM (mean 80.3 ± 14.4 µM) and the bottom concentration ranged from 55.3 – 134.5 µM (mean 82.1 ± 19.9 µM). The concentrations of surface and bottom DON were 4.8 – 11.5 µM (mean 7.2 ± 1.5 µM) and 3.0 – 13.7 µM (mean 7.0 ± 2.6 µM) respectively. In general, higher concentrations were seen in the coastal zones particularly in the Southern Bight, the German Bight and surrounding the East Anglian plume (the Thames estuary, the Humber estuary and the Wash) for both surface and bottom water, and along the coast of Norway for surface water. The highest DOC and DON concentrations in both bottom and surface waters were recorded at the same station (PSt. 6) located in the north of the Scheldt and Rhine-Meuse plume in the Southern Bight. The high concentration area generally followed the direction of the southern North Sea currents (See Figure 1.3b in chapter 1 for the North Sea current). High surface concentrations were also found near the coast of Norway. There was no significant difference of mean concentration between bottom and surface DOC ($P > 0.05$). Similarly, the mean of DON concentration in the surface and bottom water were not significantly different ($P > 0.05$) in summer 2011.

By contrast, based on analyses of three water masses, one way ANOVA test at 95% significance level, the southern well-mixed water demonstrated significantly higher mean DOC and DON concentrations ($P < 0.05$) with 97.5 ± 13.7 µM ($n = 45$) for DOC and 9.0 ± 1.8 µM ($n = 45$) for DON, followed by the stratified region in the northern surface water (DOC 73.8 ± 11.6 µM and DON 6.6 ± 1.0 µM, $n = 50$) and the northern bottom water (DOC 73.8 ± 14.7 µM and DON 5.9 ± 2.1 µM, $n = 50$).

High significant positive correlations were found between DOC and DON in the surface ($R^2 = 0.58$, $P < 0.05$, $n = 74$) and bottom water ($R^2 = 0.67$, $P < 0.05$,

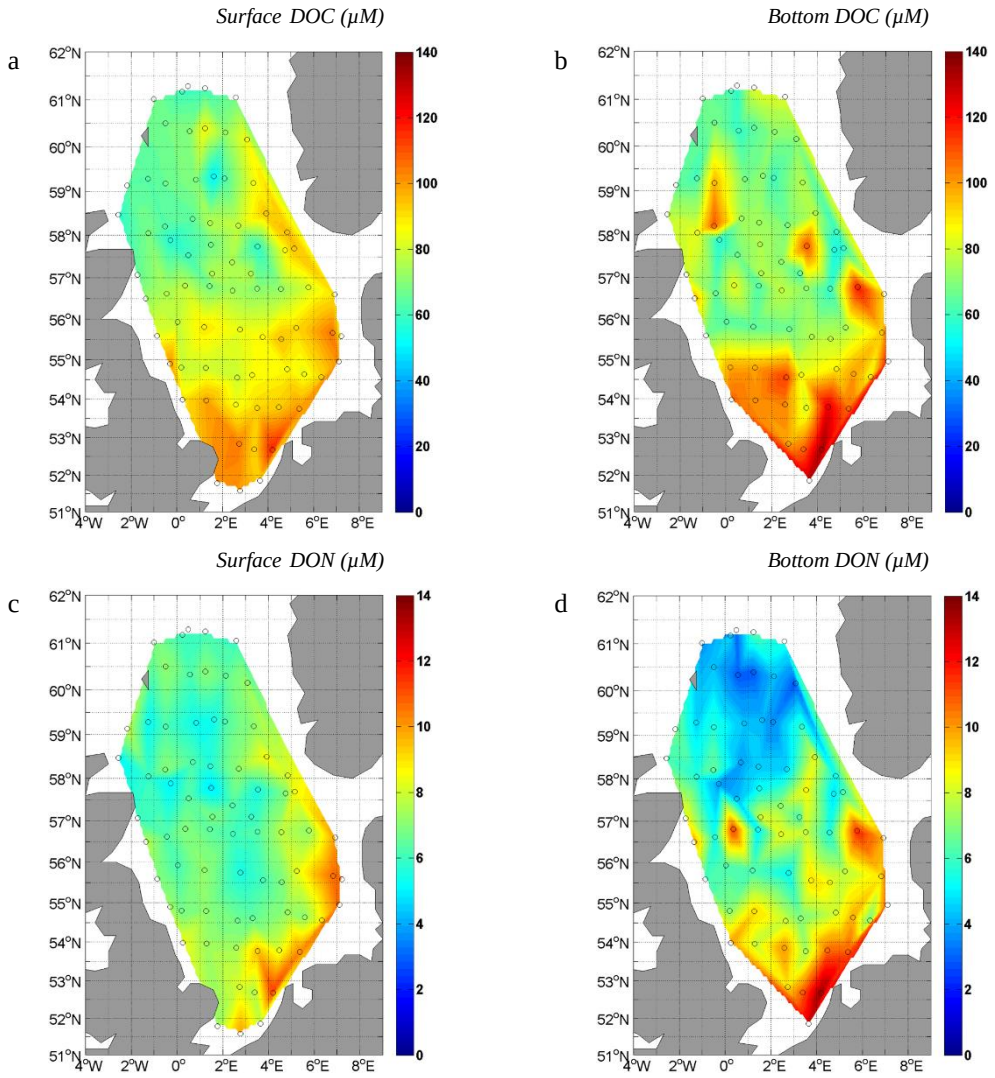


Figure 3.5 Distribution of dissolved organic nutrients (µM) in summer 2011. (a) Surface and (b) bottom DOC. (c) Surface and (d) bottom DON.

n = 70) with a slope C:N ratio of 7.4 at the surface and 6.3 at the bottom (Figure 3.6a-b). There was also a clear non zero intercept at DOC ~ 30 µM. To consider the correlation in three different water masses, the DOC and DON were plotted as shown in Figure 3.6c-e). The same pattern of the relationship was also observed for the strong correlations. The strongest significant correlation was obtained in southern well-mixed water ($R^2 = 0.54$, $P < 0.05$, n = 45) followed by northern surface ($R^2 = 0.45$, $P < 0.05$, n = 50) and northern bottom waters ($R^2 = 0.41$, $P < 0.05$, n = 49), with a slope C:N ratio of 5.7 for well-mixed southern water, and 8.1 for surface and 4.6 for bottom water of the stratified north. The slope C:N ratios and C:N molar ratios are discussed further in section 3.5.

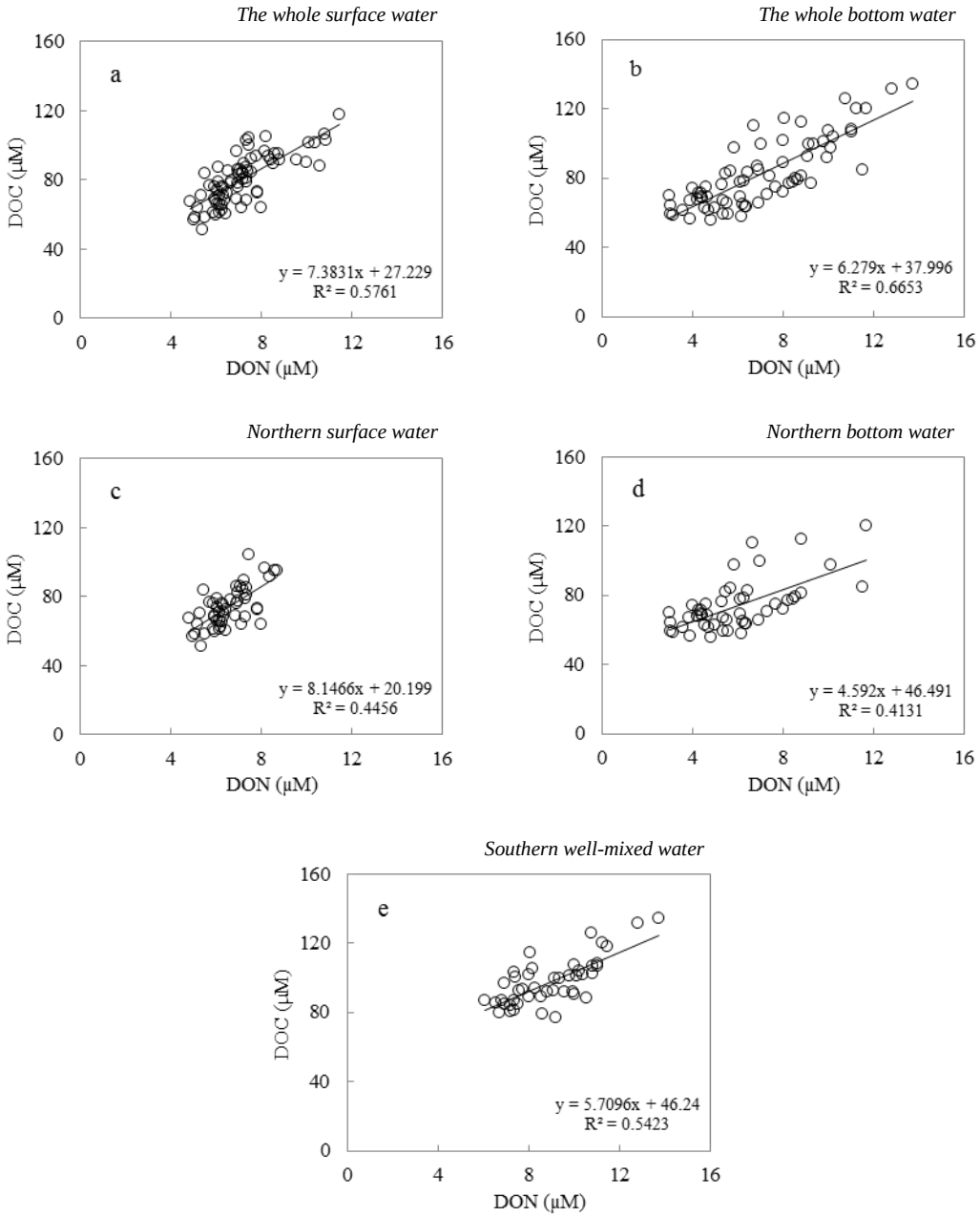


Figure 3.6 Relationship between DOC and DON (DOC = mDON + c, where m = gradient and c = intercept) for data sets of (a) the whole surface water, (b) the whole bottom water, (c) stratified northern surface water, (d) stratified northern bottom water, and (e) southern well-mixed water in summer 2011.

3.2.4 Discussion of distribution patterns in summer 2011

In general, temperature in the northern water was lower than the south, particularly in the northern bottom water where the lowest temperatures were recorded near the coast of Norway. The area surrounding coastal Norway was also dominated by the lowest surface salinity that is probably influenced by low salinity water from the Baltic Sea (salinity ~ 5 – 11) through the Kattegat (salinity ~ 21) during summer (Korth et al. 2012) which enters the North Sea by a "one-way road" via Skagerrak (Thomas et al. 2005). The difference between surface and bottom temperature corresponded with varying salinity and the stratification pattern which characterised water masses in the North Sea into three main classes including the northern surface water, the northern bottom water and the well-mixed southern water. The distribution of inorganic nutrients generally showed enhanced concentrations in the bottom stratified water column, consistent with the previous summer study (Riegman and Noordeloos 1998). The results also revealed that freshwater runoff generally does not obviously contribute TOxN, DIN, phosphate and silicate during summer into the survey area because no significant negative correlation with salinity was observed, as well as an absence of any relationship with salinity in the northern surface water and southern well-mixed water. By contrast, higher concentration of these inorganic nutrients in northern bottom water showed a strong positive correlation with salinity and water column depth. This enhanced bottom concentration implies an input of high nutrient deep water from offshore (Jickells 1998) or regeneration from sinking nutrients (Brockmann et al. 1990, Kirchman 2000). Low concentration of surface inorganic nutrients was probably associated with a minimum riverine input of nutrients during summer in the North Sea (Nedwell et al. 2002), particularly nitrate coinciding with the nutrients being consumed by phytoplankton growth near shore (Dortch 1990, Bronk et al. 1994, Tyrrell 1999, Timmermans et al. 2004).

In contrast to inorganic nutrients, higher mean concentrations of DOC and DON were found in the southern well-mixed water followed by northern surface water, and lower concentrations found in northern bottom water. In general, high levels of DOC and DON were observed in the coastal waters. A significant correlation between DOC and DON was presented in all water masses. The slope C:N ratio derived from DOC and DON correlation may suggest the C:N ratio of

bioavailable component and another recalcitrant DOC component which still persists when DON reaches zero indicated by the intercept value (Figure 1.2). The slope C:N ratio of 5.7 in the well-mixed southern water was closest to the 6.6 of the Redfield ratio (Geider and La Roche 2002) and suggested the dominant role of phytoplankton in this water mass, although the phytoplankton biomass was not investigated in this survey. The non zero intercept may indicate a background of high C:N ratio material, suggesting the high C:N ratio of recalcitrant DOC or it may occur from mixing between freshwater and seawater within the shelf sea, or a combination of both (see further discussion in section 3.5).

The summer season generally provided low concentrations of inorganic nutrients compared to other seasons and the concentrations of inorganic nutrient reported in this study agree with the levels reported by others in the North Sea (Hydes et al. 1999, Sanders et al. 2001, De Galan et al. 2004, Weston et al. 2004, Suratman et al. 2008a, Weston et al. 2008), the Celtic Sea (Robinson et al. 2009), and the Skagerrak (Rydberg et al. 1996). However, the inorganic nutrient concentrations are much lower than the estuarine levels (the Scheldt) in the southern North Sea (CabeÇadas et al. 1999) and nearby estuarine system (Torres-Valdés and Purdie 2006, Agedah et al. 2009).

Although DOC and DON concentrations are not available for the whole North Sea in previous studies for direct comparison with this study, particularly the bottom nutrients, the reported DOC and DON levels in the present study were generally similar to previous surface measurements in the central North Sea during summer (Suratman et al. 2008a, Suratman et al. 2009) and the southern North Sea (De Galan et al. 2004, Van Der Zee and Chou 2005, Van Engeland et al. 2010, Korth et al. 2012, Johnson et al. 2013), whereas, the DOC levels were lower than the value of European estuaries (the Thames, the Scheldt, the Rhine, the Ems, the Elbe) during summer (Abril et al. 2002). The DON concentration was also lower than the Marsdiep (inlet of the Wadden Sea in the southern North Sea) in summer (Moneta et al. 2014). Additionally, the DOC concentration was comparable to the Humber estuary in the plume area with salinity > 32 (Álvarez-Salgado and Miller 1998a), but much lower than the other estuarine areas closer to the river (Tipping et al. 1997, Álvarez-Salgado and Miller 1998a). DOC and DON concentrations in this study

were typically within the ranges previously reported in shelf waters of other regions (Hopkinson et al. 1997, Hopkinson et al. 2002, Ribas-Ribas et al. 2011)

To understand the influence of freshwater on DOC and DON distributions in this survey, a statistical correlation assessment was performed. The correlation between DOC and DON with salinity is summarised in Table 3.2. The results indicated high influence of salinity on DOC and DON distributions as both were inversely correlated with salinity in all water masses, except DOC in the northern bottom water which showed no statistically significant correlation with any parameter (Figure 3.7). However, note the two groups of results in Figure 3.7a and Figure 3.7b tend to drive the strong correlation. The grey highlighted area in Figure 3.7a and Figure 3.7b indicate seven surface sampling sites near the coast of Norway that provide the strongest negative significant correlation ($P < 0.05$, $n = 7$) with salinity ($R^2 = 0.55$ for DOC and $R^2 = 0.65$ for DON) and very different slopes and intercepts to the rest of the data. The high level of inorganic nutrients recorded in the northern bottom water was generally correlated to the DON pool rather than DOC.

Table 3.2 Correlations of DOC and DON with salinity for three water masses in summer 2011.

Water masses		Correlation coefficient (r)	Confidence level at 95 %
DOC	Stratified northern surface water	-0.509*	0.000
	Stratified northern bottom water	-0.233	0.107
	Southern well-mixed water	-0.408*	0.005
DON	Stratified northern surface water	-0.444*	0.001
	Stratified northern bottom water	-0.549*	0.000
	Southern well-mixed water	-0.551*	0.000

* Correlation is significant at the 0.05 confidence level.
The number of samples (n) is 50, 49 and 45 for northern bottom waters, northern surface water and southern mixed water, respectively.
Correlation to inorganic nitrogen is in Appendix 3.8.

Figure 3.8 provided the relative contribution of DON, TOxN and ammonium to the TDN pool. The results indicated that DON was the most important reservoir of nitrogen during summer in the stratified northern surface and the southern well-mixed water. The higher percentage of DON in stratified northern surface water (90%) and southern well-mixed water (85%) was comparable with previous studies in the North Sea (De Galan et al. 2004, Korth et al. 2012), whereas, the bottom water in the stratified north provided lower DON (37%) as this bottom water mass was

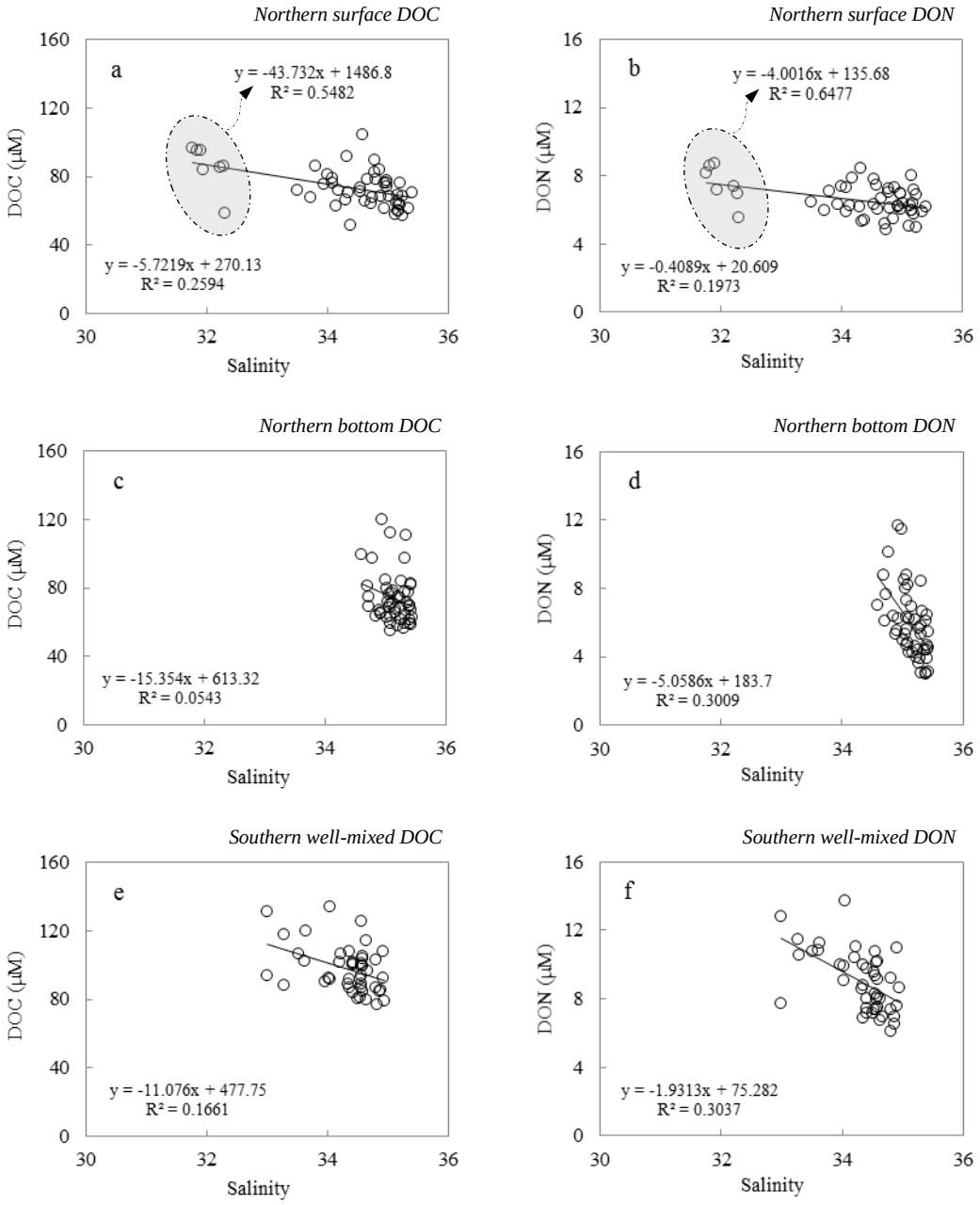


Figure 3.7 Relationship of DOC and DON with salinity (DOM = – m Salinity + c, where m = gradient and c = intercept) for data sets of (a – b) stratified northern surface water, (c – d) stratified northern bottom water, and (e – f) southern well-mixed water in summer 2011. The grey highlighted areas (a – b) indicated the seven stations near the coast of Norway.

dominated by 51% of TOxN pool. This is in line with a previous report in the continental shelf water that the proportion of DON pools contribution to TDN in surface waters was higher than in bottom waters which contained high levels of inorganic nutrients (Bradley et al. 2010). A high DON contribution to the TDN pool was found in the northern surface water and the southern well-mixed water with the similar proportion to that found in the open surface ocean (Mahaffey et al. 2004).

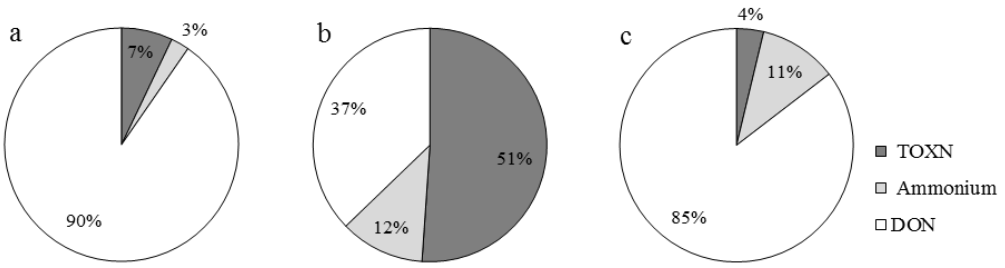


Figure 3.8 TOxN, ammonium and DON as percentage of TDN in (a) stratified northern surface water, (b) stratified northern bottom water, and (c) southern well-mixed water in summer 2011.

3.3 Winter 2011 survey

3.3.1 General hydrography

The CEND 02/12 cruise was undertaken during the winter sampling period on 20 – 31 January 2012. The surface sampling sites covered the eastern coast of the UK, approximately from the Tyne, the Tees and the East Anglian plume (the Humber, the Wash and the Thames) in the southern North Sea. While the bottom sampling site was limited by the weather conditions and only one bottom station was available in the Thames plume, seven other bottom sampling sites were collected from the Tyne through the Wash.

There were 52 stations for surface water and 8 stations for the bottom water with Figure 3.9 showing the general hydrography observed during the cruise track. The range of temperature recorded for surface and bottom water during this season were 5.8 – 8.7 °C and 5.7 – 7.9 °C respectively and the mean temperature was 7.4 ± 1.0 °C for the surface layer and 6.8 ± 0.7 °C for the bottom. There was no significant difference ($P > 0.05$) for the mean temperature between surface and bottom waters. The water column during winter was therefore well-mixed as the ratio of surface and bottom temperatures was 1.0 at all observed sampling stie. In addition, the whole water mass in winter (Figure 3.9f) generally showed the same properties in terms of temperature and salinity and much smaller range than summer. As all winter sampling sites were located near the coast, the water column depth was relatively shallow compared to the summer survey. The water column depth was recorded between 16 and 77 meters with mean depth 41 ± 17 meters. For salinity, there was no significant difference ($P > 0.05$) between surface and bottom layers. The salinity ranged between 33.3 – 35.4 with mean value of 34.8 ± 0.4.

In addition, phytoplankton biomass was investigated during winter (Figure 3.10). Statistical analysis demonstrated no significant difference ($P > 0.05$) between surface and bottom chlorophyll *a*. Concentration of chlorophyll *a* ranged between 0.3 – 1.7 µg/L with mean concentration of 0.6 ± 0.3 µg/L. The highest concentration of chlorophyll *a* (1.7 µg/L) was observed within the Thames plume. Furthermore,

chlorophyll *a* was positively correlated with salinity, showing a significant relationship ($R^2 = 0.23$, $P < 0.05$, $n = 60$).

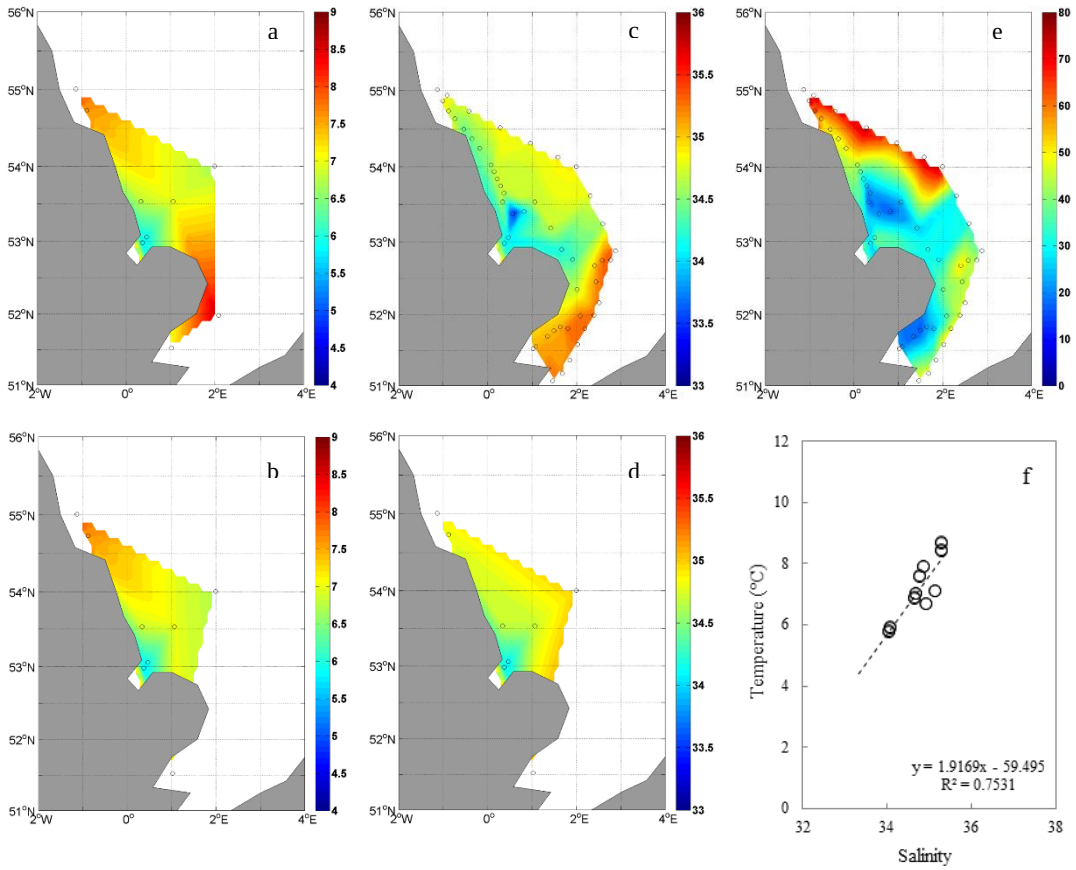


Figure 3.9 General hydrography in winter 2011. Distribution of surface and bottom (a-b) temperature (°C) and (c-d) salinity; (e) water column depth (meter); and (f) characteristic of whole water mass during winter with the line was fitted by linear regression analysis.

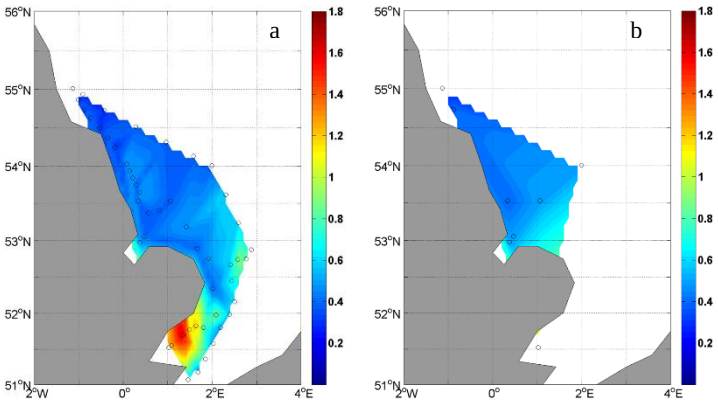


Figure 3.10 Distribution of (a) surface and (b) bottom chlorophyll *a* (µg/L) in winter 2011.

3.3.2 Dissolved inorganic nutrients

The surface and bottom inorganic nutrients are presented in Figure 3.11. There was no statistical difference (t-test, $P > 0.05$) between nutrient concentrations in surface and bottom waters. The levels of TOxN varied between 4.9 and 22.9 µM (8.5 ± 3.3 µM). For ammonium, the level was < LOD – 0.8 µM (0.3 ± 0.1 µM). The DIN concentration ranged from 5.3 to 23.0 µM, while the mean concentration was 8.8 ± 3.3 µM. The minimum and maximum concentrations for phosphate were 0.4 and 0.9 µM respectively with the mean concentration of 0.6 ± 0.1 µM. For silicate, the concentration range was 4.1 – 8.9 µM and mean concentration was 5.4 ± 1.0 µM. All maximum concentration of nutrients were found at the site located near the Humber, except ammonium where the maximum was observed within the Wash. This was followed by high TOxN, DIN concentrations near the Wash and high silicate levels in the Thames plume, while high phosphate concentrations near the Wash were comparable to the concentration in the Thames plume.

Statistical analysis revealed that inorganic nutrients were significantly correlated with salinity ($P < 0.05$, $n = 60$) for the whole data set (Figure 3.12, a-d) with the negative correlation between salinity and TOxN ($R^2 = 0.24$), DIN ($R^2 = 0.24$), phosphate ($R^2 = 0.43$) and silicate ($R^2 = 0.25$). The plots of inorganic nutrients and salinity revealed two distinct data sets of coastal areas in the western North Sea (Figure 3.12, e-h), are including the data set covering the coastal area approximately from the Tyne through the Humber and the Wash, and the other data set covering the Thames plume. The first data set provided a significant negative correlation ($P < 0.05$, $n = 37$) between salinity and TOxN ($R^2 = 0.93$), DIN ($R^2 = 0.92$), phosphate ($R^2 = 0.86$) and silicate ($R^2 = 0.84$). Similarly, the second data sets for the Thames plume also had a significant negative correlation ($P < 0.05$, $n = 23$) between salinity and TOxN ($R^2 = 0.55$), DIN ($R^2 = 0.53$), phosphate ($R^2 = 0.62$) and silicate ($R^2 = 0.64$), but different y-intercepts as discussed later. In contrast to these nutrients, no statistically significant correlation between salinity and ammonium was found at the 95% significance level ($P > 0.05$).

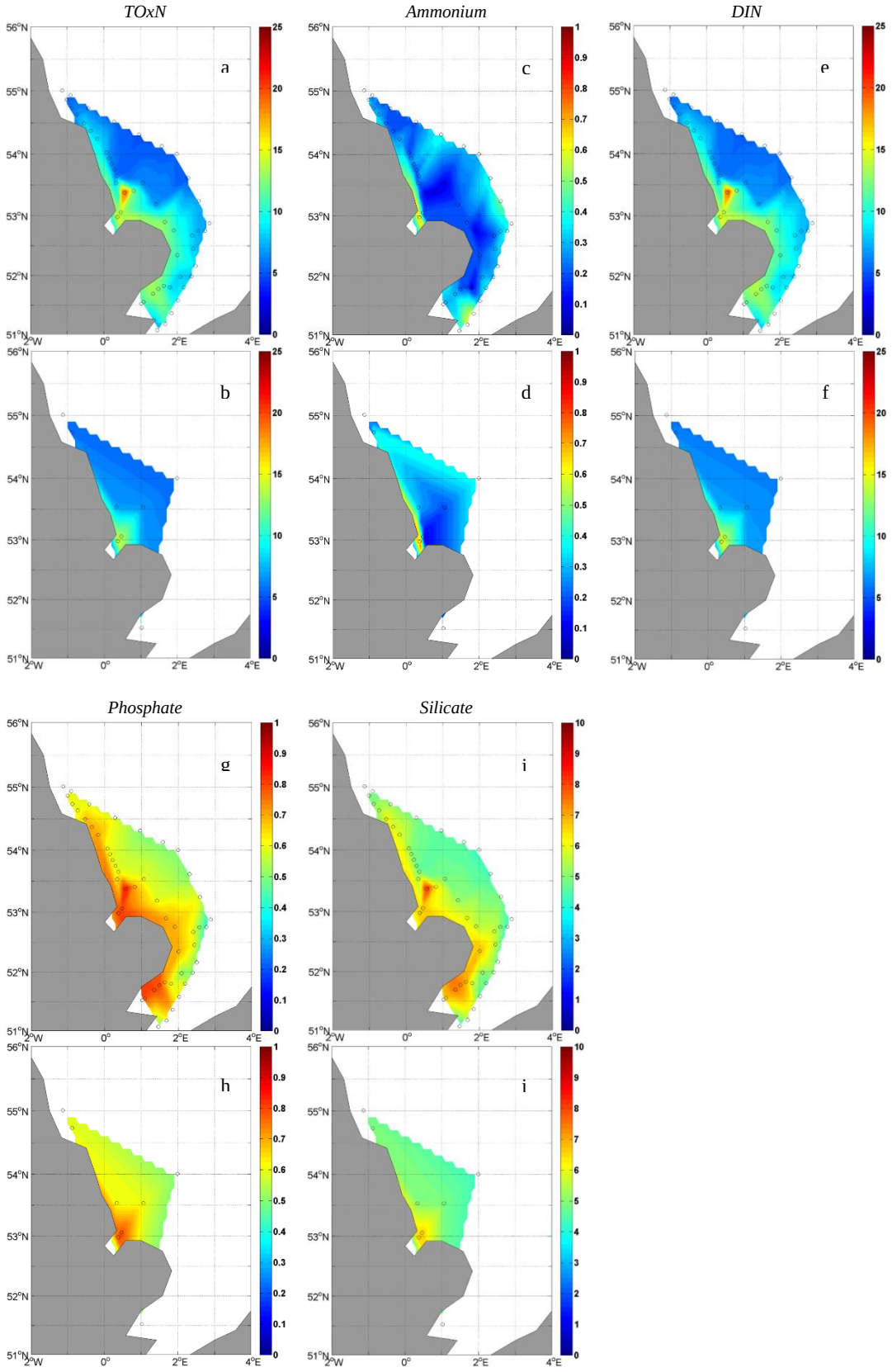


Figure 3.11 Distribution of dissolved inorganic nutrients (µM) in winter 2011 for surface and bottom (a-b) TOxN, (c-d) ammonium, (e-f) DIN, (g-h) phosphate and (i-j) silicate.

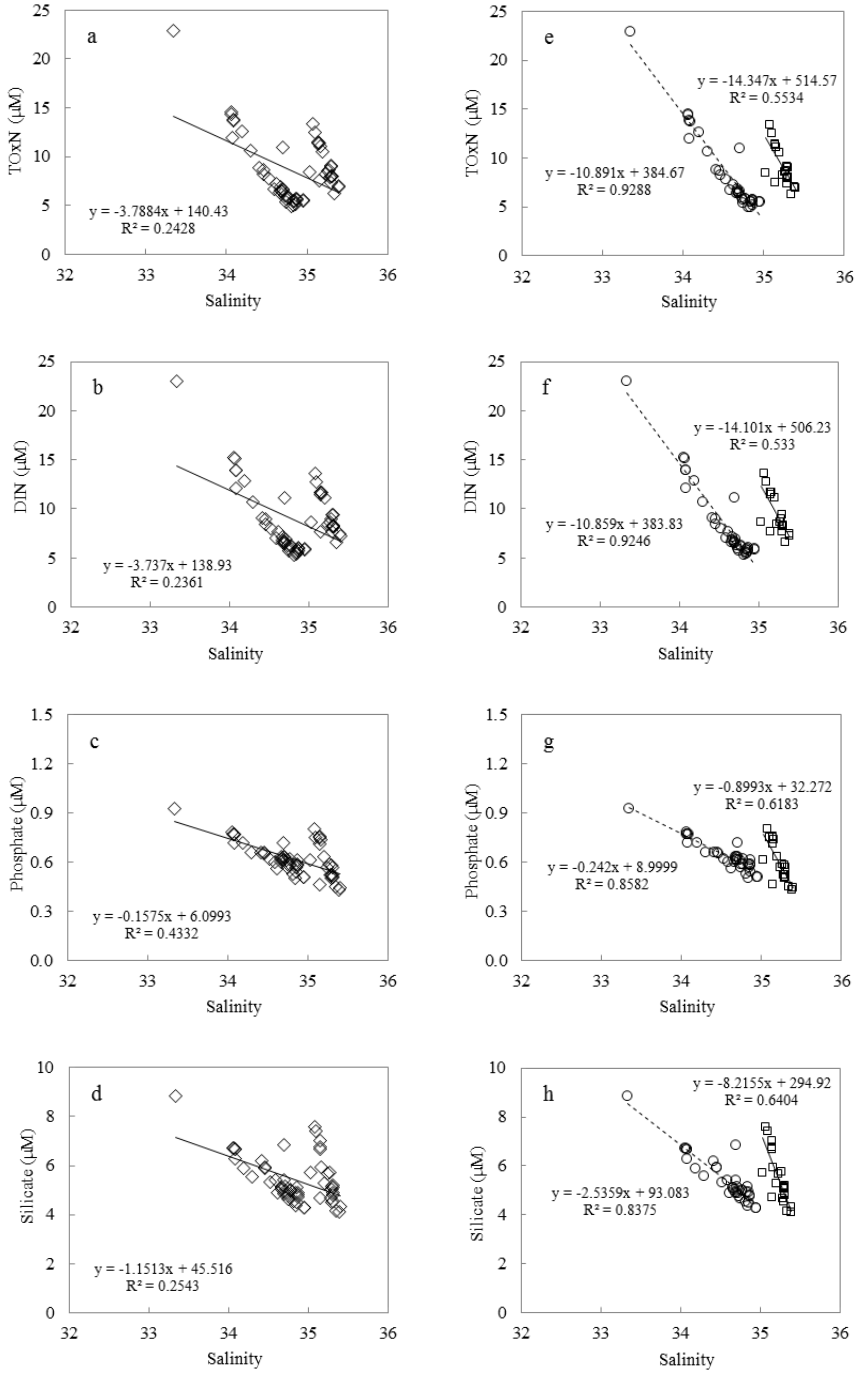


Figure 3.12 TOxN, DIN, phosphate and silicate for winter 2011 survey against salinity. In a-d the data set is treated as one and poor correlations indicated. In e-h the data is split into two groups (the Tyne through the Humber and the Wash (circles) and the Thames plume (rectangles)) with good correlation for each.

3.3.3 DOC and DON

Distributions of surface and bottom DOC, DON and DOC:DON ratios in winter are presented in Figure 3.13. The statistical test (t-test) demonstrated both DOC and DON were not significantly different ($P > 0.05$) in mean concentrations between surface and bottom waters. Similarly, there was not a significant difference ($P > 0.05$) in DOC:DON ratios between surface and bottom water. DOC concentration was 56.2 – 224.8 µM (mean 107.5 ± 29.6 µM). The level of DON ranged between 3.7 – 12.3 µM (mean 6.7 ± 2.0 µM). High level of DOC was recorded in the Wash and the Humber (175.1 – 224.8 µM), while high surface DON was generally observed in the Thames plume (10.3 – 12.3 µM). For DOC:DON ratios, the distribution pattern was similar to the DOC with high ratios near the Wash and the Humber (33.1 – 36.5). DOC:DON ratios present high variability ranging from 5.9 – 36.5 with the mean level of 17.3 ± 6.2.

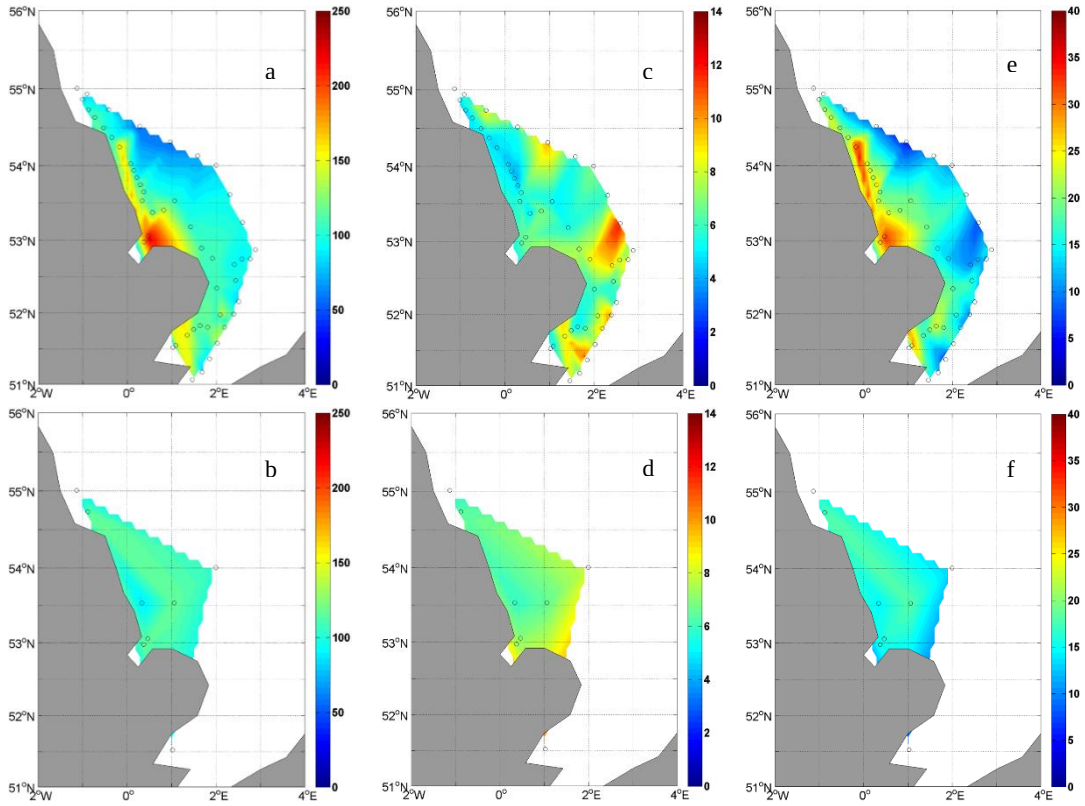


Figure 3.13 Distribution of dissolved organic nutrients (µM) and DOC:DON ratios in winter 2011. (a) Surface and (b) bottom DOC. (c) Surface and (d) bottom DON. (e) Surface and (f) bottom DOC:DON ratios.

In addition, an absence of any significant correlation ($P > 0.05$) between DOC and DON was observed during winter for both surface and bottom data sets. Similarly, the whole water mass (Figure 3.14) does not show any correlation between DOC and DON ($P > 0.05$). The slope C:N ratios and C:N molar ratios are discussed in section 3.5.

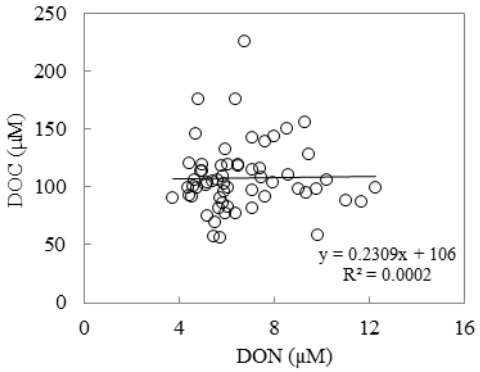


Figure 3.14 Relationship between DOC and DON (DOC = mDON + c, where m = gradient and c = intercept) for the whole water mass in winter 2011.

3.3.4 Discussion of distribution patterns in winter 2011

The absence of a significant difference between surface and bottom water of temperature, salinity, chlorophyll *a*, inorganic nutrient, DOC and DON were observed during winter as the water column was generally well-mixed during this season (Ducrotoy et al. 2000, Sharples et al. 2006). Therefore, the discussion in this section considered each parameter based on the whole water mass (mixed surface and bottom layers). The results indicate inorganic nutrients in winter were transported by freshwater to the coast as TOxN, DIN, phosphate and silicate were significantly inversely correlated with salinity ($P < 0.05$). The *y*-intercept of linear regression equations of inorganic nutrients plotted against salinity (Figure 3.12, e-h) provided estimates of nutrient levels in freshwater including 385 µM of TOxN, 384 µM of DIN, 9 µM of phosphate and 93 µM of silicate for the data sets covering the coastal area approximately from the Tyne through the Humber and the Wash. For the data sets covering the Thames plume, nutrient concentrations predicted at level of zero salinity were 515, 506, 32, 295 µM for TOxN, DIN, phosphate and silicate, respectively. These estimates of freshwater nutrients are in line with their mean

concentrations of the Wear and the rivers and tributaries entering to the Humber and the Wash reported in previous studies, 331 µM of TOxN, 360 µM of DIN, 22 µM of phosphate and 187 µM of silicate (Neal and Robson 2000). These predicted freshwater nutrients also corresponded to typical values of mean nutrient concentrations in the Thames River: 592 µM of TOxN and 595 µM of DIN (Neal and Robson 2000), 6 - 29 µM of phosphate (Neal and Robson 2000, Kinniburgh and Barnett 2010), 314 µM of silicate (Neal and Robson 2000).

In addition, a statistical correlation test was carried out to understand the influence of environmental parameters on DOC and DON distribution in winter (Table 3.3). The results indicate low influence of salinity on DOC distribution. A low negative significant correlation was shown between DOC and salinity (R^2 =0.08, $P < 0.05$, n = 60) (Figure 3.15a), thus providing no clear evidence of a strong riverine source. The contribution of DON to the TDN pool in Figure 3.16 showed the DON pool (43%) was lower than the TOxN (55%) during winter. This would be in response to higher riverine inorganic nutrient input during winter, particularly nitrate with the highest concentration recorded during winter in the Thames plume, southern North Sea (Weston et al. 2004, Weston et al. 2008) and in the central North Sea (Suratman et al. 2008a). Nitrate was the dominant inorganic nitrogen form loading to UK estuaries (Nedwell et al. 2002). In addition to the riverine input, the inputs from offshore (Jickells 1998) as the inflow from North Atlantic (Rendell et al. 1993) and seasonal nutrient regeneration (Rowe et al. 1975, Brockmann et al. 1990, Kirchman 2000) also contributed to high inorganic nutrients over the winter period.

Table 3.3 Correlations of DOC and DON with salinity and chlorophyll *a* for the whole water mass in winter 2011.

Parameters		Correlation coefficient (r)	Confidence level at 95 %
DOC	Salinity	-0.288*	0.026
	Chlorophyll *a*	0.109	0.406
DON	Salinity	0.225	0.085
	Chlorophyll *a*	0.225	0.084

* Correlation is significant at the 0.05 confidence level.
The number of samples is 60 (n = 60) for mixed surface and bottom waters.
Correlation to inorganic nitrogen is in Appendix 3.9.

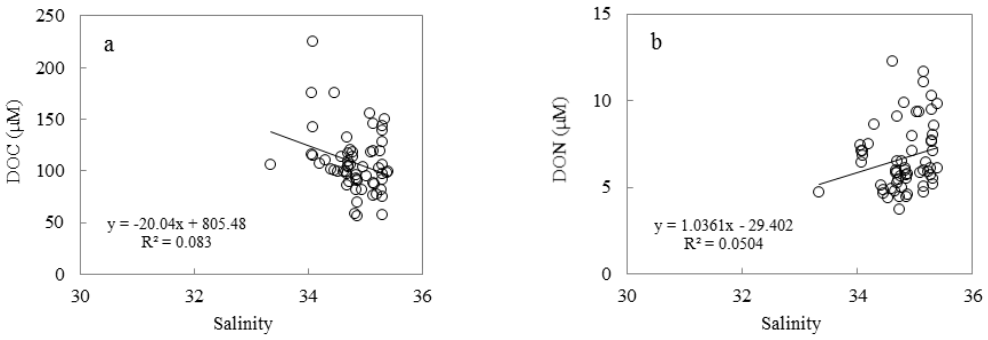


Figure 3.15 Relationship of DOC and DON with salinity in winter 2011 (DOM = – m Salinity + c, where m = gradient and c = intercept).

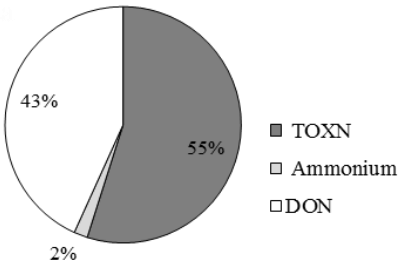


Figure 3.16 TOxN, ammonium and DON as percentage of TDN for the whole water mass in winter 2011.

High concentration of all inorganic nutrients typically revealed in the region of the Humber and the Wash followed by the Thames, probably result from highest water flows and nutrient concentration in rivers in winter (Van Bennekom and Wetsteijn 1990, Sanders et al. 1997a, Sanders et al. 1997b, Sanders et al. 2001, Nedwell et al. 2002, Weston et al. 2004). High concentration of suspended matter in this area were observed during winter in a previous study where the seasonal flux of the total suspended matter was investigated across the East Anglian plume (Dyer and Moffat 1998), together with suspended sediments over the autumn –winter period in the Humber basin which was higher than the level of the Thames basin (Neal et al. 2006). The seasonal cycle of suspended particulate matter in 2001 also showed the maximum concentration during winter in the Thames plume, as well as high phosphate and silicate concentrations, but ammonium was low (0 – 0.8 µM) (Weston et al. 2008). The low level of ammonium (Weston et al. 2008) agreed with this present study. Therefore, this suggested that inorganic nutrients in this study (not

including ammonium) and DOC were transported via freshwater, along with high particulate matter concentration during winter, probably corresponding with the transport through the estuaries to the coast.

For the DON pools, it is unclear what controls its distribution, as DON was only significantly positively correlated with ammonium. However, a low positive but insignificant correlation ($P > 0.05$) was found between DOC and DON with chlorophyll *a* consistent in previous winter studies (Suratman et al. 2008a, Suratman et al. 2009). Low levels of chlorophyll *a* (0.3 – 1.7 µg/L) recorded in this study are in line with other southern North Sea observations in winter (Bale and Morris 1998, Weston et al. 2004, Weston et al. 2008, Suratman et al. 2008a), due to a high concentration of suspended solids associated with low chlorophyll *a* concentrations during winter in the southern North Sea (Bale and Morris 1998), meaning phytoplankton productivity is probably light limited due to low light and high suspended particulate matter. Additionally, the chlorophyll *a* provided a significant positive correlation with salinity ($R^2 = 0.23$, $P < 0.05$, $n = 60$). This implied that chlorophyll *a* and phytoplankton are probably more abundant away from the coast as high particulate matter discharged from the river during the winter period leads to low light levels. Nevertheless, no significant correlation ($P > 0.05$) between DOC and DON was found during winter.

In summary, comparison with other winter studies, the inorganic nutrient concentration in this present study was in line with values in the North Sea (Riegman et al. 1990, Radach and Pätsch 1997, Dippner 1998, Hydes et al. 1999, Weston et al. 2004, Weston et al. 2008, Suratman et al. 2008a). DOC and DON levels were also in similar range to other reports in the North Sea (De Galan et al. 2004, Van Der Zee and Chou 2005, Suratman et al. 2008a, Suratman et al. 2009, Suratman et al. 2010, Van Engeland et al. 2010, Johnson et al. 2013, Moneta et al. 2014) and other continental shelf waters (Bates and Hansell 1999, Hopkinson et al. 2002, Bronk and Ward 2005, Wetz et al. 2008, Bradley et al. 2010, Ribas-Ribas et al. 2011, Knapp et al. 2012), but lower than in North Sea estuaries (Álvarez-Salgado and Miller 1998a, Spencer et al. 2007, Agedah et al. 2009) and other surrounding estuaries (Badr et al. 2008). DOC and DON were not strongly inversely related to salinity, unlike the inorganic nutrients.

3.4 Summer 2012 survey

3.4.1 General hydrography

The summer cruise in 2012 (CEND 13/12) was carried out 9 – 23 August 2012 and Figure 3.17 shows the general hydrographic pattern of the area investigated during the sampling period. Surface temperatures ranged between 13.2 and 18.5 °C with mean temperature 16.6 ± 0.9 °C. The lower mean temperature in bottom water was 11.7 ± 3.6 °C, and ranged from 7.5 °C to 18.5 °C. Both surface and bottom waters recorded the highest temperature near the Scheldt mouth (PSt. 3) where the warmest water was also found in summer 2011, while, the lowest temperature in both surface and bottom layers was recorded at the same station near the coast of Aberdeen (PSt. 40). The surface temperature had a significant higher mean level than the bottom layers ($P < 0.05$). A vertical gradient of temperature was present throughout the northern region, showing the stratification pattern of temperature (Figure 3.17, a – b) and Figure 3.17e clearly demonstrating the thermal stratification in the north with higher surface to bottom temperature ratio. By contrast, the well mixed water column in the southern North Sea had a ratio of approximately 1.0. The water column depth was 24 – 160 meter with the mean depth of 67 ± 34 meter (Figure 3.17f). For salinity, the surface layer ranged from 30.9 – 35.2 (34.4 ± 0.8) and the bottom from 33.5 – 35.4 (34.8 ± 0.4). The surface water had a significantly ($P < 0.05$) lower mean salinity than the bottom water. The surface water near the coast of Norway and the Skagerrak had the lowest surface salinity. Similarly, the other coastal areas showed low salinity in both surface and bottom waters (Figure 3.17, c – d).

Figure 3.18 shows three water masses, the stratified northern water (the surface (NS) and the bottom (NB)) and the well-mixed southern regions (SM). These were separated according to the temperature gradients between the surface and bottom layers as shown in Figure 3.17a, Figure 3.17b and Figure 3.17e. In general, the three water masses showed the characteristic features similar to the previous year in summer 2011 (Figure 3.3) described in section 3.2.1. The area A (PSt. 49, 50, 57 and 58) in the northern surface water (Figure 3.18) showed lowest salinity (30.6 – 32.6) with high temperature (16.1 – 16.7 °C) compared to other regions in the

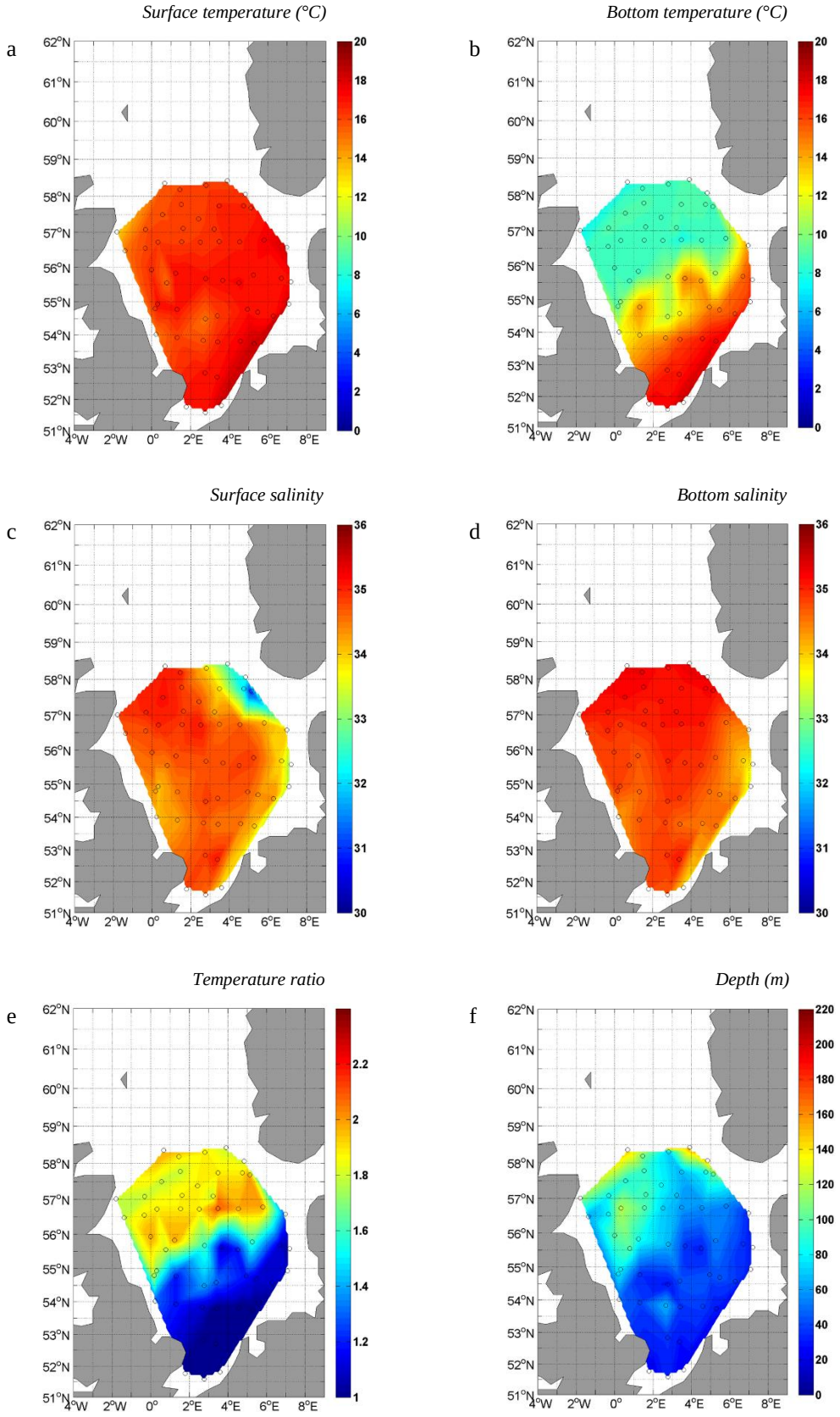


Figure 3.17 General hydrography in summer 2012. Distribution of temperature (°C) and salinity for surface and bottom (a-b) temperature and (c-d) salinity; (e) surface and bottom temperature ratio and (f) water column depth (meter).

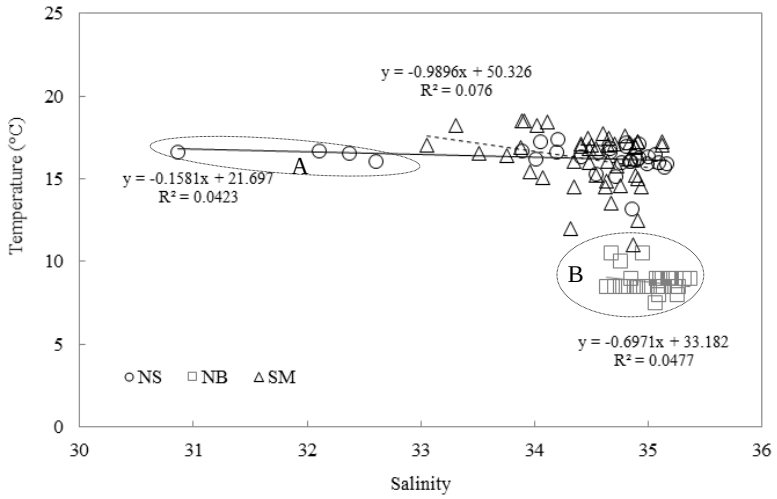


Figure 3.18 Characteristics of three water masses in the North Sea during summer 2012: northern surface water (NS), northern bottom water (NB) and southern well-mixed water (SM). The line for each water mass was fitted by linear regression analysis. The area A represents a low salinity with high temperature water mass, whereas the area B is high salinity with low temperature water mass (discussed in the text).

northern surface water where salinity and temperature were 33.9 – 35.2 and 13.2 – 17.4 °C respectively. The area A (Figure 3.18) had lowest salinity located near the Skagerrak, and the southwest coast of Norway. On the contrary, the bottom water in the north was generally high salinity (34.6 – 35.4) with the lowest temperature (7.5 – 10.5 °C) (area B in Figure 3.18). For the southern well-mixed water, the salinity ranged from 33.1 to 35.1 and temperature was 11.0 – 18.5 °C.

For the chlorophyll *a*, the distribution is presented in Figure 3.19 with generally lower mean concentration in the surface water (0.8 ± 1.2 µg/L) and range 0.2 – 7.0 µg/L, and higher mean level in the bottom water 1.4 ± 1.8 µg/L (< LOD – 7.8 µg/L). Although a higher mean value was observed in the bottom water, there was no significant difference ($P > 0.05$) between mean chlorophyll *a* concentration in the whole surface and whole bottom layer. Additionally, high bottom chlorophyll *a* concentrations generally observed in the single sampling site across the southern North Sea including the highest concentration (7.8 µg/L) observed in the bottom layer near the Skagerrak strait (PSt. 39) followed by the Scheldt (PSt.3) with 7.2 µg/L and 6.5 µg/L near the Humber (PSt.8). These high concentrations in bottom waters probably settled from the surface water and can later be stirred up to the surface in this southern well-mixed water. The highest chlorophyll *a* in the surface

layer (7.0 µg/L) was recorded near the Scheldt, the level at other sites was 3.6 µg/L or lower.

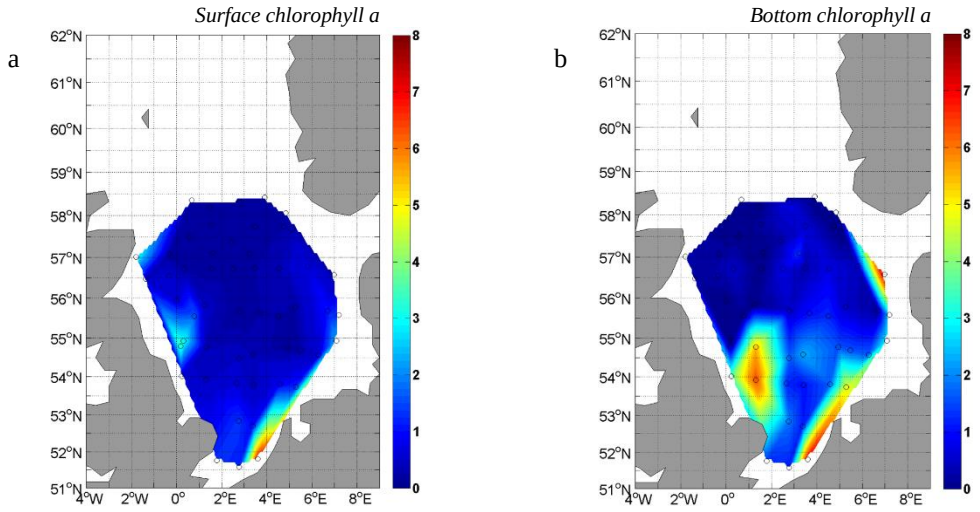


Figure 3.19 Distribution of (a) surface and (b) bottom chlorophyll *a* (µg/L) in summer 2012.

3.4.2 Dissolved inorganic nutrients

The distribution maps of inorganic nutrients are presented in Figure 3.20. In the surface water (number of sample (n) = 53), nutrient concentrations were investigated for TOxN (0.2 to 1.1 µM, 0.2 ± 0.2 µM), ammonium (< LOD to 8.1 µM, 0.5 ± 1.1 µM), DIN (0.4 to 8.3 µM, 0.7 ± 1.1 µM), phosphate (< LOD to 0.4 µM, 0.1 ± 0.1 µM) and silicate (0.1 to 2.7 µM, 1.0 ± 0.6 µM). Higher concentrations were generally found in the bottom water (n = 53) with the value of 0.2 to 10.7 µM (2.4 ± 2.9 µM) for TOxN, <LOD to 4.0 µM (1.1 ± 1.2 µM) for ammonium, 0.4 to 11.2 µM (3.4 ± 3.3 µM) for DIN, 0.1 to 0.9 µM (0.4 ± 0.3 µM) for phosphate and 0.3 to 5.2 µM (2.6 ± 1.2 µM) for silicate. The statistical analysis revealed that the mean concentration of inorganic nutrients in the bottom water was significantly higher than those in the surface water (t-test, $P < 0.05$). There was a strong separation between surface and bottom layers for all nutrients according to the seasonal stratification in the northern water mass. This same pattern was also found in the survey of summer 2011 (section 3.2.2). The distribution feature of bottom TOxN was similar to the DIN as relatively low levels of ammonium were found. However, the presence of highest ammonium concentration in the area I (Figure 3.20d) of bottom water surrounding the north Dogger Bank was the same area

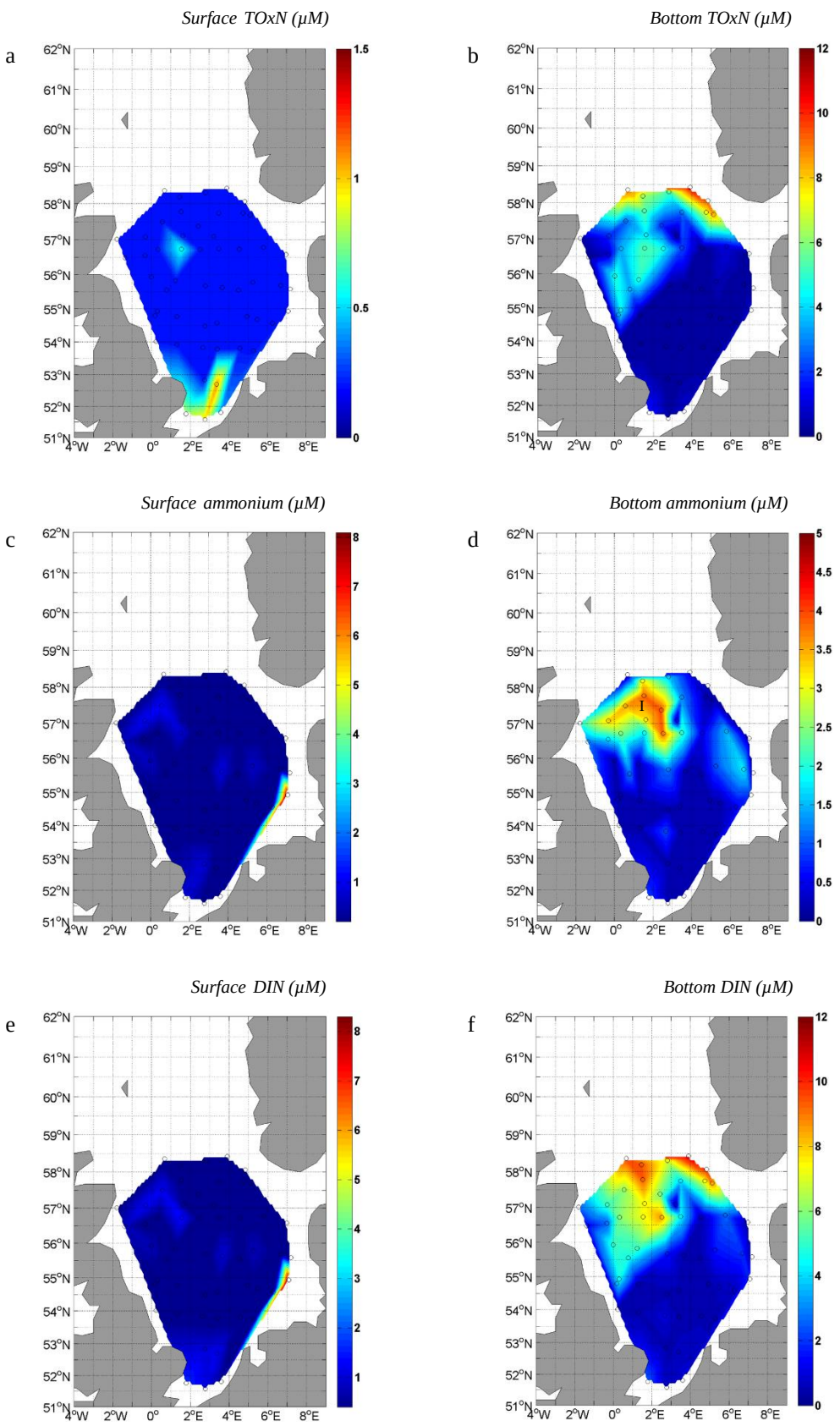


Figure 3.20 Distribution of dissolved inorganic nutrients in summer 2012 for surface and bottom (a-b) TOxN, (c-d) ammonium, (e-f) DIN, (g-h) phosphate and (i-j) silicate. Note different scales in surface and bottom concentrations.

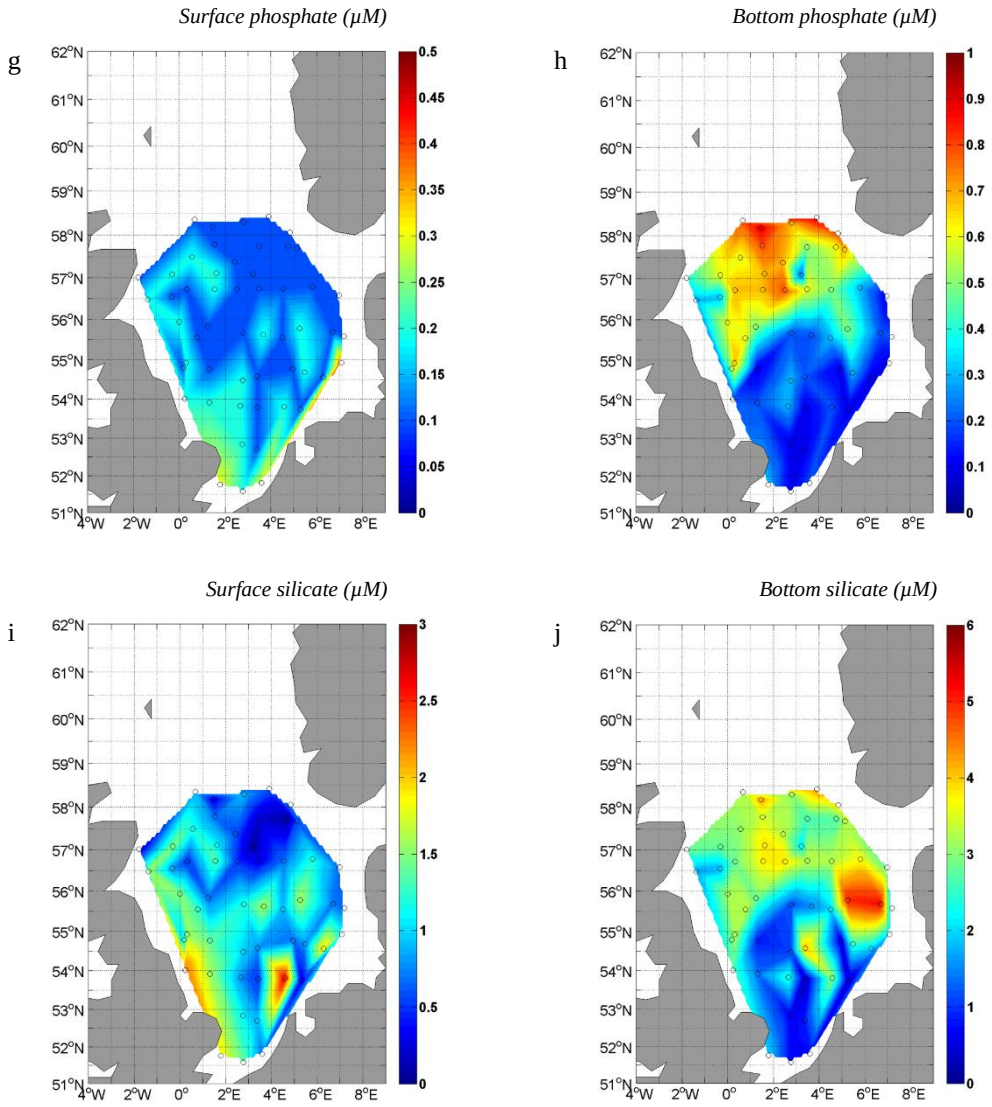


Figure 3.20 (Continued).

investigated in the summer 2011 survey of this study. This area had the lowest dissolved oxygen concentration in the North Sea in summer 2010 recorded in the previous study which suggested low advection, high water stratification and high production of organic matter from the spring bloom in this area (Queste et al. 2013).

For the consideration based on three water masses (stratified northern surface water, stratified northern bottom water and southern well-mixed water), inorganic nutrients were generally not shown to have a correlation with salinity. However in the northern bottom water, the positive significant correlation was observed between salinity and TOxN ($R^2 = 0.30$, $P < 0.05$, $n = 30$), DIN ($R^2 = 0.41$, $P < 0.05$, $n = 30$) and phosphate ($R^2 = 0.36$, $P < 0.05$, $n = 30$) as in summer 2011. In addition, a

correlation was found in the southern well-mixed water, but here there was a significant negative correlation between salinity and ammonium ($R^2 = 0.14$, $P < 0.05$, $n = 46$) and DIN ($R^2 = 0.12$, $P < 0.05$, $n = 46$). No statistically significant correlation between salinity and water column depth with inorganic nutrients were found at the 95% significance level in the northern surface water ($P > 0.05$). The correlation between water column depth and inorganic nutrients was shown in the bottom water of the northern region with significant positive correlation ($P < 0.05$, $n = 30$) of TOxN ($R^2 = 0.58$), DIN ($R^2 = 0.51$) and phosphate ($R^2 = 0.43$). In contrast, the significant negative correlation between TOxN and the depth was observed in the southern well – mixed water ($R^2 = 0.17$, $P < 0.05$, $n = 46$).

3.4.3 DOC and DON

DOC and DON measured for surface and bottom waters are shown in Figure 3.21. The concentration of DOC in the surface and bottom layers varied from 32.7 to 124.4 µM and 36.3 to 98.4 µM respectively. High surface DOC level was generally recorded in the coastal areas, particularly the highest level of surface DOC (124.4 µM) at the German Bight (PSt. 21). In addition, the high DOC levels (higher than approximately 90 µM) were found near the Skagerrak (PSt. 50, 99.5 µM), the coast of Denmark (PSt. 30, 95.2 µM) and the coast of the Netherlands in the Oyster Ground area (PSt. 11, 90.6 µM). For the bottom DOC, the highest level was recorded in the Scheldt plume (PSt. 3, 98.4 µM), followed by the coast of Denmark (PSt. 30, 93.1 µM). Concentrations of 3.0 to 9.8 µM and 2.8 to 8.2 µM were recorded for surface and bottom DON with the high DON level near the coast of Denmark (PSt. 30, 9.8 µM for surface and 8.1 µM for bottom DON) and the Scheldt plume (PSt. 3, 7.8 µM for surface and 8.2 µM for bottom DON).

The mean concentration of whole surface and whole bottom DOC were 63.7 ± 15.7 µM ($n = 53$) and 54.1 ± 13.5 µM ($n = 53$) respectively. For DON, the mean concentrations were 5.3 ± 1.2 µM ($n = 53$) for the whole surface and 5.2 ± 1.1 µM ($n = 53$) for the whole bottom layers. The mean concentration of surface DOC was significantly higher than the bottom ($P < 0.05$). Whereas, the mean of DON does not show a significant difference ($P > 0.05$) between surface and bottom waters. The one way ANOVA test at 95% significance level based on three water masses indicated

the significant difference ($P < 0.05$) in mean DOC concentration in different water mass. The southern well-mixed water provided highest mean DOC concentrations with 65.5 ± 16.4 µM (n = 46), followed by the northern surface water (60.7 ± 13.0 µM, n = 30). The northern bottom water showed the lowest mean DOC concentration with 46.9 ± 6.8 µM (n = 30). In contrast, there was no significant difference in mean DON concentration between three water masses (ANOVA, $P > 0.05$). The mean concentrations were 5.3 ± 1.1 µM (n = 30), 5.2 ± 1.0 µM (n = 30) and 5.3 ± 1.3 µM (n = 46) for the northern surface and bottom waters, and the southern well-mixed water, respectively.

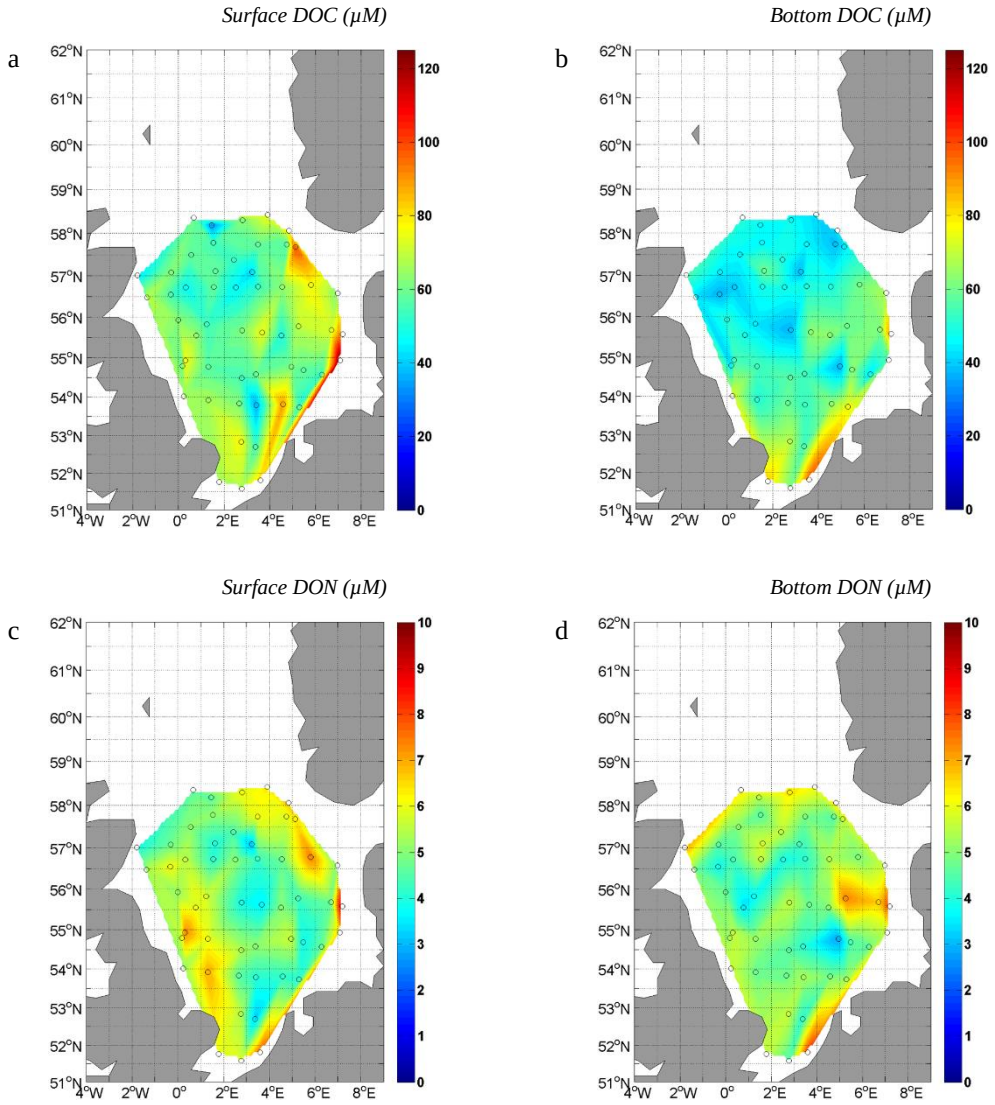


Figure 3.21 Distribution of dissolved organic nutrients (µM) in summer 2012. (a) Surface and (b) bottom DOC. (c) Surface and (d) bottom DON.

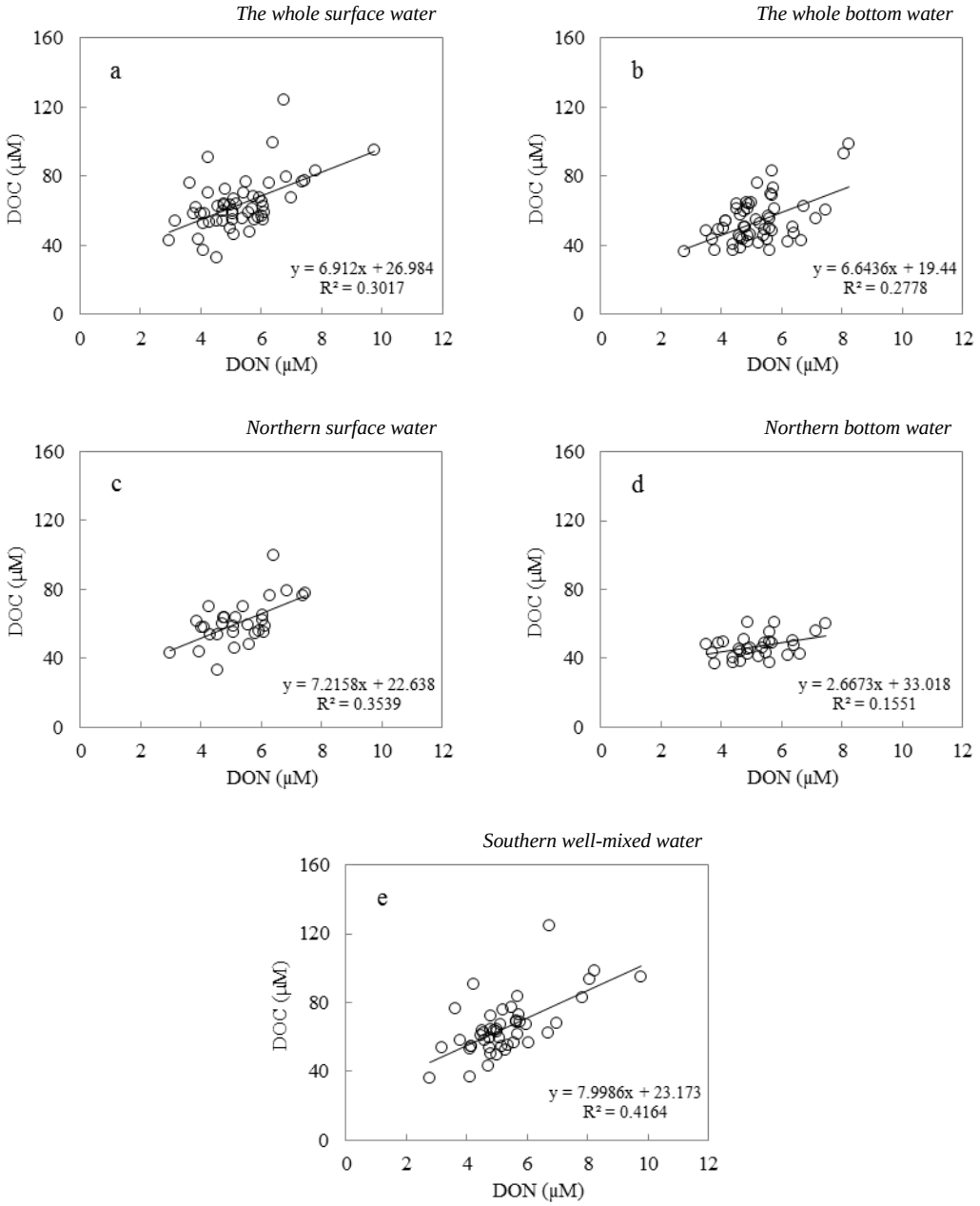


Figure 3.22 Relationship between DOC and DON (DOC = mDON + c, where m = gradient and c = intercept) for data sets of (a) the whole surface water, (b) the whole bottom water, (c) stratified northern surface water, (d) stratified northern bottom water, and (e) southern well-mixed water in summer 2012.

Figure 3.22 shows the relationship between DOC and DON in various water masses. For the regression of DOC versus DON in the surface and bottom water, the statistically significant positive correlation was found at the 95% significance level in both the surface ($R^2 = 0.30$, $P < 0.05$, $n = 53$) and bottom ($R^2 = 0.28$, $P < 0.05$, $n = 53$) waters with a slope C:N ratio of 6.9 for the surface and 6.6 for the bottom.

In addition, there were positive correlations between DOC and DON in three different water masses (Figure 3.22, c – e). The southern well-mixed water (R^2 = 0.42, $P < 0.05$, n = 46), the northern surface water (R^2 = 0.36, $P < 0.05$, n = 30) and the northern bottom water (R^2 = 0.16, $P < 0.05$, n = 30) provided the significant correlation. The slope C:N ratios were 8.0, 7.2 and 2.7 for well-mixed water in the south, the surface water and the bottom water in the stratified north, respectively. The slope C:N ratios and C:N molar ratios are discussed in section 3.5.

3.4.4 POC and PON

The whole surface and whole bottom distribution of POC and PON are shown in Figure 3.23. The POC presented high variability ranging from 2.7 to 43.8 µM (11.8 ± 6.8 µM, n = 53) for the surface water and the bottom value was 1.1 to 39.3 µM (12.2 ± 8.7 µM, n = 53). Low variation was observed in PON, the concentrations were 0.6 to 5.9 µM (1.9 ± 1.0 µM, n = 53) for surface water and 0.3 to 5.6 µM (1.9 ± 1.0 µM, n = 53) for the bottom. In general, high concentrations of POC and PON were found in the same areas as each other, near the coasts. For the surface water, high levels of POC were recorded in the German Bight (PSt. 21) and the Scheldt plume (PSt. 3) with the concentrations of 43.8 and 31.2 µM respectively, while 5.9 and 4.8 µM were observed for PON concentration at both stations, respectively. The highest concentration of bottom POC and PON was recorded in the Scheldt plume (PSt. 3). Lower bottom POC concentration was found in the Humber plume (PSt.8, 36.2 µM), the coast of Denmark near the Skagerrak (PSt. 39, 33.9 µM) and the Thames plume (PSt. 39, 30.1 µM). Lower bottom PON was recorded in the Thames plume (PSt. 1, 4.9 µM) with similar levels (3.8 µM) found in the Humber plume (PSt.8) and near the coast of Denmark and near the Skagerrak (PSt. 39). However, the absence of any significant difference of mean concentration between bottom and surface waters was shown in both POC and PON ($P > 0.05$).

To investigate differences of POC and PON concentrations in three water masses, statistical test (one way ANOVA) was carried out. The result demonstrated significant difference (ANOVA, $P < 0.05$) in POC concentration in different water masses, the PON also showed the same result. In addition, the same features were provided in both POC and PON following the sequence: the highest mean

concentration in the well-mixed southern water (16.0 ± 9.3 µM for POC and 2.2 ± 1.3 µM for PON, n = 46), lower in the stratified northern surface water (10.5 ± 4.2 µM for POC and 2.0 ± 0.7 µM for PON, n = 30) and the lowest in the stratified northern bottom water (7.3 ± 3.5 µM for POC and 1.5 ± 0.7 µM for PON, n = 30).

Figure 3.24 shows the relationship between POC and PON in various water masses. Concentrations are rather similar across much of the North Sea apart from nearer the coast. For the surface and bottom water (Figure 3.24, a – b), significant positive correlations were found for POC and PON in the surface ($R^2 = 0.56$, $P < 0.05$, n = 53) and bottom water ($R^2 = 0.71$, $P < 0.05$, n = 53) with a slope C:N ratio of 5.1 at the surface and 7.1 at the bottom and a near zero intercept.

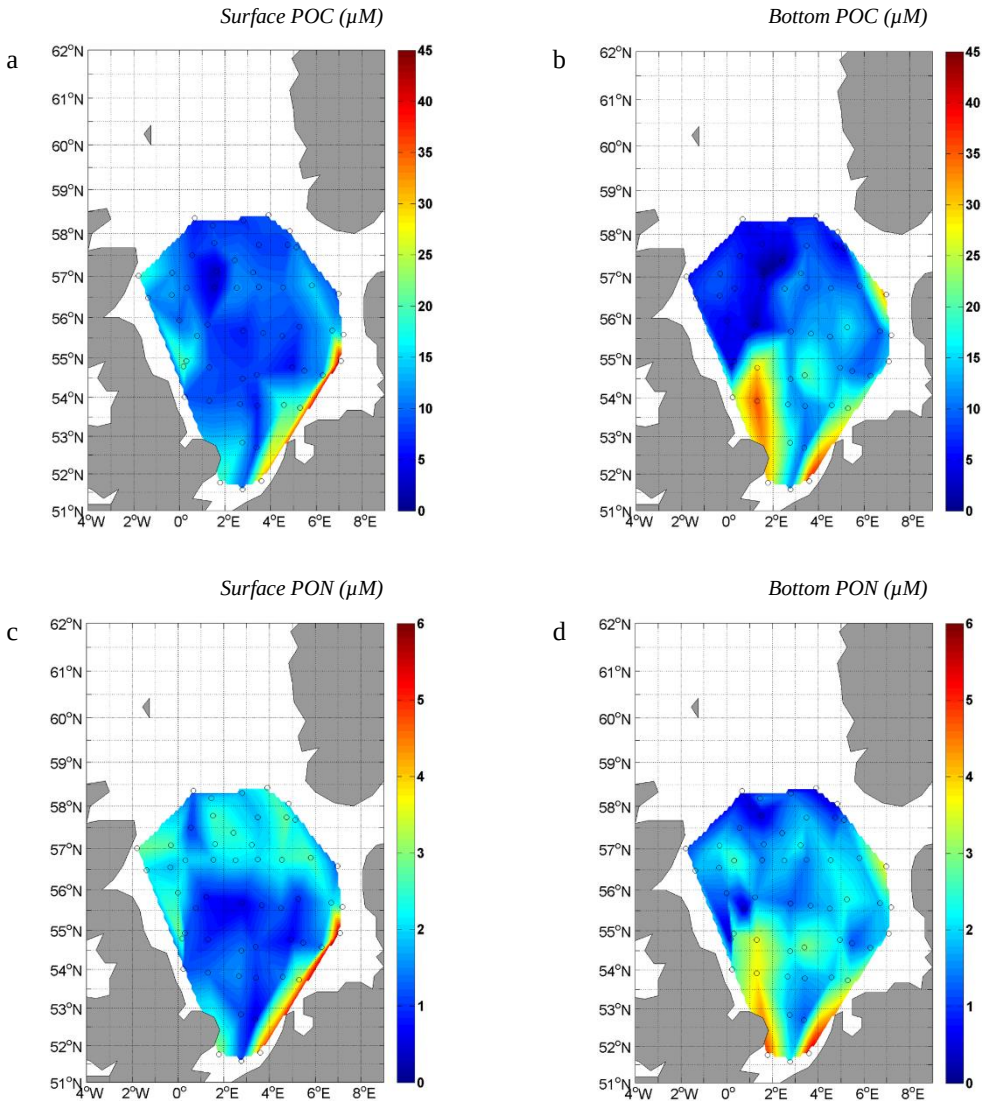


Figure 3.23 Distribution of particulate organic nutrients (µM) in summer 2012. (a) Surface and (b) bottom POC. (c) Surface and (d) bottom PON.

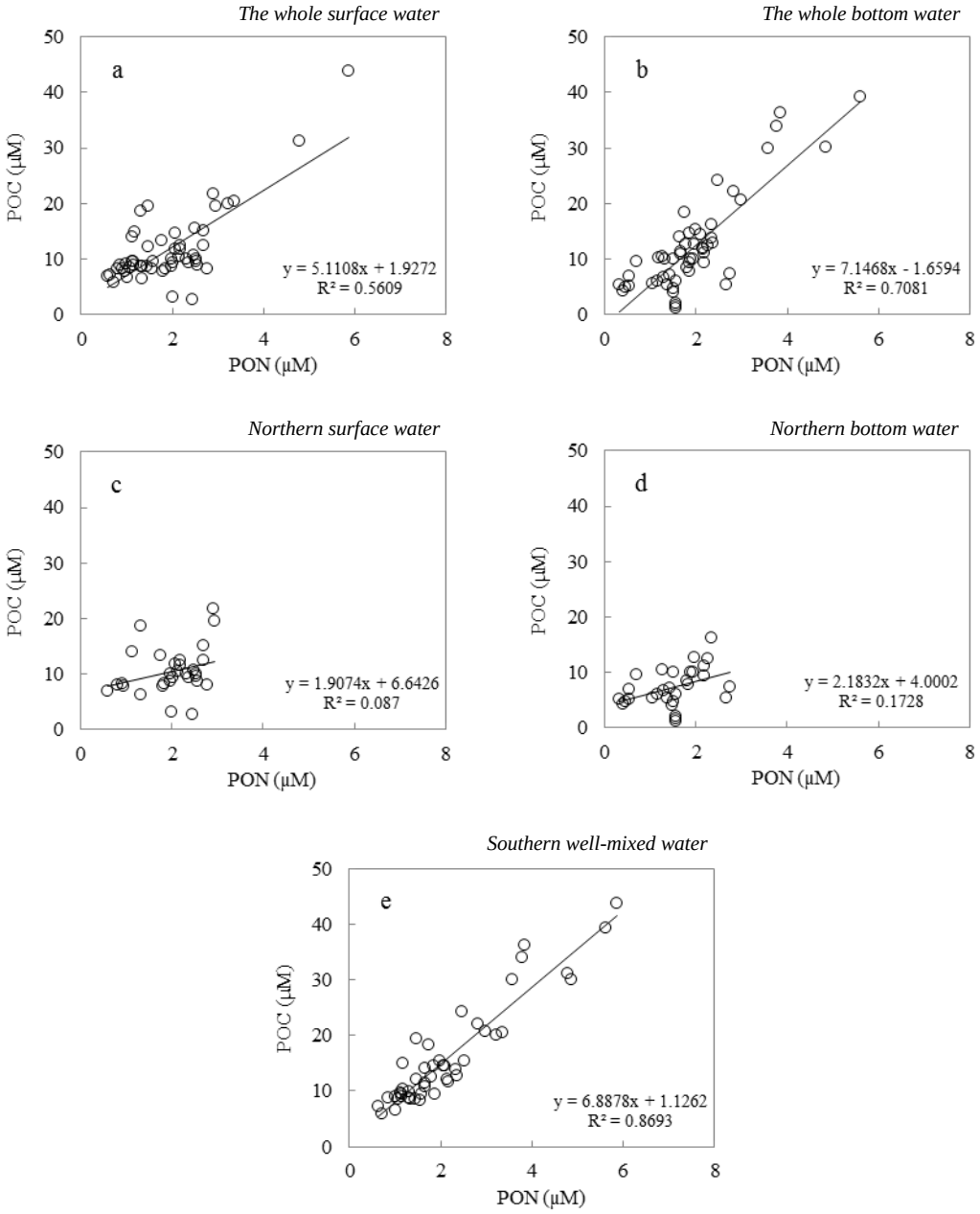


Figure 3.24 Relationship between POC and PON (POC = mPON + c, where m = gradient and c = intercept) for data sets of (a) the whole surface water, (b) the whole bottom water, (c) stratified northern surface water, (d) stratified northern bottom water, and (e) southern well-mixed water in summer 2012.

When considering the three different water masses, no significant correlation was found in the northern surface water ($P > 0.05$). Conversely, a strong significant positive relationship was seen in the well-mixed southern water ($R^2 = 0.87$, $P < 0.05$, $n = 46$). The northern bottom water also showed the same pattern with a significant correlation between POC and PON ($R^2 = 0.18$, $P < 0.05$, $n = 30$). There was a slope

C:N ratio of 6.9 in the well-mixed southern water and the ratio of 2.2 in northern bottom water. The slope C:N ratio is further discussed in section 3.5.

3.4.5 Discussion of distribution patterns in summer 2012

This section discusses results in summer 2012. Results of summer 2012 and previous investigation in summer and winter 2011 are linked together and further discussed in section 3.5. In summer 2012, general hydrography data demonstrated low temperature and salinity in the northern North Sea, showing lower temperature with higher salinity in the bottom water than the surface. The surface salinity was obviously lowest near the coast of Norway. Conversely, the southern water showed a well-mixed pattern between surface and bottom water with high temperature and salinity. However, low salinity was also recorded along the southern river plume but the low salinity water sampled here was relatively higher in salinity than the water sampled off the Norwegian coast. The low salinity in the northern North Sea was generally received from the Baltic Sea through the Skagerrak (Thomas et al. 2005, Korth et al. 2012). This pattern of features of water masses in summer allows them to be divided into three classes: the northern surface water, the northern bottom water and the well-mixed southern water. There were the same features observed in summer 2011. The chlorophyll *a* was also investigated, showing high concentrations in three coastal areas including the site near the Skagerrak/ coast of Denmark, the Scheldt and the Humber. All three sites are located in the coast of southern well-mixed water mass. Therefore, the high chlorophyll *a* was associated with river input in the southern North Sea, although negative correlation between the chlorophyll and salinity observed was insignificant. Hence the pattern could reflect chlorophyll *a* increases offshore of estuaries fed by riverine nutrients. The highest surface chlorophyll *a* (~ 7 µg/L) was found near the Scheldt where the high chlorophyll *a* was also recorded in a previous study during summer (Bale and Morris 1998). The low level of mean chlorophyll *a* (~ 1 µg/L) was at the same level as other studies during summer in the North Sea (Weston et al. 2004, Van Der Zee and Chou 2005, Suratman et al. 2008a, Moneta et al. 2014) and nearby regions (Torres-Valdés and Purdie 2006).

Inorganic nutrient concentrations generally increased with depth, particularly in the northern bottom water where the strong positive correlation between TOxN, DIN and phosphate with water column depth was observed. Low, but significant negative correlation between DIN and ammonium with salinity in the southern well-mixed water suggest this nutrient partially enters via freshwater runoff. However, all surface inorganic nutrients had relatively low concentration, consistent with other investigation during summer in the North Sea (Hydes et al. 1999, Weston et al. 2004, Weston et al. 2008, Suratman et al. 2008a, Van Engeland et al. 2010).

DOC and DON concentration showed a different pattern to inorganic nutrients as high concentration was found in the surface water. The southern well-mixed water contained highest DOC level followed by the northern surface water. The northern bottom water had the lowest DOC level. The distribution of DON was similar. High DOC and DON was generally found in the coastal area of the southern North Sea. The southern water and northern surface water showed stronger correlations between DOC and DON than the northern bottom waters. In both water masses plots of DOC and DON yield a slope C:N ratio of 7.8 and 7.2 respectively close to the Redfield of 6.6 (Geider and La Roche 2002), but also with a significant non-zero DOC intercept.

Similarly, the investigation of POC and PON provided a slope C:N ratio of 6.9 in the southern well-mixed water with strong correlation and little non-zero intercept. Both POC and PON generally showed the same distribution patterns as DOC and DON, the high concentrations were observed in coastal areas surrounding the southern North Sea. The level of DOC and DON in this study were in line with other investigations in the North Sea in summer (Van Der Zee and Chou 2005, Suratman et al. 2008a, Suratman et al. 2009, Johnson et al. 2013), and other annual mean levels in the North Sea (Van Engeland et al. 2010). DON concentrations were generally lower than the Marsdiep (inlet of the Wadden Sea in the southern North Sea) in summer (Moneta et al. 2014). However, the previous studies generally investigated the surface water of southern North Sea rather than the bottom water and have not considered the overall distribution throughout the North Sea. Concentrations of DOC and DON in this study were similar to previous investigations in other continental shelf waters (Hopkinson et al. 1997, Hopkinson et al. 2002, Ribas-Ribas et al. 2011). For the particulate form, concentrations of surface

POC and PON in this study were generally consistent with other studies during the summer period in the North Sea (Postma and Rommets 1984, Weston et al. 2004, Suratman et al. 2008a, Suratman et al. 2009).

The statistical correlation assessment in Table 3.4 provided information to understand the potential influence of freshwater, phytoplankton biomass and POM on DOC and DON distributions in this survey. The results indicated freshwater inputs were associated with DOC and DON distributions in the northern surface and southern well-mixed waters as strong inverse correlations between DOC and DON with salinity were observed in both water masses (Figure 3.25). Low correlation ($P > 0.05$) between DOC and DON with chlorophyll *a* during summer was a similar feature found in other reports in the North Sea (Suratman et al. 2008a, Suratman et al. 2009). DOC also has a strong positive correlation with POC, as well as DON correlated with PON in the southern well-mixed water suggesting a relationship between POM and DOM as an important process in the southern well-mixed water. Higher POM may indicate higher recent productivity which can then be a source of DOM.

Table 3.4 Correlations of DOC and DON with salinity, chlorophyll *a* and POM for three water masses in summer 2012.

Parameters			Correlation coefficient (r)	Confidence level at 95 %
DOC	Stratified northern surface water	Salinity	-0.637*	0.000
		Chlorophyll *a*	0.042	0.825
		POC	0.096	0.613
	Stratified northern bottom water	Salinity	-0.342	0.064
		Chlorophyll *a*	-0.050	0.794
		POC	-0.023	0.902
	Southern well-mixed water	Salinity	-0.536*	0.000
		Chlorophyll *a*	0.259	0.082
		POC	0.541*	0.000
DON	Stratified northern surface water	Salinity	-0.503*	0.005
		Chlorophyll *a*	0.212	0.261
		PON	-0.015	0.939
	Stratified northern bottom water	Salinity	0.220	0.243
		Chlorophyll *a*	-0.070	0.715
		PON	-0.105	0.581
	Southern well-mixed water	Salinity	-0.636*	0.000
		Chlorophyll *a*	0.330	0.025
		PON	0.428*	0.003

* Correlation is significant at the 0.05 confidence level. The number of samples (n) is 30, 30 and 46 for northern bottom waters, northern surface water and southern mixed water, respectively.
Correlation to inorganic nitrogen is in Appendix 3.10.

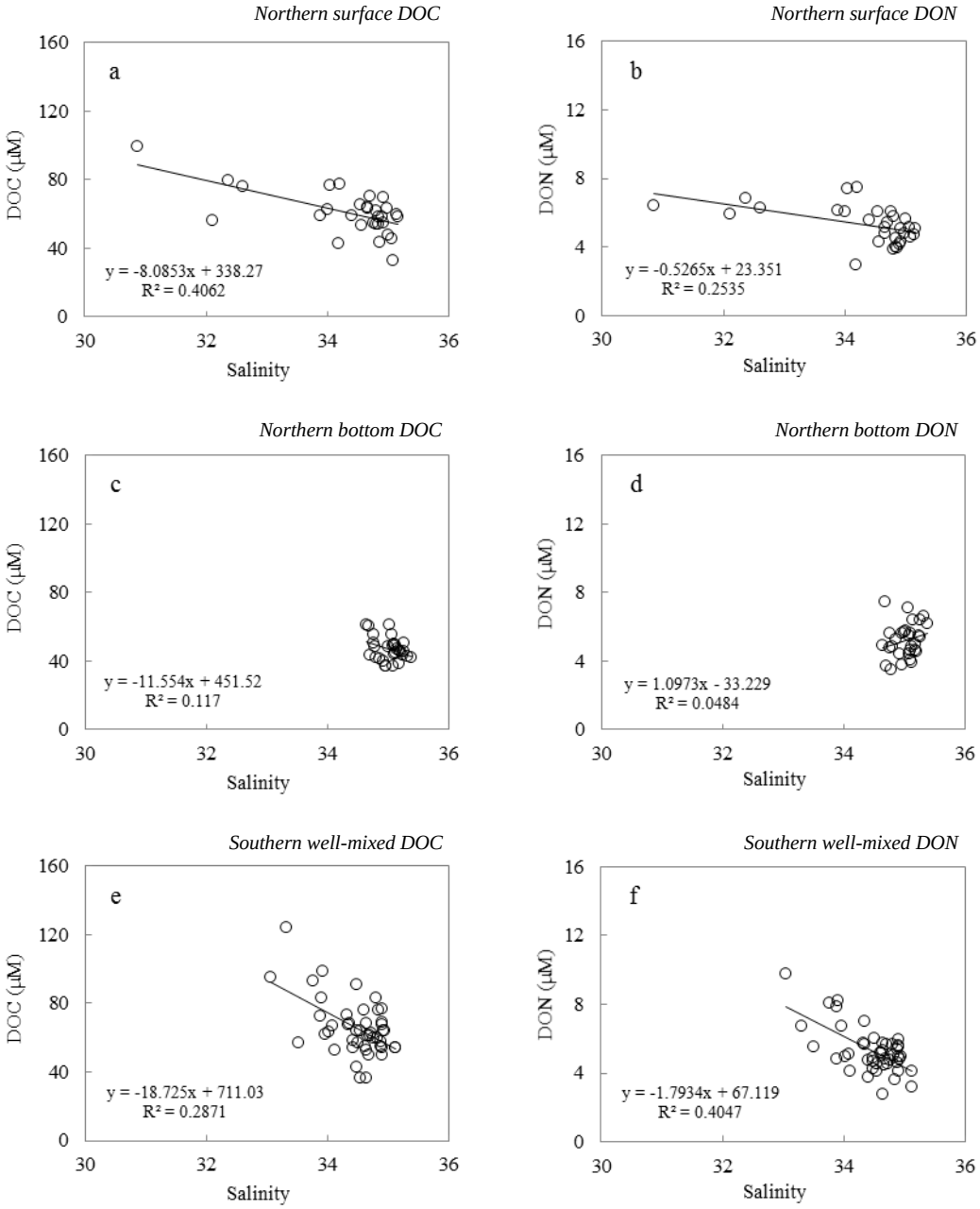


Figure 3.25 Relationship of DOC and DON with salinity (DOM = – m Salinity + c, where m = gradient and c = intercept) for data sets of (a – b) stratified northern surface water, (c – d) stratified northern bottom water, and (e – f) southern well-mixed water in summer 2012.

The statistical correlation was also carried out for POC and PON to understand the influence of freshwater and chlorophyll *a* on POC and PON distributions (Table 3.5). The results clearly showed river runoff was only associated with POC and PON in the southern well-mixed water as no significant negative correlation with salinity was observed in other water masses. The results also

indicated that both POC and PON were highly positively correlated with chlorophyll *a* in all water masses with similar slopes for POC in northern surface and southern well-mixed waters (Figure 3.26). This correlation suggested phytoplankton biomass is linked to the distribution features of POM in these water masses. Chlorophyll associated with an increase in POM concentrations is in accordance with other previous studies (Cadée 1982, Van Der Zee and Chou 2005, Suratman et al. 2008a, Suratman et al. 2009). The exception was PON in the stratified northern surface water where the absence of a relationship with chlorophyll *a* was recorded. This was probably due to the effect on the correlation of high chlorophyll *a* at four stations in the highlighted area (Figure 3.26b) located in the UK east coast near Aberdeen (PSt. 40, 3.1 µg/L), the river Tyne (PSt. 22, 1.7 µg/L), the river Tees (PSt. 13, 3.1 µg/L and PSt. 14, 3.6 µg/L). This suggests that the high chlorophyll values in these areas reflect either an algal bloom with a particularly high C:N molar ratio (e.g. phaeocystis) which can bloom across the North Sea (Rousseau et al. 2013, Desmit et al. 2015) or a post bloom situation where PON is more rapidly recycled than POC. Others have noted that POC and PON generally provided the strongest correlation with chlorophyll *a* during summer compared to other seasons (Suratman et al. 2008a, Suratman et al. 2009), POC and PON were generally much more directly connected to phytoplankton than DOC and DON.

Table 3.5 Correlations of POC and PON with salinity and chlorophyll *a* for three water masses in summer 2012.

Parameters			Correlation coefficient (r)	Confidence level at 95 %
POC	Stratified northern surface water	Salinity	-0.049	0.797
		Chlorophyll *a*	0.840*	0.000
	Stratified northern bottom water	Salinity	-0.055	0.774
		Chlorophyll *a*	0.649*	0.000
	Southern well-mixed water	Salinity	-0.317*	0.032
		Chlorophyll *a*	0.805*	0.000
PON	Stratified northern surface water	Salinity	-0.225	0.231
		Chlorophyll *a*	0.155	0.415
	Stratified northern bottom water	Salinity	-0.360	0.051
		Chlorophyll *a*	0.500*	0.005
	Southern well-mixed water	Salinity	-0.383*	0.009
		Chlorophyll *a*	0.716*	0.000

* Correlation is significant at the 0.05 confidence level. The number of samples (n) is 30, 30 and 46 for northern bottom waters, northern surface water and southern mixed water, respectively.

It has been proposed by Menzel and Goerin (1966) that the plot of POC (*y*-axis) against chlorophyll *a* (*x*-axis) can estimate the amount of the detrital carbon by the *y*-intercept of the linear regression equation assuming that the *y*-intercept represents POC not directly associated with living phytoplankton as represented by chlorophyll *a*. Therefore, correlation plots in Figure 3.26a, Figure 3.26c and Figure 3.26e can provide information on detrital carbon in each water mass. By considering the linear regression equation, the c (*y* intercept) in the equation, the detrital carbon (the carbon degraded and resuspended and not directly related to viable phytoplankton detected by chlorophyll *a*) can be estimated (Menzel and Goerin 1966). Thus, the detrital carbon in this study was highest in the southern well-mixed water with 8.9 µM followed by the northern surface water with 7.9 µM, the lowest level in the northern bottom water was 4.7 µM. This reflects increased resuspension and/or primary production in the well-mixed water and contributes an important component to the total POC.

The contribution of DON, TOxN and ammonium to the TDN pool is presented in Figure 3.27. A very high DON contribution to the TDN pool was observed in the northern surface water and the southern well-mixed water with 91% and 86% respectively. Lower proportions of DON (49%) were found in the northern bottom water, but this was still the highest contribution to the TDN pool in this water mass. This is consistent with other reports in the North Sea (De Galan et al. 2004, Korth et al. 2012), and higher proportions of DON also observed in the surface water than the bottom water in another continental shelf area (Bradley et al. 2010). Figure 3.28 provides absolute concentrations and the relative abundance of DIN, DON and PON to the total nitrogen pool. A high DON contribution to the nitrogen pool was found in the northern surface water and the southern well-mixed water with the similar proportion to that found in the open surface ocean (Berman and Bronk 2003). The DIN was slightly higher than DON pool in the northern bottom water as the DIN increases with depth in this water mass. This provided high bottom water accumulation of DIN in the northern bottom water, whereas, PON provided the lower contribution to nitrogen than DON in the three water masses.

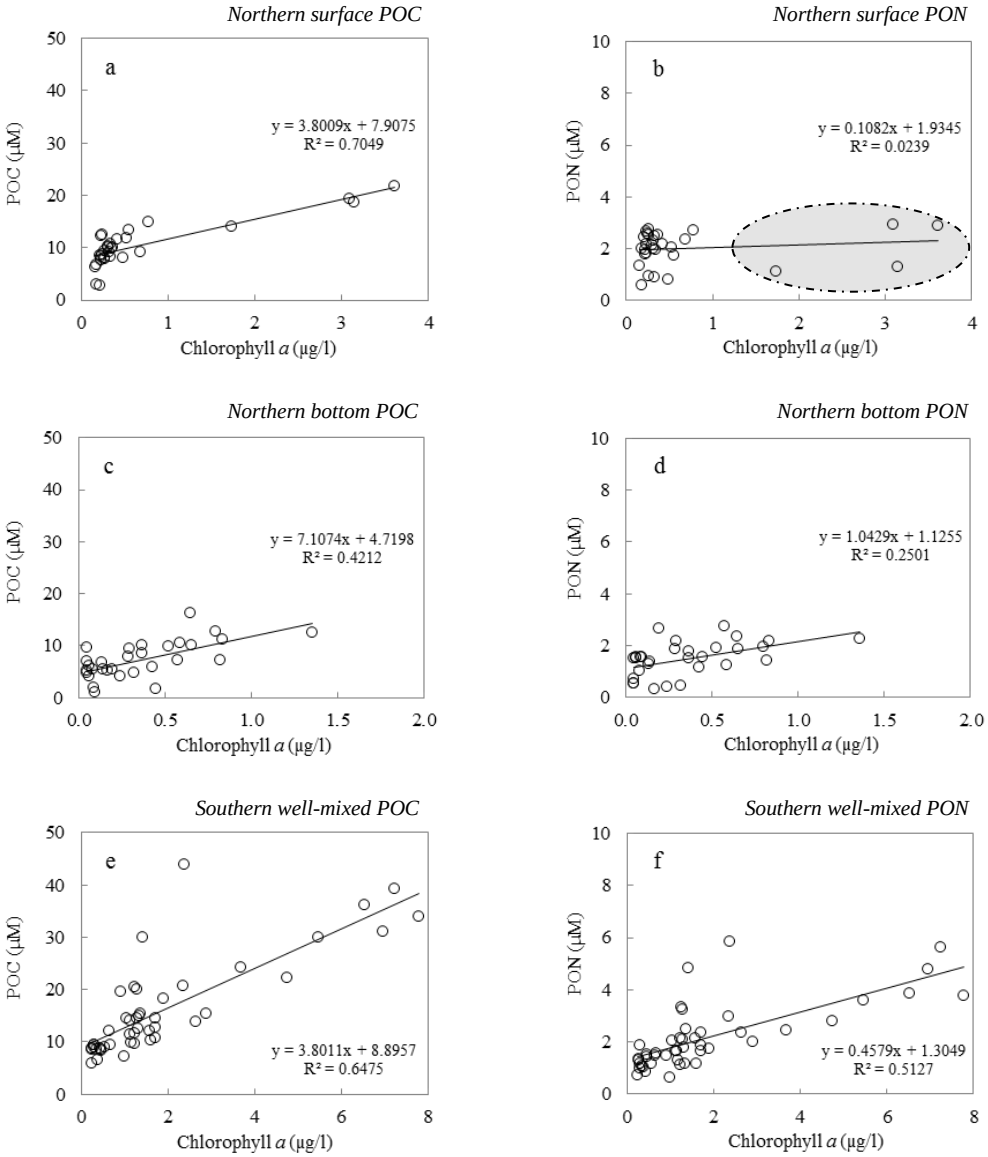


Figure 3.26 Relationship of POC and PON with chlorophyll *a* (POM = – m chlorophyll *a* + c, where m = gradient and c = intercept) for data sets of (a – b) stratified northern surface water, (c – d) stratified northern bottom water, and (e – f) southern well-mixed water in summer 2012. Note the different scales in *x*-axes. The points in the grey circle in figure b are discussed in the text.

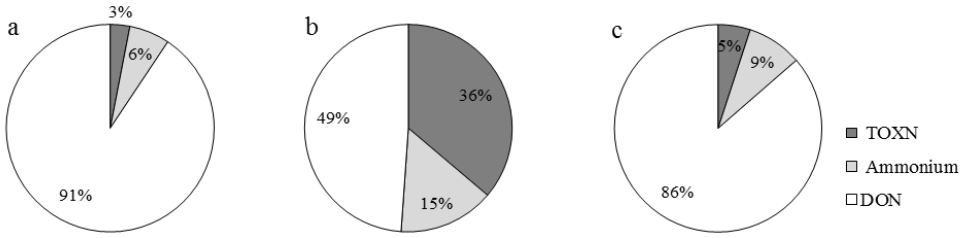


Figure 3.27 TOxN, ammonium and DON as percentage of TDN in (a) stratified northern surface water, (b) stratified northern bottom water, and (c) southern well-mixed water in summer 2012.

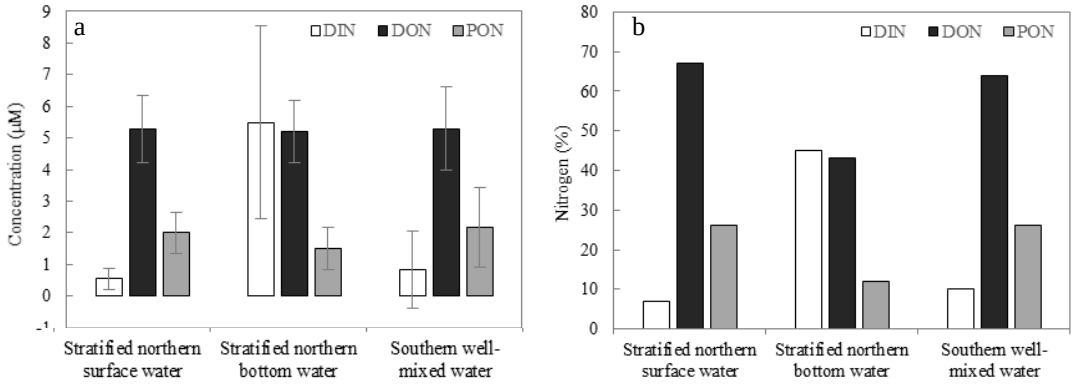


Figure 3.28 Concentrations (mean ± SD) of DIN, DON and PON (a) and relative abundance of nitrogen compounds (b) for three water masses in summer 2012. Error bars are standard deviation (SD) of concentrations in each water mass.

3.5 Discussion of spatial distribution patterns

The three surveys are linked together in this section by considering the features of water masses. In summer, the North Sea water was characterised into three water masses. In the north, the water column was stratified with warmer water staying on top and cooler water staying on the bottom due to seasonal stratification as observed in previous studies (Greenwood et al. 2010, Queste et al. 2013), the stratification was then reduced in the autumn (Knight et al. 2002, Van Haren and Howarth 2004). By contrast, the shallow water in the south is characterised by a vertically well-mixed water mass. The southern water investigated in this study showed a well-mixed water column in both summer and winter seasons. The southern North Sea is generally well-mixed year round as the shallow depth and strong tides allow vertical mixing (Emeis et al. 2015).

By considering the three features of water (Figure 3.29), the stratified northern bottom water provided a high stock of inorganic nutrients in summer. Inorganic nutrients were partly transported by river runoff during winter in the southern well mixed water which showed higher levels of inorganic nutrients than the summer period. In deep waters, all inorganic nutrients accumulated during the thermal stratification and strong temperature gradients make it difficult to mix this water to the surface as the stratification in the shelf sea generally depends on gradients of vertical temperature and salinity, as well as depth and tidal mixing

(Simpson et al. 1977). The mean inorganic N:P ratios (DIN/phosphate) in this study were substantially lower than the Redfield ratio of 16 in all water masses of summer 2011 (~ 7), summer 2012 (~ 6) and winter 2011 (~ 14), indicating potential nitrogen limit of water column for phytoplankton growth.

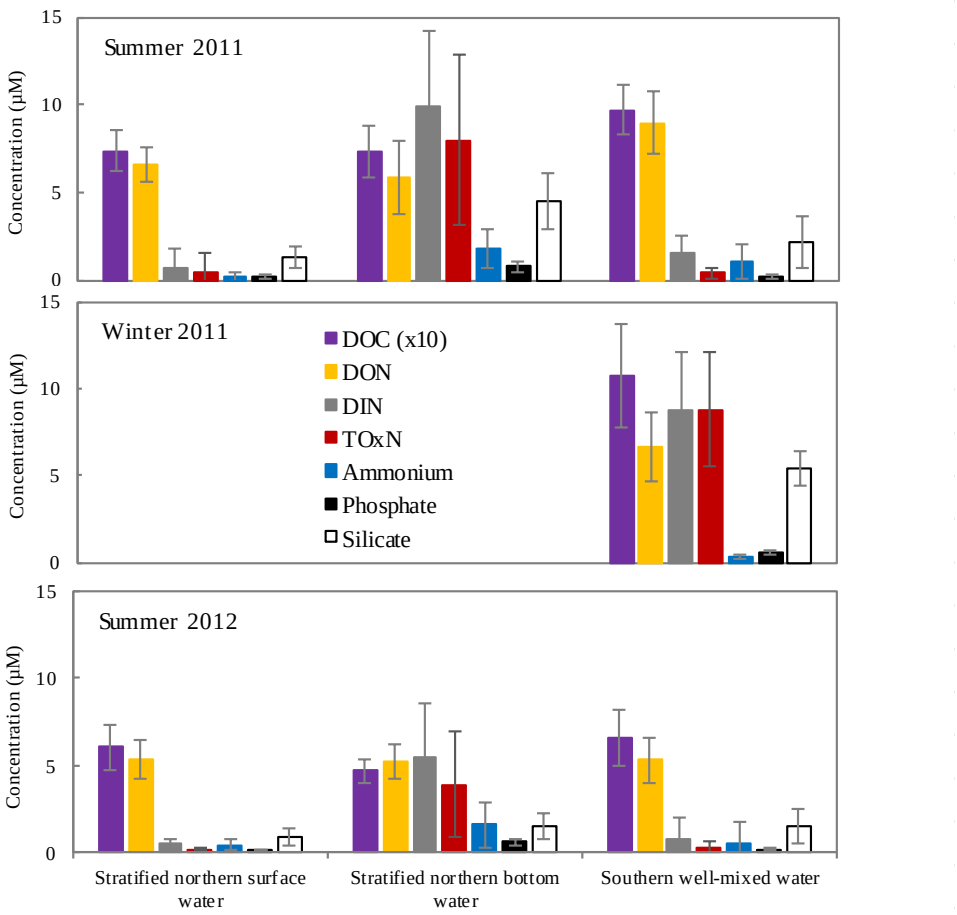


Figure 3.29 Variation of mean nutrients in three different water masses. Error bars are standard deviation. Similar scales are used in summer 2011, winter 2011 and summer 2012 surveys. Note the concentration unit of DOC is multiplied by 10.

In contrast to inorganic nutrients, high DOC and DON concentration generally were found in the surface layer and shallow depth well mixed water, rather than the northern bottom water. River plumes from the coastal area were related to the distribution of DOC and DON, and salinity was a key factor to control their distribution. This is indicated by the inverse correlation between DOC and salinity in the stratified northern surface water and the southern well-mixed water, and between DON and salinity in all water masses (Table 3.6). Generally, the chlorophyll *a* was not associated with the DOC and DON distribution (low correlation, $P > 0.05$) at

least in summer and winter, but highly correlated with POC and PON. Furthermore, salinity was also associated with the POC and PON distribution in the southern well-mixed water. This suggests that an important control on the higher DOC and DON in surface northern and southern waters is an input from rivers or at least the lower salinity region. In general, the high level of DOC in the rivers is decreased when entering to the coastal area and open sea by mixing and dilution with coastal waters (Ferrari et al. 1996). DOC and DON concentrations in offshore water were generally lower than the level near shore (Van Engeland et al. 2010, Yamashita et al. 2011), DIN and other inorganic nutrients also showed that their concentrations in offshore were lower than the near shore water (Hydes et al. 1999).

Table 3.6 Correlation of DOC, DON, POC and PON with salinity in each water mass. Note only significant correlation is presented.

Parametesr	Surveys	Water mass [a]	Correlation coefficient (r) [b]	Regression analysis			
				R-square (R^2)	Slope	Intercept	n [c]
DOC	Summer 2011	NS	-0.509	0.2594	-5.7	270.1	50
		SM	-0.408	0.1661	-11.1	477.7	45
	Winter 2011	SM	-0.288	0.0830	-20.0	805.5	60
	Summer 2012	NS	-0.637	0.4062	-8.1	338.3	30
		SM	-0.536	0.2871	-18.7	711.0	46
DON	Summer 2011	NS	-0.444	0.1973	-0.4	20.6	50
		NB	-0.549	0.3009	-5.1	183.7	49
		SM	-0.551	0.3037	-1.9	75.3	45
	Summer 2012	NS	-0.503	0.2535	-0.5	23.4	30
		SM	-0.636	0.4047	-1.8	67.1	46
POC	Summer 2012	SM	-0.317	0.1004	-6.3	233.6	46
PON	Summer 2012	SM	-0.383	0.1469	-1.0	37.8	46

[a] Water masses: NS = stratified northern surface water, NB = stratified northern bottom water, SM = southern well-mixed water

[b] All presented correlation is significant at the 0.05 confidence level

[c] Number of sample (n)

Based on extrapolation of the observed relationship of DOC and DON to salinity to zero salinity and assuming conservative mixing, the intercept value in Table 3.6 provides the approximate concentrations of DOC, DON, POC and PON in the average river entering the region. The results suggest higher riverine DOC concentration in the south than the northern area in both years. DON generally followed the same pattern. However in summer 2011, a much higher DON (~ 184 µM DON) was seen in the bottom water in the north for which the range of salinity (Figure 3.7d) is very small so the intercept is uncertain. The current from the Baltic

Sea flowed into the North Sea via Skagerrak was the main low salinity water entering to the Northern North Sea (Thomas et al. 2005). In winter, there was little evidence of DOC and DON correlation with salinity but the range of sampled salinity was small.

DOC and DON concentrations and C:N molar ratios in summer and winter 2011 and summer 2012 surveys are presented in box-whisker plots in Figure 3.30. Difference in concentrations of DOC and DON in summer may reflect interannual variability. DOM in both summer surveys reaches the maximum level in the southern well-mixed water, while the highest DOC and C:N molar ratio were

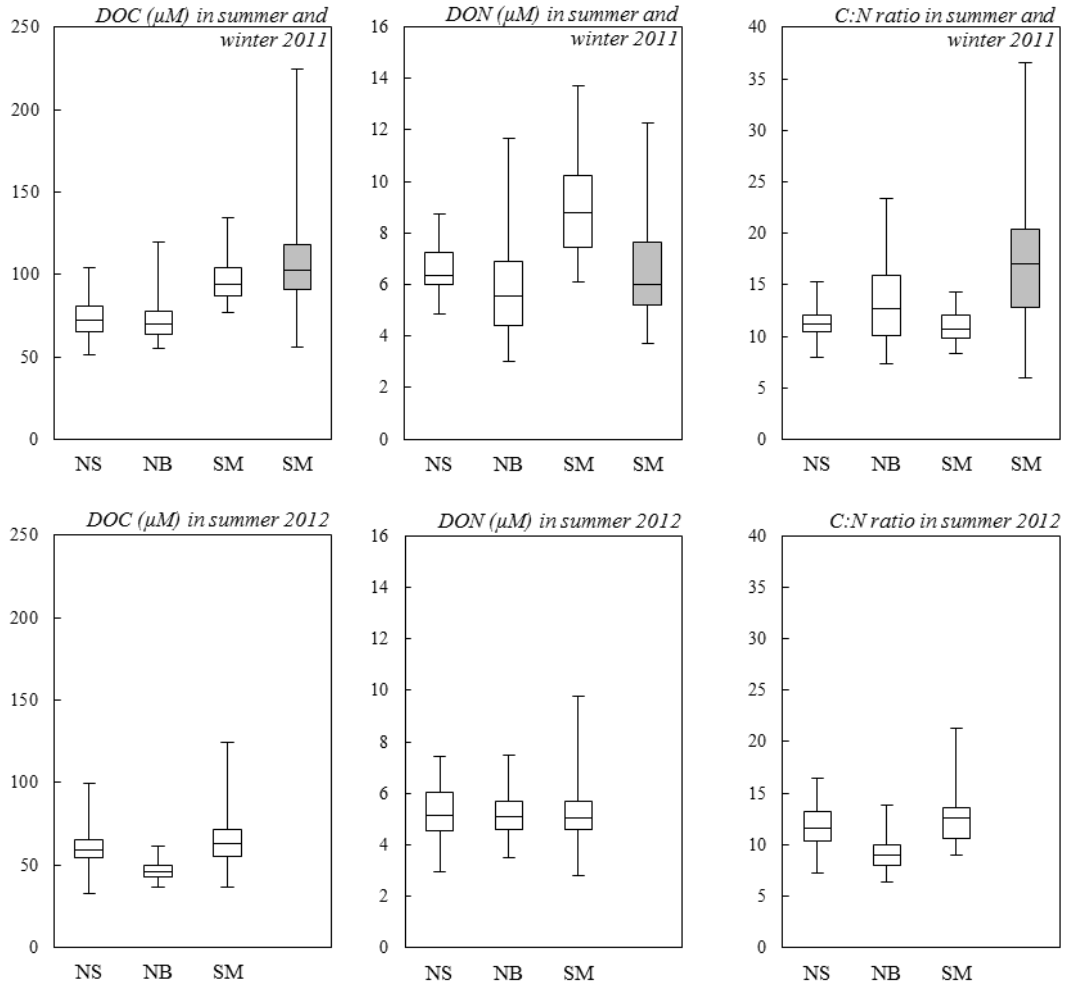


Figure 3.30 Box – whisker plot of DOC and DON concentrations (μM) and C:N molar ratios of DOM in summer 2011-2012 (blank boxes) and winter 2011(grey boxes). In each data set, the box indicates the lower (Q_1, 25%) to the upper (Q_3, 75%) quartile and the median (the horizontal line within the box). The lowest and highest data points indicate by the whiskers. Three water masses in the North Sea include NS (the northern surface water), NB (the northern bottom water) and SM (the southern well mixed water).

recorded during winter. During summer 2011, mean C:N molar ratio in the northern bottom water showed significantly higher ratio (ANOVA, $P < 0.05$) than in other water masses (Figure 3.31(a, c and e)). This implied the preferential remineralisation of N compare to C and/or high C:N molar ratio materials input from offshore as mean C:N molar ratio in the northern bottom water agreed with the mean value in the North Atlantic (~13-14) (Aminot and Kérouel 2004) and C:N molar ratios in the northern bottom water showed a significant positive correlation with salinity ($R^2 = 0.32$, $P < 0.05$, $n = 49$). In contrast to summer 2011, mean C:N molar ratio in summer 2012 showed significantly lower levels in the northern bottom water (ANOVA, $P < 0.05$), than the northern surface and southern well mixed waters (Figure 3.31(b, d and f)). This was probably due to the areas above 58°N not being covered in summer 2012 and that area exhibited substantially high C:N molar ratio in the northern bottom water in summer 2011 (Figure 3.31c).

In comparison to the Redfield ratio of 6.6, the C:N molar ratio in this study was generally enriched in carbon relative to nitrogen (Table 3.7), and their mean values (~ 9 to 17) were comparable to the previous report in in the southern North Sea (10.8 – 14.8) (Van Engeland et al. 2010) and other continental shelf waters (11 – 19) (Hansell et al. 1993, Hopkinson et al. 1997, Bates and Hansell 1999, Hopkinson et al. 2002, Wetz et al. 2008, Kim and Kim 2013). The elevated C:N molar ratio in winter (Table 3.7) was probably due to the riverine input of high C:N materials as a significant inverse relationship with salinity in C:N molar ratio ($R^2 = 0.15$, $P < 0.05$, $n = 60$) has been shown.

The comparison of C:N molar ratios and slope C:N ratios are summarised in Table 3.7. Data of slope C:N ratio in winter 2011 were not available because there was not a significant correlation ($P > 0.05$) between DOC and DON concentrations (Figure 3.14). Although statistical test showed no significant difference (ANOVA, $P > 0.05$) between slope C:N ratios in the three water masses, the slope C:N ratios in both summer 2011 (Table 3.7, Figure 3.6) and summer 2012 (Table 3.7, Figure 3.22) showed C-rich in the surface relative to bottom water. There was no statistical difference (t-test, $P > 0.05$) between summer 2011 and summer 2012 for the slope C:N ratios. The slope C:N ratio was close to the Redfield proportion of 6.6, particularly in the northern surface and southern well mixed waters, implying a

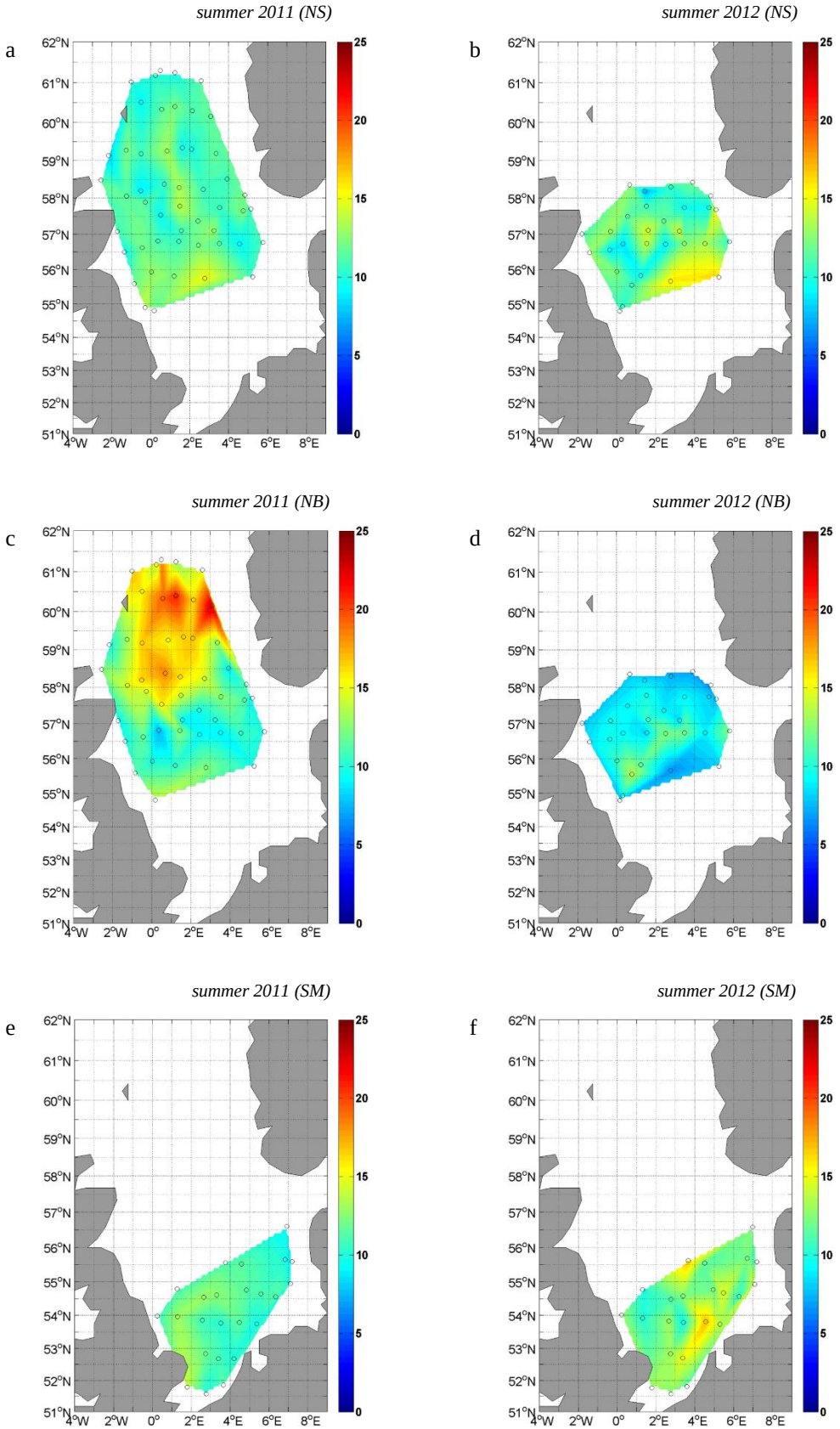


Figure 3.31 Distribution of C:N molar ratios of DOM in summer 2011 (a, c and e) and summer 2012 (b, d and f) in three water masses including NS (the northern surface water), NB (the northern bottom water) and SM (the southern well mixed water).

Table 3.7 The slope C:N ratio and C:N molar ratio of DOM from cruise survey samples in summer 2011-2012 and winter 2011.

Water mass [a]	C:N molar ratio [b] (Range, mean ± SD)			Slope C:N ratio [c]	
	Summer 2011	Summer 2012	Winter 2011	Summer 2011	Summer 2012
NS	8.0 – 15.3, 11.3 ± 1.4, n = 50	7.2 – 16.4, 11.7 ± 2.3, n = 30	*na*	8.1	7.2
NB	7.4 – 23.3, 13.4 ± 3.6, n = 49	6.4 – 13.8, 9.3 ± 1.8, n = 30	*na*	4.6	2.7
SM	8.3 – 14.3, 11.1 ± 1.6, n = 45	8.9 – 21.3, 12.6 ± 2.8, n = 46	5.9 – 36.5, 17.3 ± 6.2, n = 60	5.7	8.0
Whole surface	8.0 – 15.3, 11.3 ± 1.5, n = 74	7.2 – 21.3, 12.3 ± 3.0, n = 53	5.9 – 36.5, 17.6 ± 6.5, n = 52	7.4	6.9
Whole bottom	7.4 – 23.3, 12.6 ± 3.3, n = 70	6.4 – 14.7, 10.5 ± 2.3, n = 53	8.0 – 18.2, 14.9 ± 3.3, n = 8	6.3	6.6

[a] NS = the northern surface water, NB = the northern bottom water and SM = the southern well-mixed water.

[b] DOC:DON ratio are reported in range and mean ± SD (standard deviation), n = number of samples

[c] Data were taken from the slope of DOC and DON plot in Figure 3.6 for summer 2011and Figure 3.22 for summer 2012. Data of slope C:N ratio in winter 2011 was not available because there was not significant correlation between DOC and DON concentrtion (Figure 3.14).

na = data is not available,

dominant role of phytoplankton in the water column, plus a high C:N background. This background level of DOC ~ 30 µM still persisted when DON reaches zero.

Previous studies has proposed that the slope C:N ratio (derived from linear regressions of the bulk DOC and DON plot as described in section 1.5) is the C:N stoichiometry of labile/decomposable DOM (Hopkinson and Vallino 2005) or the stoichiometry of production and remineralization that the DOM altered because of difference in its composition (Aminot and Kérouel 2004). This slope C:N ratio therefore provided a value lower than the bulk C:N molar ratio observed in this study (Table 3.7) and other previous observations in the central North Sea (Suratman et al. 2009), the other shelf waters (Hopkinson et al. 1997, Hopkinson and Vallino 2005, Lønborg et al. 2010).

For the C:N stoichiometry of POM, the value was only available in summer 2012 when the POC and PON concentration were measured. The slope C:N ratio of POM was comparable to the bulk C:N molar ratio of POM, particularly in the southern well-mixed water. POC and PON in the southern well-mixed waters were a strong significant positive correlation ($R^2 = 0.87$, $P < 0.05$, n = 46) with a slope C:N ratio of 6.9 with a background level of POC 1.1 µM still persisted when PON reaches zero. This is similar to the bulk C:N molar ratio of 7.7 (7.7 ± 1.8, n=46) and the Redfield ratio of 6.6. The possible explanation for these similar ratios found in this study is that they were due to phytoplankton derived POM dominating in the

water column as the chlorophyll *a* is linked to the distribution features of POM. The agreement of slope C:N ratios of POM, bulk C:N molar ratios of POM and the Redfield ratio was also found in previous studies in the North Sea during summer (Weston et al. 2004, Suratman et al. 2009).

The C:N molar ratio of POM in the northern surface water (5.9 ± 3.1, n=30) was similar to the northern bottom water (6.0 ± 3.9, n=30) implying no preferential remineralisation of N or C. Both ratios were also close to the Redfield proportions as found in the southern well-mixed water. The C:N molar ratio of POM which is similar to the canonical Redfield ratio is also observed in the North Sea during summer (Weston et al. 2004, Suratman et al. 2009) and spring (Tungaraza et al. 2003) as well as a recent report for the global ocean (Martiny et al 2013). Although a median value of 6.5 for C:N molar ratio of POM in the global ocean was reported (Martiny et al 2013), the authors indicated that the ratio was regionally variable, the upwelling regions and higher latitude cold waters generally had lower ratios than the warm oligotrophic gyres.

In summary, during the summer, dead organisms sink to the bottom and bacterioplankton breaks down the tissues in the process of decay. This decomposition releases inorganic nutrients, which concentrate in the bottom water, whereas, phytoplankton assemblages that need them are on the top of the water column. This results in most of the dissolved inorganic nutrients in this study being found in high concentration in the northern bottom waters in summer. In contrast, high concentration of organic compounds in both dissolved and particulate forms (DOC, DON, POC and PON) and chlorophyll *a* were generally found at highest level in the southern well-mixed water, particularly near the coast where there was more influence by river plumes from continental Europe, the coastal area near Skagerrak and the eastern coast of UK. The stratified northern surface water had higher DOC and DON concentrations than the bottom. The stratified northern bottom water had higher DOC:DON molar ratios than the surface in summer 2011 implying the preferential remineralisation of N compared to C and/or high C:N molar ratio materials input from offshore. The highest C:N molar ratio of DOM recorded in winter was partly influenced by riverine input of high C:N materials. Although no clear relation of DOC and DON to salinity was seen, but the sample salinity range was small in winter. In general, the C:N molar ratio of DOM in this

study was enriched in carbon relative to nitrogen, compared to the Redfield ratio. The slope C:N ratio of DOM was close to the Redfield proportion of 6.6, particularly in the northern surface and southern well mixed waters, implying a dominant role of phytoplankton in the water column. This agreed with the POM pool in which the slope C:N ratios and the bulk C:N molar ratios were similar to the Redfield ratio. No preferential remineralisation of N or C showed in the POM pool.

3.6 Discussion of temporal distribution patterns

The temporal pattern is considered in two parts, the difference between the summer and winter seasons and difference between summer 2011 and summer 2012 survey. The difference in nutrient pool during winter and summer period is illustrated in the southern well-mixed water, by the black bars in Figure 3.32. In comparison to summer, the results indicated higher DOC concentration during winter, while low DON concentration was observed. The TDN shows a similar seasonal pattern to DON. All inorganic nutrients clearly demonstrated much higher levels in winter, except ammonium for which the summer had slightly higher concentration. The seasonal nutrient cycle for DIN was greater than for DOC and DON. The enrichment of inorganic nutrients in winter when sampling was near the coast was strongly correlated with the salinity with a negative correlation (Figure 3.12, e-h). This indicated riverine runoff was an important source to support inorganic nutrient entering via the coast in winter. There was no clear evidence of a strong riverine source for DOC in the winter (Figure 3.15a).

In summer, the distribution pattern of DOC and DON showed a significant influence of riverine input although the relationship showed variability (Figure 3.33) indicating that other factors besides salinity are important. There was a difference of mean DOC and DON concentration between summer 2011 and summer 2012. The survey in 2011 presented significantly higher concentrations of DOC and DON than the summer 2012 survey in both the whole water data set and each data set separated by three different water masses (t-test, $P < 0.05$). In addition, Figure 3.33 and Figure 3.34 were plotted based on the whole data set (whole three water masses) for each

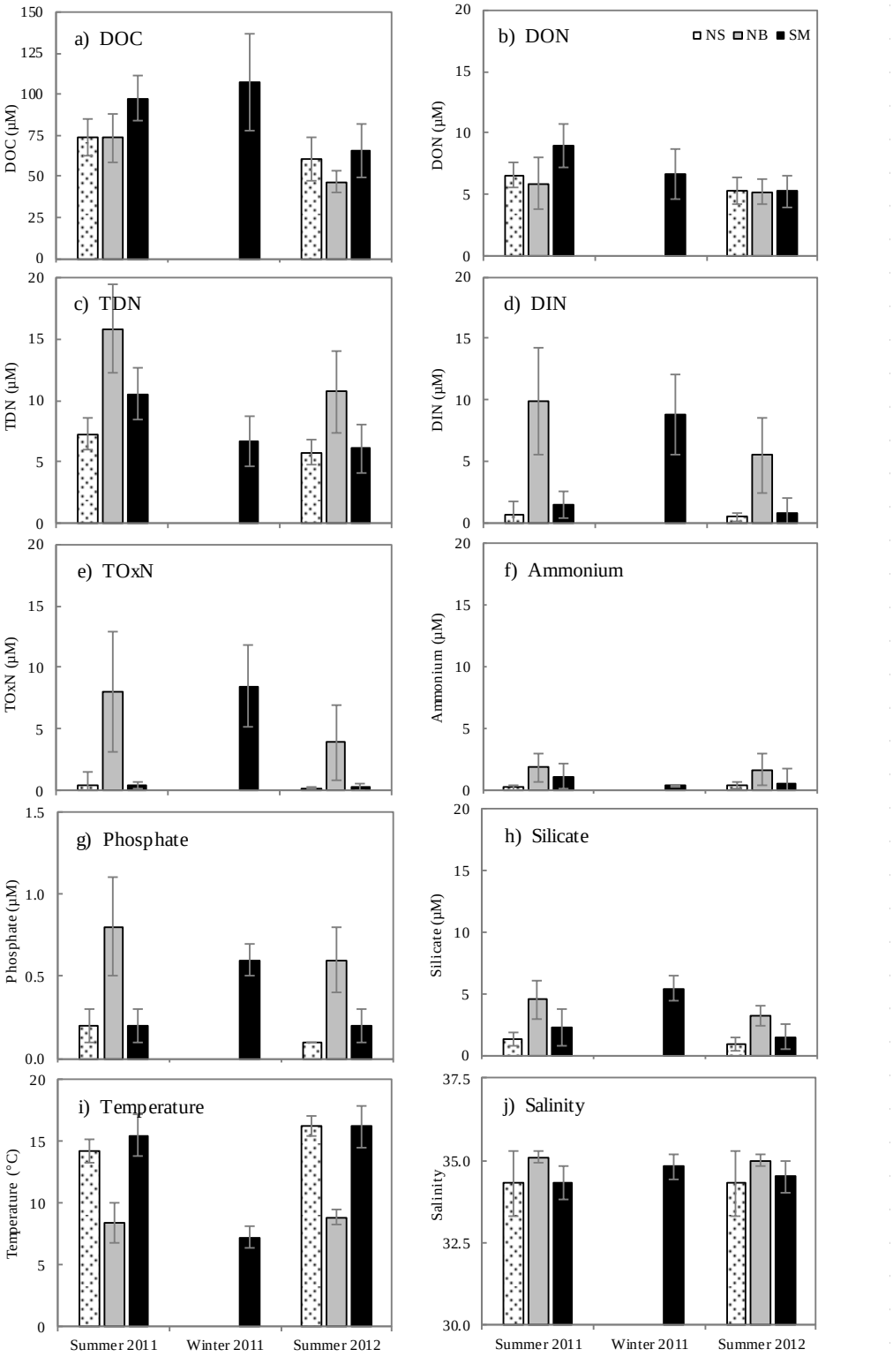
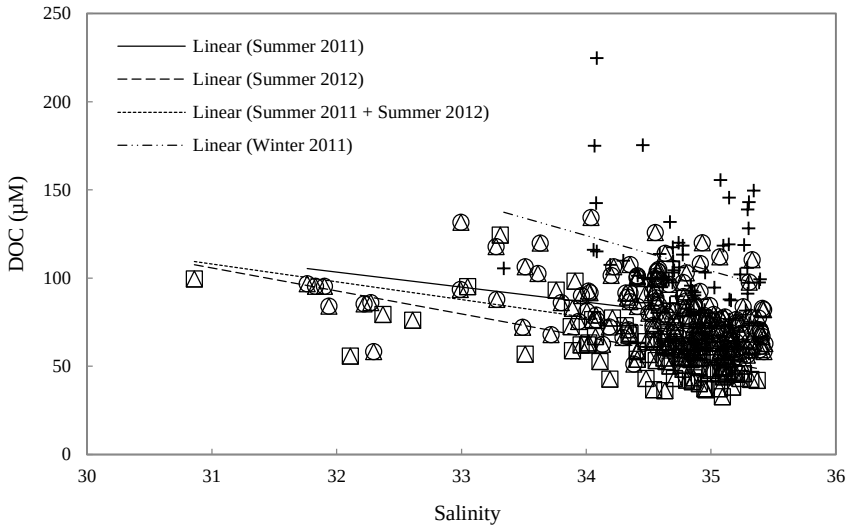


Figure 3.32 Variation of mean nutrients, temperature and salinity in summer 2011, winter 2011 and summer 2012. Error bars are standard deviation. Note different scale in *y*-axis. All parameters in the southern well-mixed water (SM, black bars) show a significant difference (ANOVA, $P < 0.05$) in concentration between three surveys. For summer surveys in 2011 and 2012, all parameters show a significant difference (t-test, $P < 0.05$) in concentration between two summer surveys for each water mass (northern surface water (NS), northern bottom water (NB) and SM), except DIN and salinity in NS, ammonium and temperature in NB, and TOxN, temperature and salinity in SM.

a)



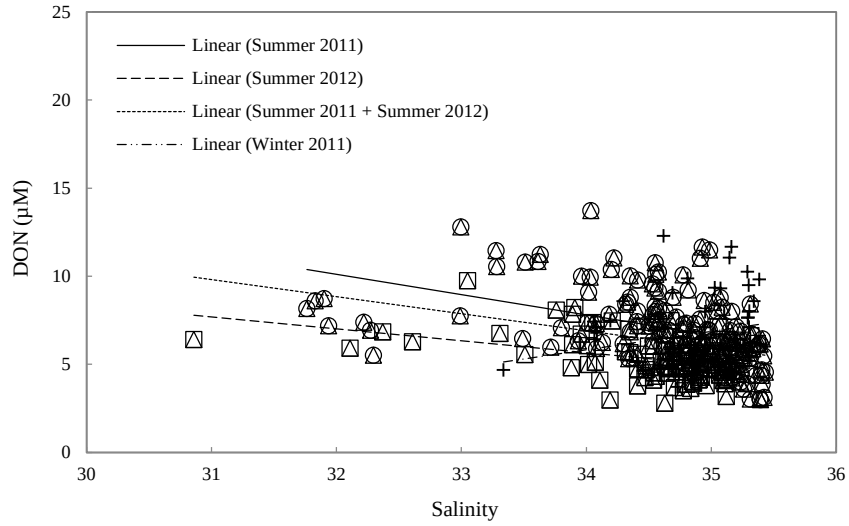
○ Summer 2011 y = -8.5433x + 376.8
R² = 0.1503

□ Summer 2012 y = -13.071x + 510.97
R² = 0.3433

△ Summer 2011 + Summer 2012 y = -10.059x + 419.72
R² = 0.1423

+ Winter 2011 y = -20.04x + 805.48
R² = 0.083

b)



○ Summer 2011 y = -1.1524x + 46.984
R² = 0.1872

□ Summer 2012 y = -0.6749x + 28.607
R² = 0.1606

△ Summer 2011 + Summer 2012 y = -0.9698x + 39.877
R² = 0.133

+ Winter 2011 y = 1.0361x - 29.402
R² = 0.0504

Figure 3.33 Relationship between DOC and DON with salinity for the whole water mass in each survey. The line was fitted by linear regression analysis. (a) DOC and salinity. (b) DON and salinity

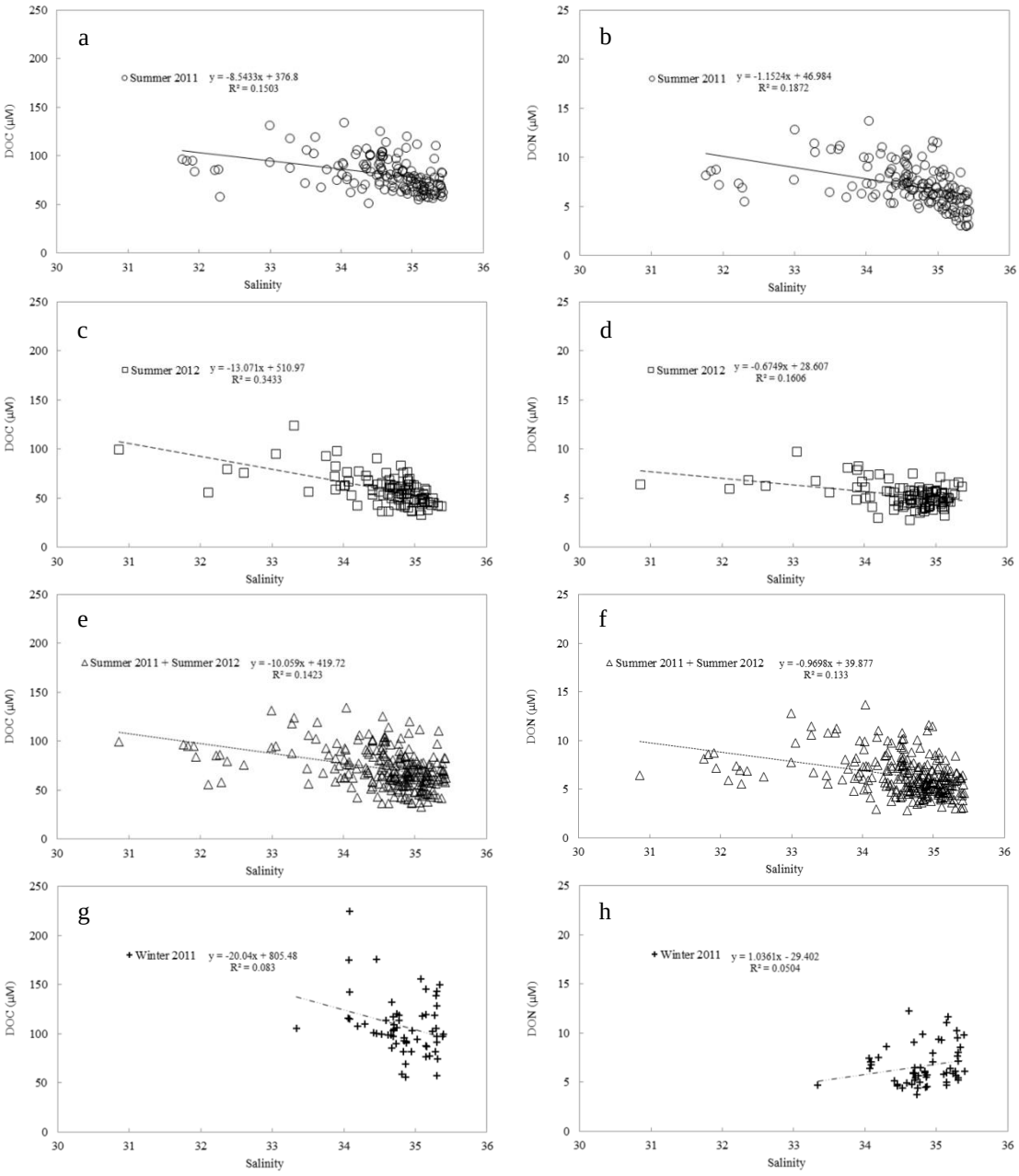


Figure 3.34 Relationship between DOC and DON with salinity for the whole water mass in each survey: (a-b) summer 2011, (c-d) summer 2012, (e-f) summer 2011 + summer 2012, and (g-h) winter 2011. The line was fitted by linear regression analysis.

Table 3.8 The *y*-intercept values and the estimated uncertainty of the relationship between DOC and DON with salinity for the whole water mass in summer 2011 and summer 2012 survey.

Parameters	Season	*y*-intercept ± uncertainty
DOC	Summer 2011	376.8 ± 59.0
	Summer 2012	511.0 ±61.3
DON	Summer 2011	47.0 ± 7.0
	Summer 2012	28.6 ± 5.2

survey. The DOC and DON concentration was plotted against salinity in Figure 3.33 to determine the distinction between two surveys in summer. The same plots separated by surveys were shown in Figure 3.34. The *y*-intercept of the linear regression equation in both figures provide estimates DOC and DON levels in freshwater of each survey. Thus, the estimated levels of DOC in freshwater were 377 µM and 511 µM for summer surveys in 2011 and 2012 respectively (Figure 3.34a, Figure 3.34c and Table 3.8). For DON, the estimated freshwater concentration was 47 µM in summer 2011 and lower concentration in summer 2012 with 29 µM (Figure 3.34b, Figure 3.34d and Table 3.8). These are statistically significant difference (t-test) between two years (summer 2011 and 2012). These freshwater estimates are based on large extrapolation and so must be treated cautiously but they do suggest that while freshwater inputs are important sources of DOC and DON, those sources may themselves vary with time and potentially from river to river. The Baltic looks different to the North Sea for instance as discussed below.

The combination of two surveys in summer demonstrated approximately 420 µM DOC and 40 µM DON for estimated freshwater concentrations (as intercepts of the best fit lines of summer 2011 + summer 2012 plotted in Figure 3.34e and Figure 3.34f respectively). This agreed reasonably well with the mean DOC concentration in the eastern UK rivers draining to the North Sea with 458 µM (Neal and Robson 2000). DON river data is more limited, but high riverine DON can be seen in an individual river, for instance DON concentration in August 2002 was ~ 150 µM in the river Colne which is subject to sewage pollution (Agedah et al. 2009). In surrounding areas, mean DOC levels in freshwater discharged to the Horsens Fjord (Belt Sea, Kattegat) in Denmark was 591 µM, while DON concentration was 84 µM (Markager et al. 2011). While freshwater inputs are important sources of DOC and DON, these sources may vary with time and place. In addition, the results in Figure 3.33 – Figure 3.34 also show higher estimate end-member DOC concentration in freshwater during winter (805 µM). However, information on estimated freshwater DON concentration during winter was not considered as there was no significant correlation ($P > 0.05$) between DON and salinity.

3.7 SmartBuoy time series

The SmartBuoy is an instrumented moored buoy operated by CEFAS. The mooring networks are in the UK shelf sea and have been used to study physical and biogeochemical parameters (Mills et al. 2003, Mills et al. 2005, Greenwood et al. 2010, Suratman et al. 2010, Panton et al. 2012, Johnson et al. 2013). The SmartBuoy provided high frequency measurements of the water column for both in situ measured data (by continuous sensors) and routine autonomous water sampling (by preserved water samples) which are difficult to obtain by cruise based sampling. The data recorded by in situ sensors (e.g. temperature, salinity, oxygen, chlorophyll fluorescence etc.) can be directly used, while the preserved water samples (within the sample bags preserved with mercuric chloride ($HgCl_2$) (Suratman et al. 2010, Johnson et al. 2013) have to be analysed later at the laboratory.

In this present study sample bags were collected during the Smartbuoy cruises serviced at West Gabbard and Dowsing SmartBuoy sites. Location of the sites are shown again here in Figure 3.35, while details of bag samples was previously shown in Table 2.2 of chapter 2. The two SmartBuoy site represents the coastal waters in the well-mixed southern North Sea. The West Gabbard is situated in a region influenced by river inputs from both the UK and the European continent. According to the direction of the southern North Sea current, the Dowsing sites located in the south western Dogger Bank is generally less directly influenced by the river inputs from the UK and less impacted by European continental coastal rivers (see Figure 1.3b in chapter 1 for the North Sea currents). Samples used here were collected from autumn 2013 to spring 2014. Details of the SmartBuoy instruments can be found elsewhere in Mills et al. (2003) and Mills et al. (2005), however, a brief detail is provided here. An automated sampler collects 150 ml water samples in polyethylene bags at 1 meter depth at both mooring sites and they are immediately preserved with 375 µl 0.05 M $HgCl_2$. After retrieval of the mooring, the preserved sample was then filtered through 0.4 µm pore size polycarbonate (PC) filters (Whatman, UK) in the laboratory (P. Nelson (CEFAS), personal communication). Discrete filtered bag samples were kept in 50 ml polycarbonate bottles at 4 °C during transport and analysed at UEA laboratory.

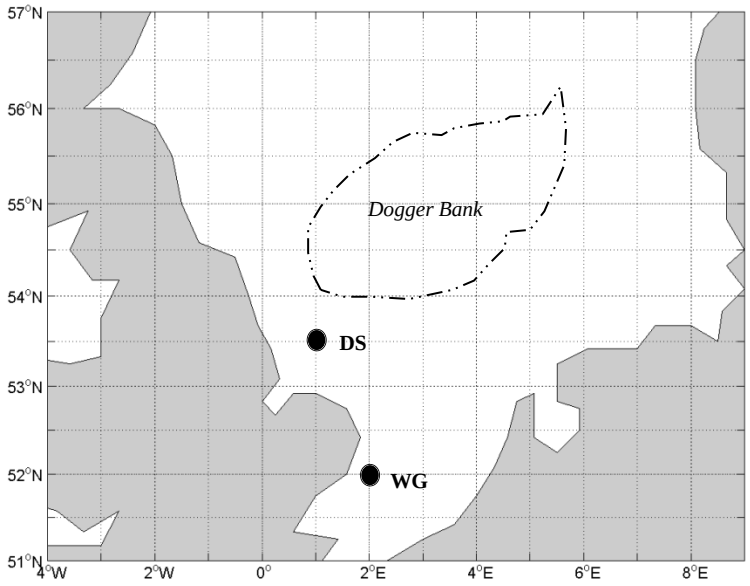


Figure 3.35 Location of the West Gabbard and Dowsing SmartBuoy in the Southern North Sea. The Dogger Bank is approximately located within the broken line area.

Data collected at both sites in this present study are divided into two parts:

1) Data from in situ measurements by the moored buoys, these data are continuous sensor monitoring of 7 parameters (T. Hull (CEFAS), personal communication). The parameters are temperature, salinity, chlorophyll florescence, oxygen concentration, oxygen saturation, wave height and optical backscatter (for turbidity). Data were measured at high frequency (every 30 minutes) over the study periods. The parameters are calibrated by CEFAS, fluorescence is not currently available as calibrated output, therefore arbitrary instrument outputs are used here.

2) Data from preserved bag samples. These data are for the measurement of preserved samples at the UEA laboratory. Water samples from each bag were used to measure 6 parameters including DOC, DON, TOxN, ammonium, phosphate, silicate, by methods described in chapter 2 (section 2.6 – 2.7). The integrity of preservation technique and the value of the SmartBuoy samples for studying temporal variability of DON have been demonstrated previously (Suratman et al. 2010, Johnson et al. 2013).

The archive of preserved bag samples in this study contained a number of samples within different time periods that were deployed and recovered including WG 94 and WG 96 for the West Gabbard site and DS 33, DS 34 and DS 35 for the

Dowsing site. Samples were recorded by CEFAS code with the site (WG and DS) and the deployment period number e.g. WG94. Samples were collected every 4 days in each deployment. There was a break in the record for West Gabbard site (no bag samples from WG 95) as well as a biofouling problem on in situ sensors meaning some data are not available for whole deployments. There were 31 bag samples from West Gabbard and 69 bag samples from Dowsing sites analysed for 6 nutrient parameters. All results of analysed bag samples and related in situ results are presented in Appendix 3.11 and the missing data is indicated. The results and discussion of SmartBuoy samples at West Gabbard and Dowsing site are presented in section 3.7.1 and 3.7.2, respectively. Basically, details start with in situ measurements by continuous sensors. Then, the exact date and time sensor data were chosen to agree with the date and time collection of preserved bag samples in order to study nutrient variations with related environmental parameters over the time period. A statistical correlation assessment was then performed in order to understand the influence of the in situ parameters and dissolved inorganic nutrients on DOC and DON variations in this study. Overall discussion of the two SmartBuoy sites is provided in section 3.7.3.

3.7.1 West Gabbard SmartBuoy

The West Gabbard SmartBuoy in the southern North Sea is located in between the plumes of the Thames and Scheldt/Rhine estuaries. The in situ measurements of temperature, salinity, chlorophyll fluorescence, oxygen concentration and oxygen saturation are presented in Figure 3.36. Each parameter was recorded every half-hour during the collection period of preserved bag samples on WG 94 and WG 96. Data were not available in between WG 94 and WG 96 as there was no services on the WG 95 time period (P. Nelson (CEFAS), personal communication). Based on data available, the high frequency data from the in situ sensors was aligned with date and time collection of bag samples to study their variation with data from bag samples (Figure 3.37).

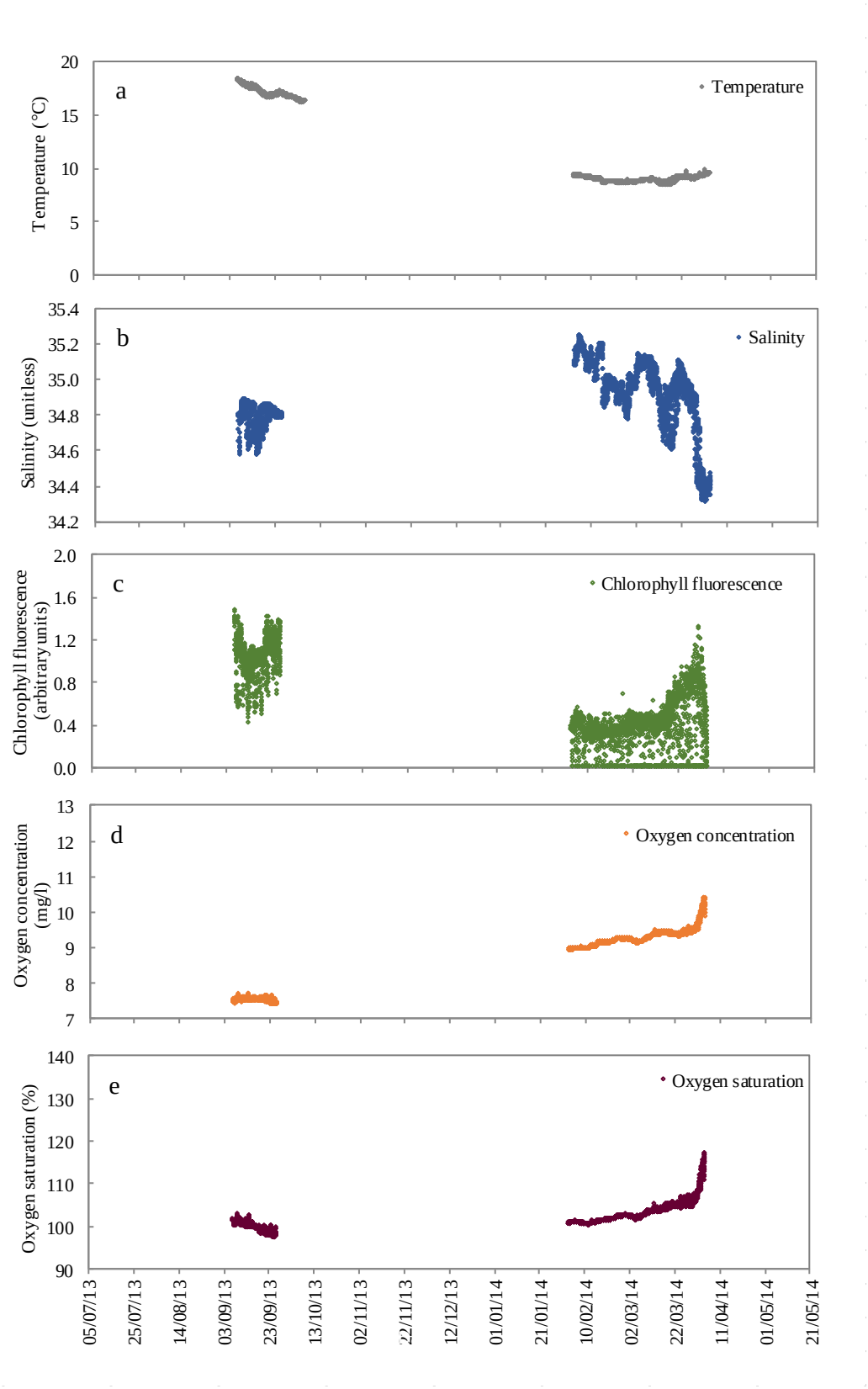


Figure 3.36 Variation of in situ parameters during September 2013 – April 2014 from West Gabbard SmartBuoy: (a) temperature, (b) salinity, (c) chlorophyll fluorescence, (d) oxygen concentration, and (e) oxygen saturation.

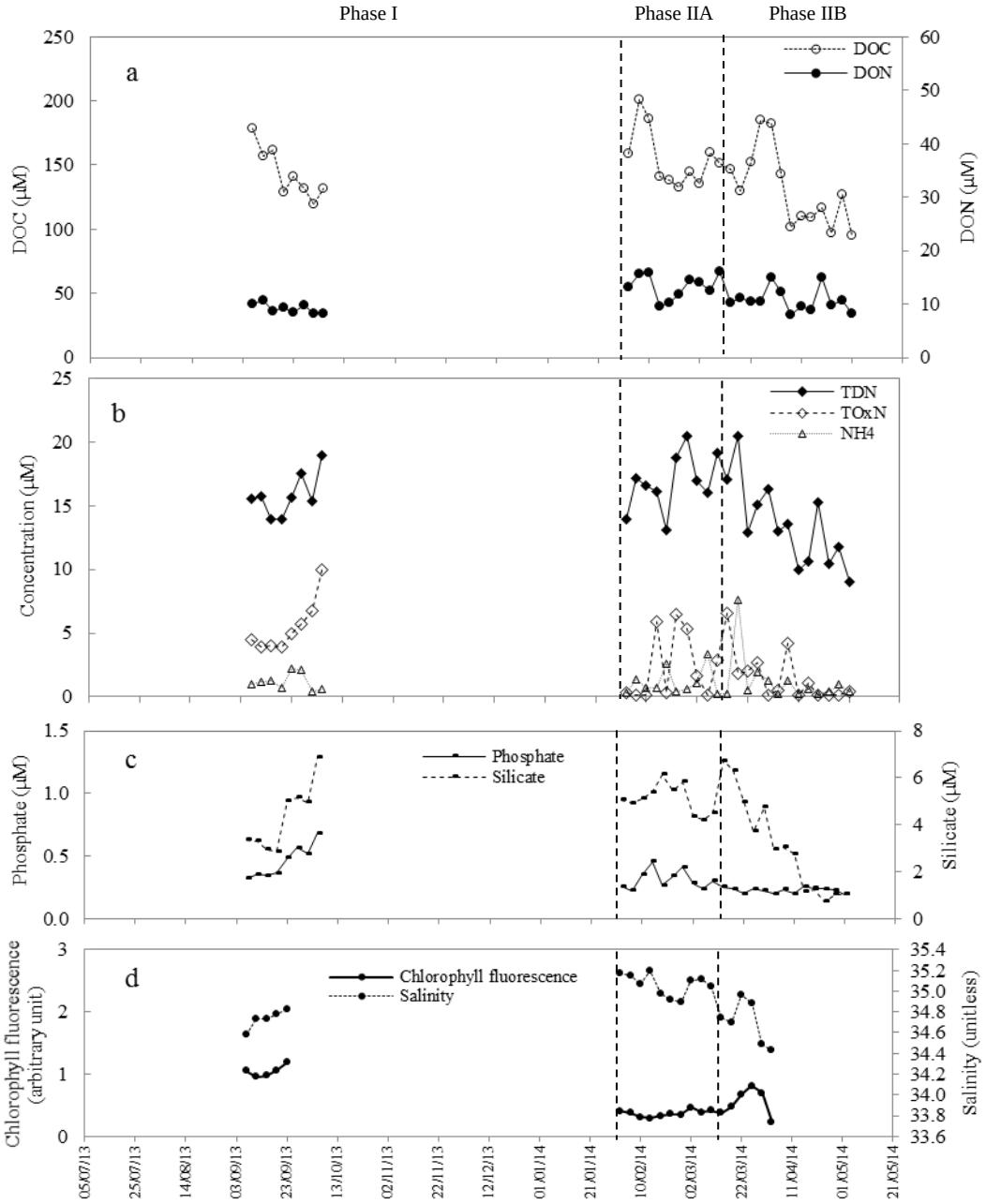


Figure 3.37 Variation of nutrients (a) DOC and DON; (b) TDN, TOxN and ammonium; (c) phosphate and silicate; and (d) in situ measurement of chlorophyll fluorescence and salinity during September 2013 – April 2014 from the West Gabbard SmartBuoy site.

Figure 3.37 presents the cycles of DOC, DON, TDN, TOxN, ammonium, phosphate and silicate from bag sample with the in situ parameters (chlorophyll fluorescence and salinity) over the main two periods (phase I (WG 94 samples) and phase II (WG 96 samples)). Additionally phase II, has been divided into two sub-periods (phase IIA and phase IIB). All phases were indicated by vertical dashed lines separating the record into seasonal pattern. Phase I is interpreted a 'post-bloom'

condition in autumn (07/09/13 – 05/10/13) where TOxN and chlorophyll flurorescence are increasing, whereas DOC and DON are decreasing. Phase IIA is the period starting from 02/02/14 in winter to 10/03/14 which is before the spring bloom period in Phase IIB where chlorophyll fluorescence starts to rise and TOxN declines from 14/03/14. Phase IIB is the period of the developing bloom as shown by fluorescence in Figure 3.36 and declining nutrients (particularly silicate, Figure 3.37c), but probably does not include the full spring bloom period. Each phase also showed different characteristics of water masses as shown in Figure 3.38 reflecting the complex circulation in the area. Variations of all nutrients and in situ parameters over the three phases are summarised in Table 3.9. The three phases were also applied later for the Dowsing sites.

Low (~0.4 – 1) fluorescence was recorded during the three phases of study period although calibration may change between deployments. However, the mean fluorescence measurement in early autumn of Phase I was significantly higher than later phases in winter and spring (ANOVA, $P < 0.05$). In Phase IIB, a slight increase of fluorescence was observed between 14/03/14 and 03/04/14 with a maximum reading of 0.8. This coincided with the steady decrease of TOxN concentration from 6.5 µM to below the detection limit (< 0.2 µM).

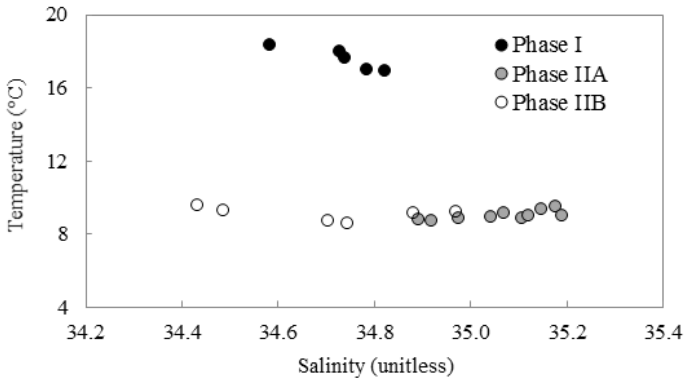


Figure 3.38 Characteristics of water masses in three phases at the West Gabbard SmartBuoy site.

Table 3.9 Summary of concentration of nutrient pools and in situ parameters over the study period at the West Gabbard SmartBuoy site.

Parameters *	Mean ± SD			Range		
	Phase I	Phase IIA	Phase IIB	Phase I	Phase IIA	Phase IIB
DOC (µM)	143.8 ± 20.1	155.0 ± 22.6	130.6 ± 30.0	119.2 – 178.7	132.8 - 201.3	95.6 - 185.0
DON (µM)	9.2 ± 0.9	13.4 ± 2.3	10.8 ± 2.2	8.2 – 10.6	9.5 – 16.0	8.0 – 15.0
DOC:DON ratio	15.7 ± 1.8	11.8 ± 1.8	12.3 ± 2.3	13.5 – 18.5	9.4 – 14.8	7.8 – 17.5
TOxN (µM)	5.5 ± 2.1	2.3 ± 2.6	1.5 ± 2.0	3.9 – 10.0	0.1 – 6.5	0.1 – 6.5
Ammonium (µM)	1.2 ± 0.7	1.1 ± 1.0	1.2 ± 2.0	0.4 – 2.2	0.2 – 3.3	0.2 – 7.6
Phosphate (µM)	0.5 ± 0.1	0.3 ± 0.1	0.2 ± 0.0	0.3 – 0.7	0.2 – 0.5	0.2 – 0.3
Silicate (µM)	4.3 ± 1.4	5.1 ± 0.6	3.1 ± 2.1	2. 9 -6.9	4.2 – 6.1	0.7 – 6.7
TDN (µM)	15.8 ± 1.7	16.8 ± 2.3	13.5 ± 3.3	13.9 – 18.9	13.1 – 20.5	9.0 – 20.5
DIN (µM)	6.6 ± 2.0	3.5 ± 2.3	2.7 ± 2.9	4.7 – 10.6	0.7 – 6.9	0.3 – 9.5
Temperature (°C)	17.3 ± 0.7	9.0 ± 0.3	9.1 ± 0.4	16.4 – 18.3	8.8 – 9.5	8.6 – 9.6
Salinity (unitless)	34.7 ± 0.1	35.1 ± 0.1	34.7 ± 0.2	34.6 – 34.8	34.9 – 35.2	34.5 – 35.0
Chlorophyll fluorescence (arbitrary unit)	1.0 ± 0.1	0.4 ± 0.1	0.5 ± 0.2	1.0 – 1.2	0.3 – 0.5	0.2 – 0.8
Oxygen concentration (mg/l)	7.5 ± 0.0	9.1 ± 0.1	9.6 ± 0.3	7.5 – 7.6	9.0 – 9.3	9.4 – 10.2
Oxygen saturation (%)	99.7 ± 1.1	101.8 ± 1.0	106.5 ± 4.1	98.0 – 100.7	100.5 – 103.6	103.5 – 114.8
Turbidity (FTU)	6.4 ± 3.0	10.2 ± 3.0	6.7 ± 2.9	3.8 – 12.3	5.4 – 14.2	4.2 – 12.2
Wave height (m)	1.4 ± 0.7	1.8 ± 1.1	0.9 ± 0.4	0.3 – 2.8	0.7 – 3.8	0.3 – 1.6

* Each parameter was significant difference between phases (ANOVA, $P < 0.05$), except ammonium.

Date collection of bag samples:

Phase I 07/09/2013 – 05/10/2013
Phase IIA 02/02/2014 – 10/03/2014
Phase IIB 14/03/2014 – 01/05/2014

TOxN, phosphate, DIN and the DOC:DON ratio had significantly higher levels in Phase I similar to the fluorescence, while silicate, TDN, DOC and DON showed the highest level in Phase IIA (ANOVA, $P < 0.05$). There was no significant difference between phases for ammonium concentration and the N:P ratio (DIN/phosphate) (ANOVA, $P > 0.05$). The N:P ratio (~11 to 15) was lower than the Redfield ratio of 16 suggesting potential nitrogen limit of the water column for phytoplankton growth. The salinity, turbidity and wave height showed significantly higher level in Phase IIA, whereas, significantly highest oxygen concentration and oxygen saturation was recorded in Phase IIB (ANOVA, $P < 0.05$). The mean temperature in early autumn of Phase I was significantly higher than later phases in winter and spring (ANOVA, $P < 0.05$). There was no significant difference between winter and spring for mean temperature (t-test, $P > 0.05$).

DOC and DON concentration declined in Phase I and Phase II (Figure 3.39). This is consistent with the decay of DON produced during the spring and summer, as previously reported (Suratman et al. 2010, Johnson et al. 2013). In Phase I, DOC and DON started to decay from 07/09/13 with initial concentration of 178.7 µM (DOC) and 10.1 µM (DON) to 05/10/13 with final concentration of 132.0 µM (DOC) and

8.3 µM (DON). To determine DOC and DON degradation rate, the linear regression analysis with time was used (as the best fit lines with gradients of -1.77 for DOC and -0.06 for DON in Figure 3.39). The approach has been used previously by Johnson et al. (2013) to obtain the rate of DON degradation. This yields net degradation rate of 1.77 µM d^{-1} for DOC and 0.06 µM d^{-1} for DON during Phase I. Similarly, the net degradation pattern is still present across Phase IIA and Phase IIB although the increase in DOC and DON between September and February periods, indicate an input of DOC and DON probably either from rivers or from biological processes. During the decay period (06/02/14 – 01 /05/14), DOC and DON decreased from 201.3 µM to 95.6 µM and from 15.7 µM to 8.3 µM, respectively. The decay rates during Phase II (A+B) determined by the linear regression analysis showed the best fit lines with gradients of -0.74 for DOC and -0.05 for DON (Figure 3.39). This yields the net decay rate of 0.74 µM d^{-1} and 0.05 µM d^{-1} for DOC and DON respectively. The results provided evidence of no DOC and DON production during the "spring bloom" period in Phase IIB as low fluorescence level (0.2 – 0.8) was recorded in this phase.

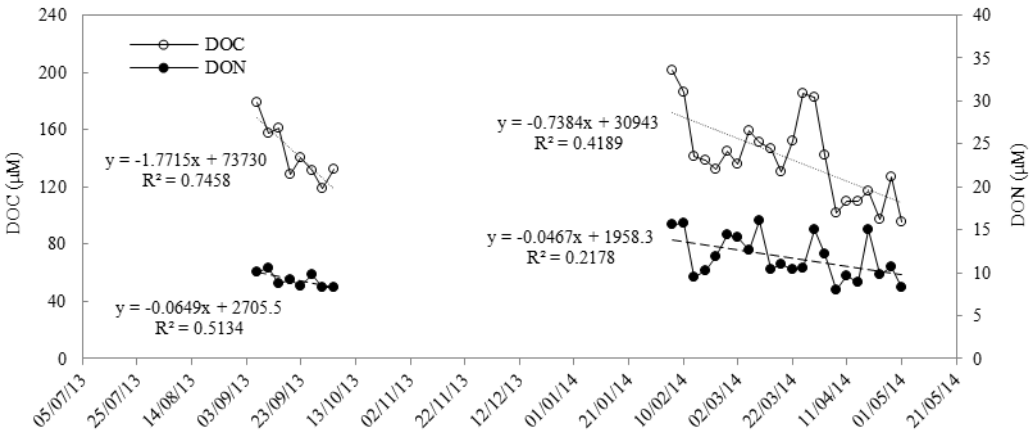


Figure 3.39 The DOC and DON degradation during 07/09/13 to 05/10/13 and 06/02/14 to 01/05/14 at the West Gabbard SmartBuoy site. The degradation rate is shown as gradients of the best fit line.

When considering the in situ parameter, Phase I demonstrated strong significant positive relationship between DOC and temperature ($R^2 = 0.81$, $P < 0.05$, $n = 8$). The DOC also showed strong significant negative correlation to salinity ($R^2 = 0.77$, $P < 0.05$, $n = 5$). For DON, the only significant positive correlation was

observed with temperature (R^2 = 0.60, P < 0.05, n = 8). In Phase IIA, DOC also presented strong significant positive correlation with temperature (R^2 = 0.51, P < 0.05, n = 10), but DON was not significantly correlated (P > 0.05). In the same pattern, DON had an insignificant correlation to salinity, temperature and chlorophyll fluorescence (P > 0.05) in Phase IIB, as well as DOC.

Although DOC and DON mostly showed no significant relationship at the 95% significance level (P > 0.05) with in situ parameters, their relationships with some variables are illustrated in Figure 3.40. The limit of the in situ data leads to low number of samples (n) available to test the correlation with DOC and DON and other data. In this present study, there was a biofouling problem on the in situ instruments which led to data not being available for the whole deployment (e.g. salinity and fluorescence). Data were then limited particularly at the end of each deployment (T. Hull (CEFAS), personal communication). The missing data are indicated in Appendix 3.11 where the results of SmartBuoy data was summarised.

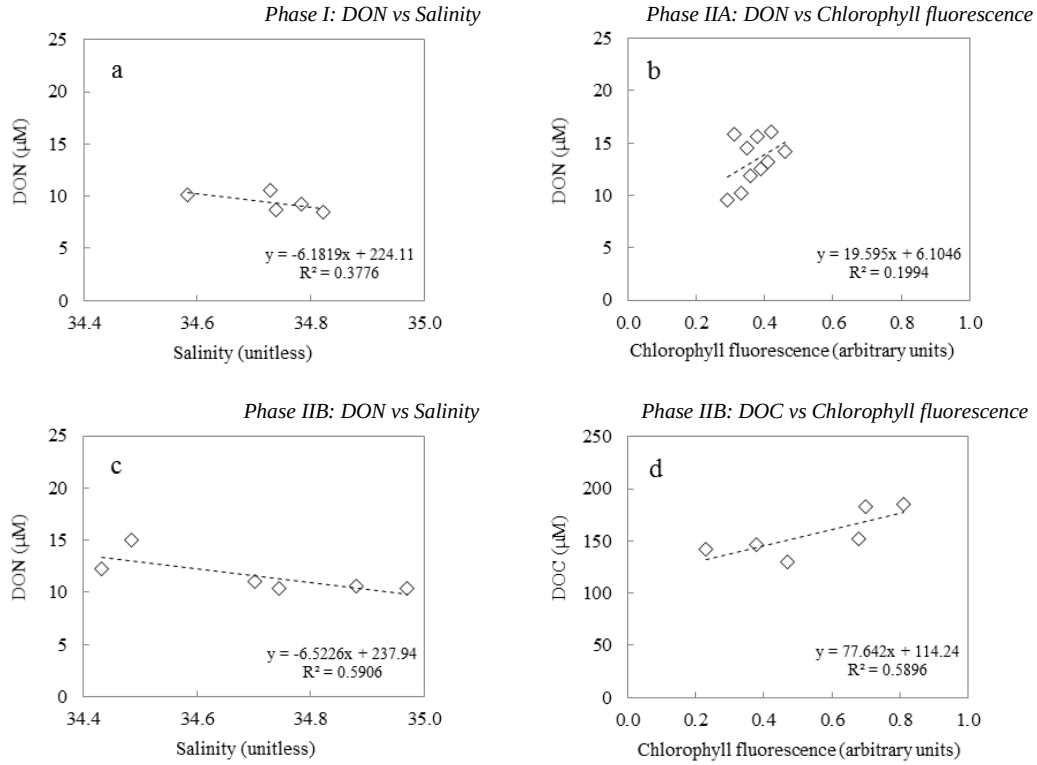


Figure 3.40 Relationship of DON with (a) salinity in Phase I, (b) chlorophyll fluorescence in Phase IIA and (c) salinity in Phase IIB; and relationship of DOC with chlorophyll fluorescence in Phase IIB at West Gabbard SmartBuoy site. Note a – b are not statistically significant correlated (P > 0.05)

3.7.2 Dowsing SmartBuoy

The Dowsing SmartBuoy in the southern North Sea is situated at a site where the water column is more impacted by water masses from the North than the West Gabbard, and also receives the river runoff from the UK mainland being located near the Humber and the Wash (Figure 3.35 and the current map in chapter 1 Figure 1.3b). The variation of in situ measurements is shown in Figure 3.41 including temperature, salinity, chlorophyll fluorescence, oxygen concentration and oxygen saturation; each parameter was recorded every 30 minutes during the time periods as at the West Gabbard SmartBuoy site. The data set considered here is much more complete than for the West Gabbard site. This high frequency data shows increasing chlorophyll fluorescence after the middle of March 2014, with associated increase of dissolved oxygen. The fluorescence level shows the spring bloom as an increase of the fluorescence lasting for two months from the middle of March to the middle of May with a maximum level of ~8 in the middle of April. The salinity in winter began to fluctuate considerably approximately two months before the spring bloom period. By contrast, the temperature shows the expected seasonal pattern with the highest temperature in summer and a decline to autumn and lowest value in winter. The temperature then increased again in the spring period.

Each in situ parameter was then subsequently chosen for the same date and time as bag samples were collected, in order to study their relationship (if any) to nutrients measured in bag samples. The seasonal cycles of DOC, DON, TDN, TOxN, ammonium, phosphate and silicate from the bag samples plotted with the in situ parameters (chlorophyll fluorescence and salinity) at the same date and time of nutrient collection are depicted Figure 3.42. The plot is divided into two main time periods (phase I and phase II) and two sub-periods in phase II (phase IIA and phase IIB) by vertical dashed lines, which are based on the salinity, chlorophyll fluorescence and TOxN data. Phase I is the period up to 24/01/14. Nutrients and chlorophyll fluorescence remain at low and steady levels, whereas DOC and DON decrease. Phase IIA is the period from 25/01/14 to 14/03/14 in which the salinity and TOxN are clearly fluctuating. The TOxN is subsequently depleted in Phase IIB (from 15/03/14) when the spring bloom develops with the chlorophyll fluorescence starts to rise up and eventually decline (Figure 3.41c). Figure 3.43 suggests different

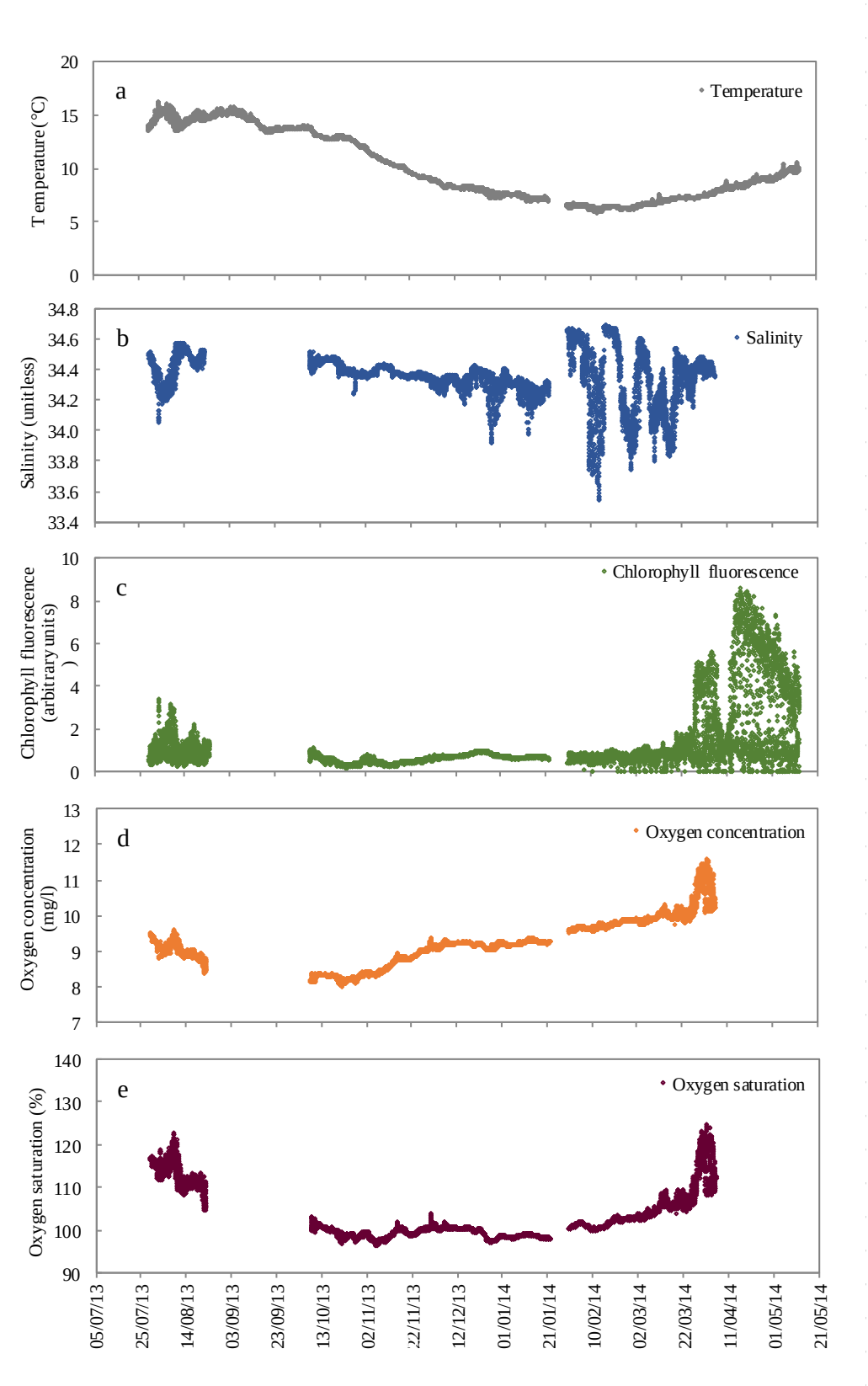


Figure 3.41 Variation of in situ parameters during July 2013 – May 2014 from Dowsing SmartBuoy: (a) temperature, (b) salinity, (c) chlorophyll fluorescence, (d) oxygen concentration, and (e) oxygen saturation.

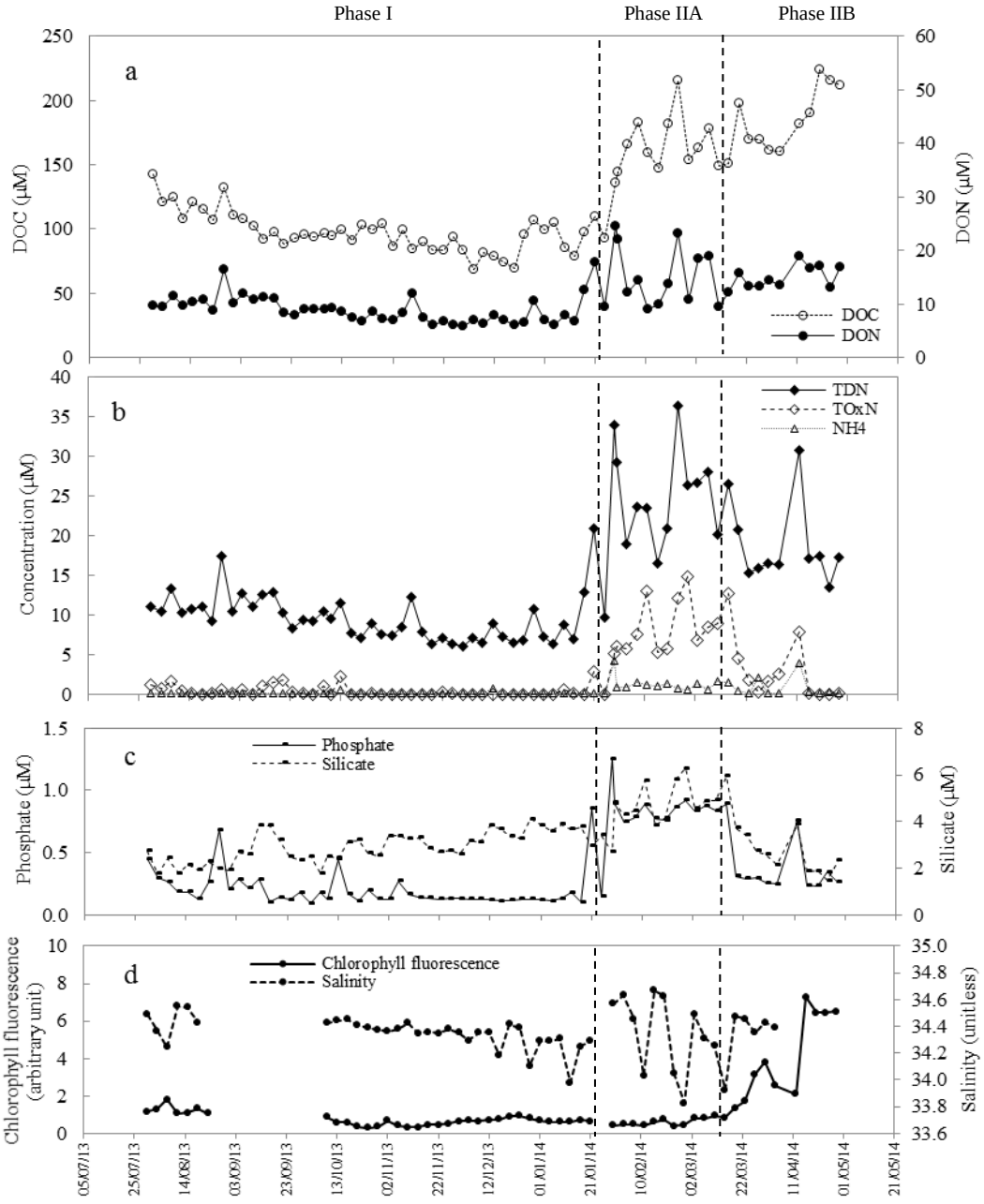


Figure 3.42 Variation of nutrients (a) DOC and DON; (b) TDN, TOxN and ammonium; (c) phosphate and silicate; and (d) in situ measurement of chlorophyll fluorescence and salinity during July 2013 – May 2014 from the Dowsing SmartBuoy site.

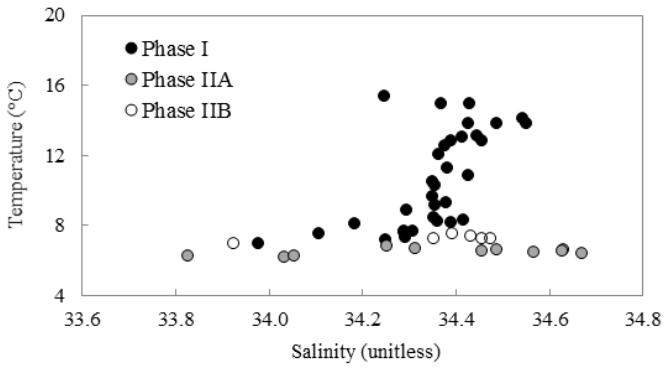


Figure 3.43 Characteristics of water masses in three phases at the Dowsing SmartBuoy site.

characteristic of the water mass in each phase. The mean level of all nutrients and in situ parameters over the three phases are summarised in Table 3.10

Table 3.10 Summary of concentration of nutrient pools and in situ parameters over the study period at the Dowsing SmartBuoy site.

Parameters [a]	Mean ± SD			Range		
	Phase I	Phase IIA	Phase IIB	Phase I	Phase IIA	Phase IIB
DOC (µM)	97.7 ± 15.6	159.3 ± 28.9	184.8 ± 24.9	68.3 – 142.6	93.3 – 215.7	150.7 – 224.0
DON (µM)	8.9 ± 2.6	15.1 ± 5.7	15.0 ± 2.1	5.8 – 17.8	9.1 – 24.5	12.2 – 18.9
DOC:DON ratio	11.4 ± 2.3	11.6 ± 3.6	12.4 ± 1.7	6.2 – 17.1	5.5 – 17.5	9.6 – 16.4
TOxN (µM)	0.5 ± 0.7	7.7 ± 3.9	2.9 ± 4.0	0.1 – 3.0	0.1 – 14.9	0.1 – 12.7
Ammonium (µM)	0.2 ± 0.1	1.3 ± 1.0	0.9 ± 1.2	0.2 – 0.9	0.2 – 4.3	0.2 – 3.9
Phosphate (µM)	0.2 ± 0.1	0.8 ± 0.2	0.4 ± 0.2	0.1 – 0.9	0.1 – 1.3	0.2 – 0.9
Silicate (µM)	2.9 ± 0.7	4.6 ± 1.0	2.9 ± 1.3	1.8 – 4.1	2.7 – 6.3	1.5 – 5.9
TDN (µM)	9.7 ± 3.0	24.2 ± 7.2	18.8 ± 5.2	6.1 – 20.9	9.7 – 36.3	13.6 – 30.7
DIN (µM)	0.7 ± 0.7	9.1 ± 3.9	3.8 ± 4.8	0.3 – 3.2	0.3 – 15.6	0.3 – 14.3
Temperature (°C)	11.9 ± 2.7	6.5 ± 0.2	7.9 ± 0.8	7.0 – 15.4	6.2 – 6.9	7.0 – 9.1
Salinity (unitless)	34.4 ± 0.1	34.4 ± 0.3	34.3 ± 0.2	34.0 – 34.5	33.8 – 34.7	33.9 – 34.5
Chlorophyll fluorescence (arbitrary unit)	0.7 ± 0.3	0.6 ± 0.2	3.8 ± 3.4	0.3 – 1.8	0.4 – 1.0	0.8 – 7.3
Oxygen concentration (mg/l)	8.9 ± 0.4	9.8 ± 0.1	10.3 ± 0.3	8.1 – 9.4	9.6 – 10.0	10.0 – 10.7
Oxygen saturation (%)	101.4 ± 5.5	102.0 ± 1.6	109.4 ± 3.3	96.7 – 116.1	100.1 – 105.7	105.1 – 114.7
Turbidity (FTU)	2.9 ± 2.1	3.1 ± 1.0	4.4 [b]	0.4 – 8.6	1.6 – 4.8	4.4 [b]
Wave height (m)	1.2 ± 0.8	1.3 ± 0.5	1.2 ± 0.6	0.3 – 4.3	0.6 – 2.3	0.4 – 2.6

[a] Each parameter was significant difference between phases (ANOVA, $P < 0.05$), except DOC/DON ratio, salinity, turbidity and wave height.

[b] no SD as only one data available during the period

Date collection of bag samples:
Phase I 30/07/2013 – 21/01/2014
Phase IIA 25/01/2014 – 11/03/2014
Phase IIB 15/03/2014 – 28/04/2014

Although there were variations with time during each phase, it is possible to compare the average concentration during each phase. Within the three phases, there was no statistical difference (ANOVA, $P > 0.05$) of the DOC:DON ratio, salinity, turbidity and wave height between phases. In contrast, all inorganic nutrients demonstrated a significant difference (ANOVA, $P < 0.05$) in concentration between phases, with the highest level in Phase IIA and the lowest level in Phase I. The same pattern was also found in TDN concentration and the N:P ratio (DIN/phosphate). The N:P ratio (~4 (Phase I), ~11 (Phase IIA) and ~8 (Phase IIB)) was lower than the Redfield ratio of 16 suggesting potential nitrogen limitation of water column for phytoplankton growth. By contrast, chlorophyll fluorescence had a significantly higher level (ANOVA, $P < 0.05$) in Phase IIB corresponding with the highest oxygen concentration and oxygen saturation recorded. There was no statistical difference (t-test, $P > 0.05$) between Phase I and Phase IIA for the value of chlorophyll

fluorescence, oxygen concentration and oxygen saturation. Similar to the fluorescence, DOC concentration was significantly higher (ANOVA, $P < 0.05$) in Phase IIB, with lower DOC values found in Phase IIA and Phase I respectively. No statistical difference (t-test, $P > 0.05$) was observed for DON concentration between PhaseIIA and Phase IIB. However, mean DON of Phase I showed significantly lower concentration ($P < 0.05$) than in Phase IIA and IIB. Only temperature showed significantly higher levels in Phase I (ANOVA, $P < 0.05$), lower temperatures were recorded in Phase IIB and IIA respectively, following the seasonal cycle.

During Phase I, the DOC and DON concentration declined (Figure 3.44). The DOC concentration continually decreased from 131.9 µM on 27 August 2013 to 69.7 µM on 20 December 2013, and the concentration of DON declined from 16.5 µM to 6.2 µM in the same period. This decline is suggested to reflect the degradation of DOC and DON produced earlier in the season by phytoplankton (Johnson et al. 2013). The linear regression analysis was used to determine DOC and DON net decay rate (as the best fit lines with gradients of -0.29 for DOC and -0.05 for DON). Rates calculated in this way are very sensitive to the chosen start and finish points. Here the slope has been calculated from the date after which the concentration showed a continuous decline (Figure 3.42a and Figure 3.44). This post autumn bloom period (27/08/13 – 20/12/13) yields net degradation rate of 0.29 µM d^{-1} and 0.05 µM d^{-1} for DOC and DON, respectively. The net degradation rate of DOC was approximately six times higher than the net rate of DON degradation and the mean concentration of DOC during Phase I was approximately eleven times higher than that of DON.

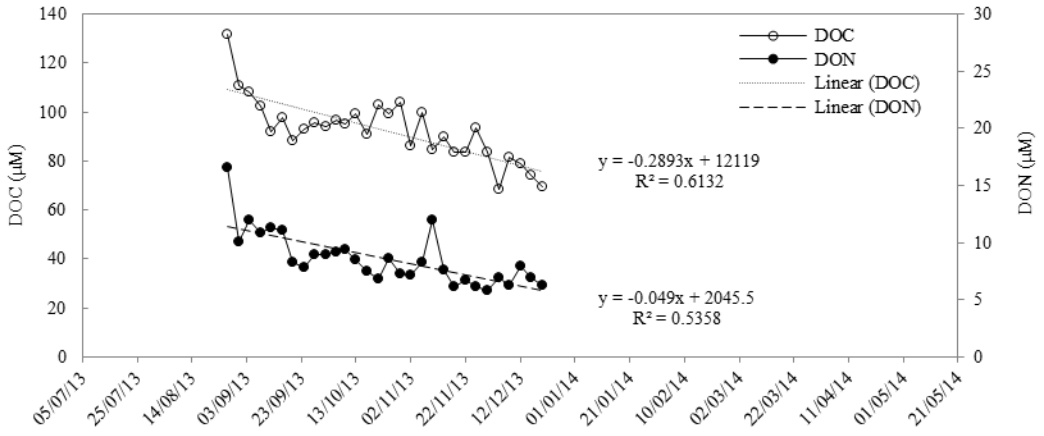


Figure 3.44 The DOC and DON degradation during 27/08/13 – 20/12/13 at the Dowsing SmartBuoy site. The degradation rate is shown as gradients of the best fit line.

In phase IIA, the concentration of DOC and DON were very variable and fluctuated between 93.3 – 215.7 µM for DOC and 9.1 – 24.5 µM for DON (Table 3.10). The variability was probably influenced by the environment rather than the DOM measurement as analytical precision (expressed as a coefficient of variation (CV)) was 2%, 4%, and 1% to 4% for DOC, TDN, and inorganic nutrient measurements, respectively (chapter 2). The salinity (Figure 3.41b),TDN and inorganic nutrients also fluctuated compared to the previous phase. These rapid fluctuations include not just pulses of low salinity water, as might be expected with major rain events loading to high river flow, but also particularly high salinity period (Figure 3.41b and Figure 3.43). The Dowsing site is located in the areas impacted by water masses from the north (Figure 3.35 and the North Sea current map in chapter 1 (Figure 1.3b). It is therefore suggested that a frontal boundary between low salinity southern North Sea water and higher salinity northern North Sea water may have passed backward and forward over this SmartBuoy several times during the period. The concentration of inorganic nutrients was significantly negatively correlated with salinity, showing strong relationships for TOxN ($R^2 = 0.98$, $P < 0.05$, $n = 11$), silicate ($R^2 = 0.93$, $P < 0.05$, $n = 11$) and phosphate ($R^2 = 0.58$, $P < 0.05$, $n = 11$). This indicated inorganic nutrient concentrations are influenced by riverine runoff.

It is clear that in Phase IIB the spring bloom developed with chlorophyll fluorescence rising. This bloom lasted for two months from the middle of March to the middle of May (Figure 3.41c). The fluorescence measured which corresponded with the time when nutrients from bag samples were available (Figure 3.42) also showed an increase in fluorescence level from 0.8 on 15/03/14 to the highest level of 7.3 on 16/04/14, the level then started to decline after the middle of April. This bloom coincided with a sharp decrease in TOxN concentration from 12.7 µM (15/03/14) to below the detection limit (< 0.2 µM) in the middle of April when the highest level of chlorophyll fluorescence was recorded. The statistical analysis also showed a significant negative correlation between TOxN and chlorophyll fluorescence ($R^2 = 0.51$, $P < 0.05$, $n = 11$) in this period. The results indicated TOxN was removed by phytoplankton during the spring bloom. In the same way, other inorganic nutrients presented the same declining pattern as TOxN, particularly silicate that had strong significant negative correlation with the fluorescence ($R^2 = 0.63$, $P < 0.05$, $n = 11$).

By contrast, DOC and DON concentrations increased during the spring bloom with a positive relationship with chlorophyll fluorescence. The DOC concentration increased from 150.7 µM on 15 March 2014 to the maximum 224.0 µM on 20 April 2014 (four days after the fluorescence reached its highest level), the DOC then slightly decreased to 211.6 µM on 28 April 2014. There was a small increase in concentration of the DON from 12.2 µM to the final 16.9 µM in the same period. Thus it seems that Phase IIB represents the spring bloom with increasing chlorophyll, declines in inorganic nutrients, and the net production of DOC and DON associated with the bloom as was seen by Johnson et al. (2013). There is no evidence of a lag between the bloom and DOC production, suggesting DOC is released during the growth phase and not just the bloom decline.

DOC and DON production rate during the spring bloom determined by the linear regression analysis showed the best fit lines with gradients of 1.23 for DOC and 0.08 for DON (Figure 3.45). This yields net production rate of 1.23 µM d^{-1} and 0.08 µM d^{-1} for DOC and DON respectively. In considering the fluorescence signal, the significant correlation was only found to DOC ($R^2 = 0.50$, $P < 0.05$, $n = 11$), the DON was not significantly correlated with the fluorescence ($R^2 = 0.13$, $P > 0.05$, $n = 11$). Highest mean oxygen concentrations (10.3 ± 0.3 mg/l) were also recorded in this phase as well as the highest mean oxygen saturation (109.4 ± 3.3 %). This was in agreement with a strong significant positive relationship between oxygen concentration and chlorophyll fluorescence ($R^2 = 0.94$, $P < 0.05$, $n = 6$), and oxygen saturation and fluorescence ($R^2 = 0.96$, $P < 0.05$, $n = 6$) reflecting net oxygen production during the spring bloom.

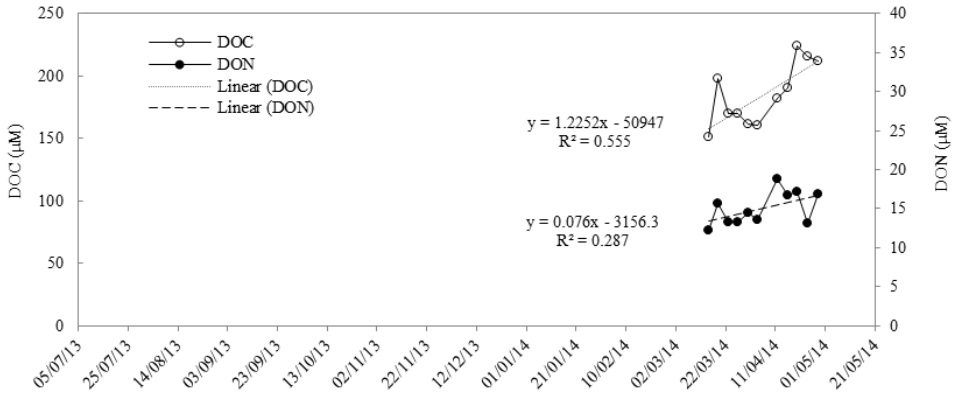


Figure 3.45 The DOC and DON production during the spring bloom period (15/03/14 – 28/04/14) at the Dowsing Smartbuoy site. The production rate is shown as gradients of the best fit line.

3.7.3 Discussion of the SmartBuoy samples

The feature of nutrient variation at the West Gabbard and Dowsing sites is presented in Figure 3.46. West Gabbard contained the highest mean TOxN and phosphate in Phase I covering early autumn 2013, while the lowest mean concentration of all inorganic nutrients was recorded at Dowsing as a result of an earlier and longer collection period starting from mid-summer 2013 when inorganic nutrients were low. However, both locations contained a higher inorganic nutrient stock in Phase IIA during the winter period compared to later Phase IIB in spring as the bloom started. Higher TOxN continually decreased to levels below the detection limit at the end of Phase IIB in response to phytoplankton uptake and growth during the spring bloom, as is most obviously seen at Dowsing. The West Gabbard site also showed a decline of TOxN but the signal of phytoplankton bloom was relatively less clear compared to the Dowsing, partly because sampling stopped before the full spring bloom period. In a similar pattern, phosphate and silicate declined during the spring bloom, with a slight decrease for phosphate at West Gabbard. Ammonium stayed at low concentrations at both locations over the study period.

The higher values of inorganic nutrients in winter than the spring agrees well with other studies in the North Sea (Riegman et al. 1990, Radach and Pätsch 1997, Dippner 1998, CabeÇadas et al. 1999, Hydes et al. 1999, Weston et al. 2004, Weston et al. 2008, Suratman et al. 2008a, Suratman et al. 2010, Johnson et al. 2013). The cruise surveys in this study also provided higher mean levels of TOxN, phosphate and silicate in winter than the summer (see subsection 3.1), whereas, ammonium was at low concentration over winter and summer and was at similar levels to those measured on the SmartBuoy samples. For phase IIA (i.e. winter before the spring bloom), TOxN, phosphate and silicate were influenced by riverine runoff during this period as shown by a negative correlation with salinity at Dowsing SmartBuoy site.

There was evidence of two distinct patterns for DOC and DON, net production during the spring bloom and net consumption in autumn. DOC and DON demonstrated different cycles between West Gabbard and Dowsing stations over the study phases. Although both sites had higher winter concentration in Phase IIA,

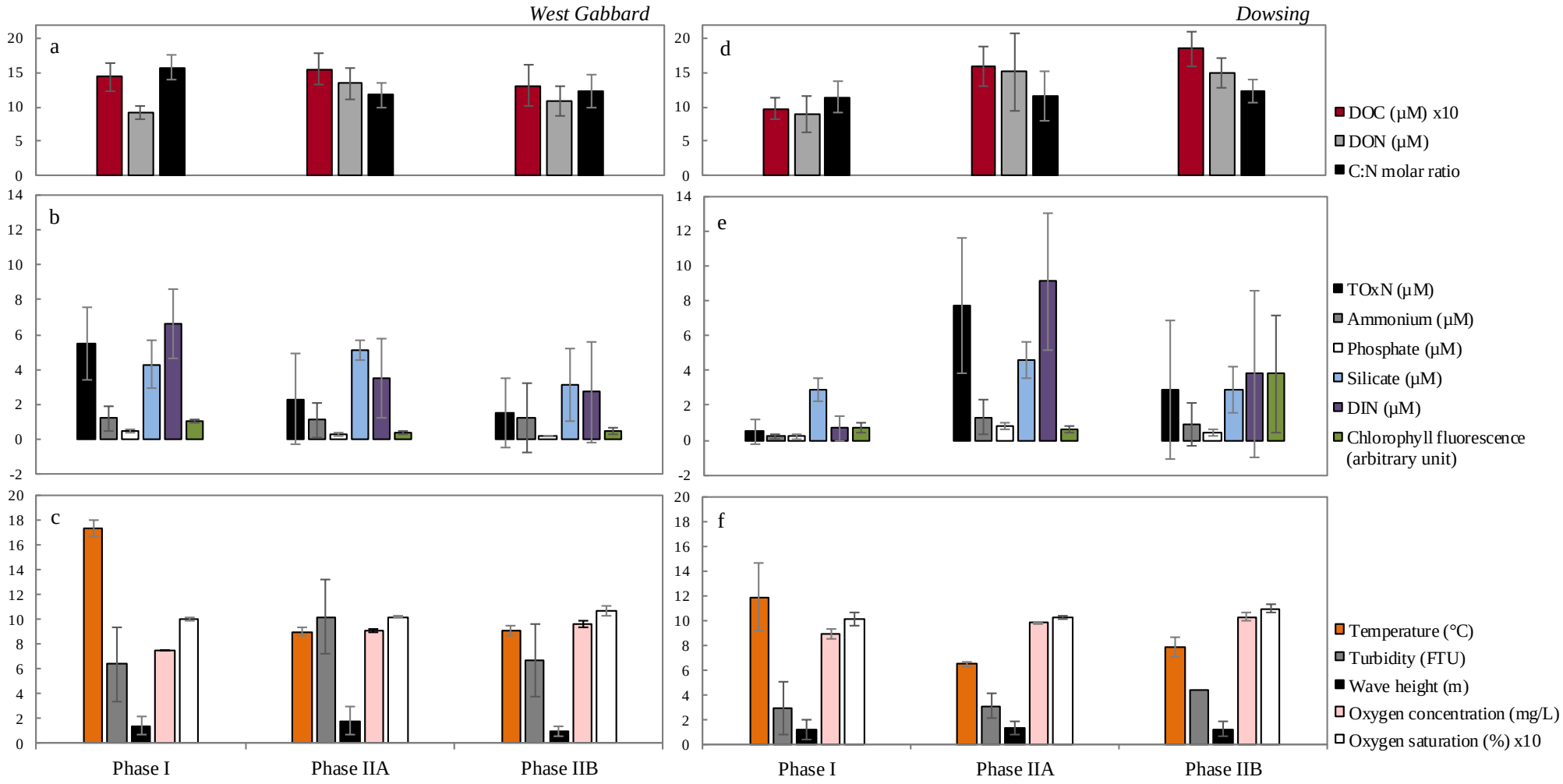


Figure 3.46 Variation of mean nutrients and in situ parameters in the three period (Phase I, Phase IIA and Phae IIB) at West Gabbard (a – c) and Dowsing (d – f) SmartBuoy sites. Error bars are standard deviation of samples in each phase. The absent error bar of turbidity in Phase IIB (f). Note units of DOC and oxygen saturation are multiplied by 10.

DOC and DON gradually decreased in spring (Phase IIB) at West Gabbard. By contrast, both organic pools increased over the spring bloom period at Dowsing. The increase in spring at Dowsing is expected as a result of the release of both DOC and DON by phytoplankton in the spring bloom period (Bronk and Glibert 1991, Collos 1992, Bronk et al. 1994, Hu and Smith 1998, Diaz and Raimbault 2000, Bode et al. 2004, Varela et al. 2005, Sintes et al. 2010, Suratman et al. 2010, Johnson et al. 2013). DON increased by approximately 5 µM during the spring bloom coinciding with the decrease of TOxN from ~13 µM to ~ 5µM during the spring bloom and then falling to below detection limit at the end of the period. This indicates a considerable part (~ 60%) of the TOxN uptake by phytoplankton was then released as the DON. DOC increased during the bloom by approximately 73 µM. The previous study reported 25 – 41 % of ammonium and nitrate taken up by phytoplankton is then released as DON (Bronk et al. 1994), while the percentage DON release was higher for a nitrate substrate (~ 42%) and lower (~ 22%) when ammonium was taken up by phytoplankton in another study (Varela et al. 2005).

The chlorophyll fluorescence peak of 7.3 during the spring bloom in Phase IIB at Dowsing site (Figure 3.42) in this present study was recorded. The highest level of chlorophyll fluorescence at the West Gabbard site (Figure 3.37) was notably lower for the same period with the value of 0.8 recorded. Therefore, different patterns in both DOC and DON at West Gabbard may be due to the evidence of a smaller spring bloom at this location corresponding with the higher turbidity observed and hence less light for phytoplankton, or that the spring bloom at the West Gabbard was later. The West Gabbard site illustrated a net degradation pattern for the whole of Phase II (A+B) with the net decay rate of 0.74 µM d^{-1} and 0.05 µM d^{-1} for DOC and DON respectively.

During the spring bloom in Phase IIB, Dowsing provided a net production rate of 1.23 µM d^{-1} DOC and 0.08 µM d^{-1} DON. Additionally, when the TOxN level fell to below the detection limit during this phase (after the middle of April in Figure 3.42), the results show a decline of DON (while DOC is still rising up) coinciding with the bloom starting to decrease. This may imply that phytoplankton used DON as an alternative source of nitrogen (Bronk et al. 2007).

A clear net degradation pattern of DOC and DON was observed during Phase I. At the Dowsing site, the post bloom yields net degradation rates of 0.29 µM d^{-1} and 0.05 µM d^{-1} for DOC and DON respectively. For the West Gabbard site, the net decay rate was higher, 1.77 µM d^{-1}, for DOC but this is for a short time period investigated, and the DON net decay rate of 0.06 µM d^{-1} was comparable with the Dowsing site. The DON rate at both SmartBuoy sites are in the similar order of DON net degradation rate at the Dowsing Smartbuoy site during the secondary bloom period in 2010 with a rate of 0.06 µM d^{-1} (Johnson et al. 2013). However, there are no DOC decay rate in the North Sea available to compare with the results calculated for this study. The decay rates of SmartBouy samples will be compared to incubated samples rates and discussed further in chapter 4 (section 4.2.4.1).

For DOM stoichiometry in each phase at West Gabbard and Dowsing SmartBuoy sites, a bulk C:N molar ratio was considered, instead of a slope C:N ratio, because only DOC and DON in Phase I at the Dowsing site were statistically significant relationship ($R^2 = 0.32$, $P < 0.05$, $n = 45$) with a regression equation $y = 3.44x + 66.97$. Hence no slope C:N ratio can be calculated in each phase. The variation of bulk C:N molar ratios in each phase at West Gabbard and Dowsing SmartBuoy sites are presented in Figure 3.47 and Figure 3.48 respectively. Each figure was separated based on phases described in previous section (section 3.7.1 and section 3.7.2). Mean C:N molar ratio of Phase I at West Gabbard site showed significantly higher concentration (ANOVA, $P < 0.05$) than in Phase IIA and IIB, while no statistical difference (ANOVA, $P > 0.05$) was observed for mean C:N molar ratio between phases at the Dowsing site. The C:N molar ratio in this study was in the range of other continental shelf waters and the mean ratio in this study (12.0 ± 2.6, $n = 100$ for both SmartBuoy sites) was in agreement with previous report in the southern North Sea (10.8 – 14.8) observed for 10 years during 1995-2004 (Van Engeland et al. 2010) and reports in this study from the survey cruises observed in the southern North Sea during summer 2011 (11.1 ± 1.6, $n = 45$) and summer 2012 (12.6 ± 2.8, $n = 46$). Values for C:N molar ratio in the continental shelf waters generally range between 11 and 19 in the surface water (Hansell et al. 1993, Hopkinson et al. 1997, Bates and Hansell 1999, Hopkinson et al. 2002, Wetz et al. 2008, Kim and Kim 2013), however, higher ratios can also be observed, for instance, 13 – 30 in the northeastern shelf of the Gulf of Cádiz (Ribas-Ribas et al. 2011), 27.6

in the eastern Gulf of Mexico (Sipler et al. 2013) and 4.9-25.1 in the East China Sea (Chen et al. 2016). There were substantially higher C:N molar ratios in this study (12.0 ± 2.6, n = 100) than the Redfield ratio of 6.6, implying that the DOM in both SmartBuoy sites are C-rich and N-poor.

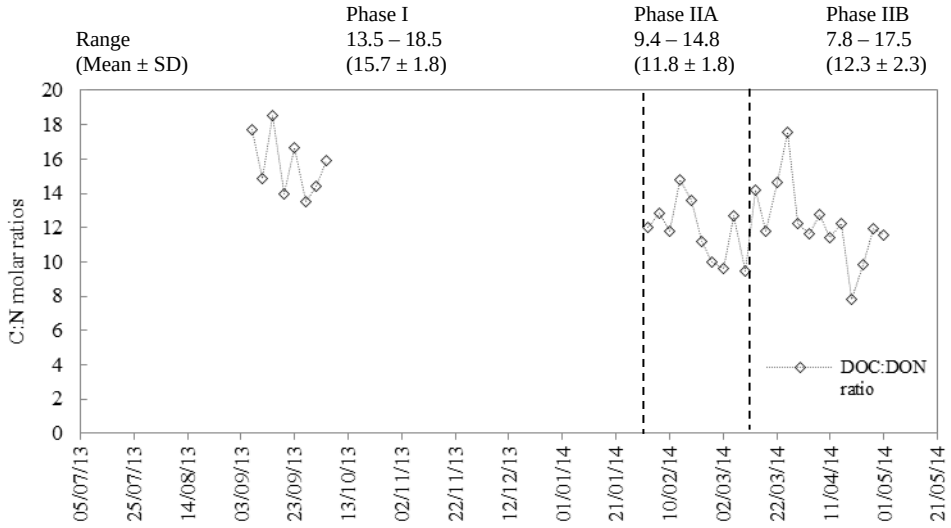


Figure 3.47 Variation of molar stoichiometry of the bulk DOM pool for DOC:DON ratios during September 2013 – April 2014 at the West Gabbard SmartBuoy site.

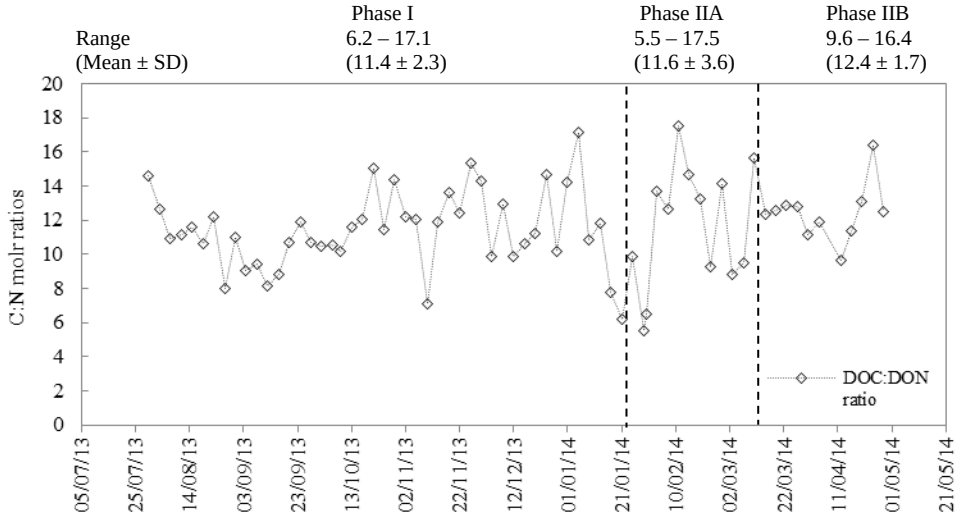


Figure 3.48 Variation of molar stoichiometry of the bulk DOM pool for DOC:DON ratios during July 2013 – May 2014 at the Dowsing SmartBuoy site.

Although DOC and DON in each phase generally did not show a significant correlation (P > 0.05), Figure 3.49 shows the correlation between DOC and DON of

the whole data sets at West Gabbard and Dowsing SmartBuoy site. For the regression of DOC versus DON at West Gabbard, the statistically significant positive correlation was found at the 95% significance level ($R^2 = 0.28$, $P < 0.05$, $n = 31$), a slope C:N ratio of 5.6. In addition, the Dowsing site provided the significant correlation ($R^2 = 0.53$, $P < 0.05$, $n = 69$) with the slope C:N ratios of 6.8.
In comparison with mean bulk C:N molar ratio of the whole data sets in each SmartBuoy site (13.0 ± 2.6, n =31 for West Gabbard and 11.6 ± 2.5, n =31 for Dowsing), the slope C:N ratio for each site was lower as the slope C:N ratio is the C:N stoichiometry of degradable DOM which is generally lower than a bulk C:N molar ratio (Hopkinson and Vallino, 2005). This pattern of the slope C:N ratio being lower than bulk C:N molar ratio is also reported in the central North Sea (Suratman et al. 2009) and other shelf waters (Hopkinson et al. 1997, Hopkinson and Vallino 2005, Lønborg et al. 2010). The slope C:N ratio of the whole data sets (Figure 3.49) was close to the Redfield ratio of 6.6 suggesting an important role of phytoplankton in the water column at both sites that the labile DOM is partly released from phytoplankton in the water column.

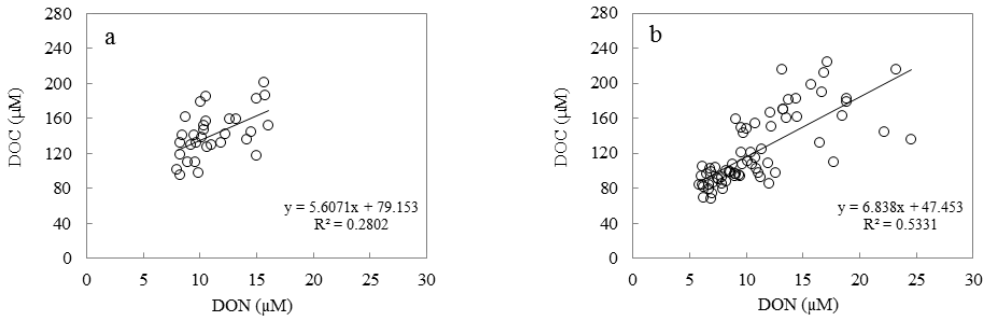


Figure 3.49 Relationship between DOC and DON (DOC = mDON + c, where m = gradient and c = intercept) for the whole data sets of (a) West Gabbard and (b) Dowsing SmartBuoy site.

The N:P ratios (DIN/phosphate) was also investigated at both SmartBuoy sites. The N:P ratios of~11 to 15 at West Gabbard and ~ 4 to 11 at Dowsing SmartBuoy site were lower than the Redfield ratio of 16 suggesting potential nitrogen limit of water column for phytoplankton growth.

The most obvious difference between West Gabbard and Dowsing sites is that the spring bloom was clearly seen at the Dowsing site in Phase IIB as the sharp increase of chlorophyll fluorescence coinciding with the decrease in inorganic nutrients and increase of DOC and DON. The West Gabbard also showed a decrease in inorganic nutrients in the same period but the DOC and DON decreased with only a slight increase of the fluorescence reading. Low chlorophyll fluorescence at West Gabbard in all three phases (0.2 – 1.2), particularly in the spring (0.2 – 0.8) compared to the Dowsing site (0.8 – 7.3) was expected in response to higher turbidity at West Gabbard location. The turbidity for all three phases at West Gabbard ranged from 3.8 -14.2 FTU (Phase IIA 5.4 – 14.2 FTU), higher than the range of Dowsing with 0.4 – 8.6 FTU. This is the normal turbidity distribution pattern as shown in Figure 1.4 (chapter 1). Additionally, mean chlorophyll fluorescence at West Gabbard (0.6 ± 0.3) was significantly ($p < 0.05$) lower than Dowsing (1.3 ± 1.6). Conversely, West Gabbard had significant higher mean turbidity (8.0 ± 3.4 FTU) than Dowsing (2.9 ± 1.9 FTU) ($p < 0.05$). Therefore, higher turbidity seen at West Gabbard during late winter probably influenced the fluorescence by prolonged light inhibition, leading to the low spring bloom at West Gabbard during the study period, although it may have occurred later and not been seen in this study.

Concentrations of TOxN recorded in Phase IIA at West Gabbard (0.1 – 6.5 µM, mean 2.3 ± 2.6 µM) were lower than at Dowsing (0.1 – 14.9, mean 7.7 ± 3.9 µM). This may lead to less nutrients available for the spring bloom occurring in the next phase. Thus, lower TOxN in winter probably also played a role in the low chlorophyll fluorescence obtained at West Gabbard. The low growth of phytoplankton in this site during Phase IIB influenced the low release of DOC and DON at the time and possibly explained why DOC and DON showed the degradation pattern rather than the production pattern as Dowsing site. Additionally, a previous study in the Marsdiep tidal basin (Wadden Sea) also showed that the spring – summer DOC and DON stock was related to elevated extracellular release by phytoplankton and this was almost the only way to support the bacterial carbon demand (BCD) over the spring – summer period, while BCD during autumn – winter was supported by both release by phytoplankton and the DOC – DON stock from spring – summer (Sintes et al. 2010). This suggests that less phytoplankton at West

Gabbard site during the study period, particularly in spring, provided less DOC and DON available for bacteria. Thus, the pattern of DOC and DON at this site demonstrated a decreasing trend with time in all the studied phases, while an increasing concentration was shown in spring at Dowsing site and decreasing at other times.

In conclusion, in situ high frequency data combined with nutrient data from bag samples obtained from the SmartBuoy, provides useful time series information in addition to the survey data. The seasonal cycle is dominated by the spring bloom which develops when light condition is first allow. This consumes inorganic nutrients stocked during the winter period which are influenced by riverine runoff. In general, there is a net production of DOC and DON during the spring bloom and net consumption in autumn. The N:P ratios at both sites were lower than the Redfield ratio of 16 suggesting potential nitrogen limitation of water column phytoplankton growth. The DOM in both SmartBuoy sites is C-rich implied by a substantially higher bulk C:N molar ratio in this study than the Redfield ratio of 6.6, while the slope C:N ratio of the whole data set at each site was close to the Redfield ratio suggesting an important role of phytoplankton in the water column. To the best of our knowledge, this present study was the first in the North Sea to measure DOC and DON along with inorganic nutrients and in situ parameters from SmartBuoys. The previous studies of SmartBuoy samples in the North Sea did not include the DOC pool (Suratman et al. 2010, Johnson et al. 2013). The growth of phytoplankton was responsible for both the release and consumption of organic nutrients under the available of inorganic nutrients condition at both sites but at different rates and extents.

3.8 Summary discussion

This study is the first attempt to investigate both DOC and DON and inorganic nutrient together in the whole North Sea. The investigation provided useful information on nutrient distribution patterns over the summer period as the thermal stratification occurred in the water column. While inorganic nutrients concentrate in the bottom water, organic compounds (DOC, DON, POC and PON) and chlorophyll *a* were found high concentration in the surface, particularly in the southern well-mixed water. DIN was removed and returned as DON, and DON became the main nitrogen

form in the water column. In comparison to the Redfield ratio, the bulk C:N molar ratio of DOM in this study was enriched in carbon relative to nitrogen, while the slope C:N ratio was close to the Redfield ratio with a background level of DOC of ~ 30 µM when DON reaches zero. The stratified bottom water had higher DOC:DON molar ratios than the surface in summer 2011 implying the preferential remineralisation of N compared to C and/or high C:N molar ratio material input from offshore. No preferential remineralisation of N or C observed in the POM pool as C:N molar ratio of POM was similarly in all water masses with close to the Redfield ratio. The data obtained from the winter survey were used to determine the different distribution pattern between winter and summer seasons in the southern North Sea. A significantly higher DOC and C:N molar ratio in winter than the summer in 2011 was partly influenced by riverine input of high C:N materials.

The cruise survey results reveal a clear coherent DOC and DON distribution which concentrated in the southern North Sea. The overall results revealed salinity as a key factor controlling both DOC and DON via riverine runoff. There are two components to the DOM, a biologically cycled component with phytoplankton derived like composition and a background high DOC:DON component. In addition, chlorophyll *a* was associated with POC and PON distribution during summer. Although the survey result did not show the influence of chlorophyll *a* on DOC and DON distribution pattern, the SmartBuoy samples clearly identified that the chlorophyll *a* was the important factor producing DOC and DON to the water column, particularly at the Dowsing site during the spring bloom. There is a net production of DOC and DON during the spring bloom, while net consumption in autumn. A substantially higher bulk C:N molar ratios in this study than the Redfield ratio of 6.6, implying that DOM pool in both West Gabbard and Dowsing SmartBuoys are C-rich as found in the cruise survey results.

4 INCUBATION EXPERIMENTS

In this chapter, results and discussion of incubation experiments including experiments onboard in summer and laboratory based experiments in autumn, winter and spring are presented. The experiments onboard (section 4.1) were performed on Smart Buoy cruise (CEND 12/12) and IBTS cruise (CEND 13/12) during summer 2012. Samples were collected from 3-4 m depth surface water with Niskin bottles at three stations including station WG, 9 and 24 (Figure 2.1 in chapter 2) to estimate degradation of DOC and DON based on ship board incubation experiments.

Later experiments in 2013-2014, with incubations started onboard and continued at the UEA laboratory are detailed in section 4.2. In this experiment, water samples were collected with Niskin bottles from surface water (2-4 m depth) of WG and DS (Figure 2.1 in chapter 2) on Smart Buoy cruise CEND 19/13, CEND 3/14 and CEND 08/14 for autumn 2013, winter 2013 and spring 2014, respectively. This work provides the data for the determination of DOC and DON degradation and production rate constants over the course of incubation for these laboratory based experiment. Although the summer 2012 experiments showed some procedures were not suitable to continue without modification, valuable information was obtained to help design the later three seasonal experiments. The rationale for the experiment is described in chapter 2. The results and discussion of all experiments are presented here; first for the summer 2012 onboard experiment (section 4.1) and then the later onboard-laboratory experiment (section 4.2).

4.1 Incubation experiments onboard

4.1.1 Initial conditions of samples

The seawater used to initiate the experiment was first filtered through 200 µm mesh to remove large zooplankton, while phytoplankton and microzooplankton (< 200 µm) were still contained in the filtrate (Sieburth et al. 1978, Calbet 2008). Sub-samples of incubated water were analysed on day 0, 2, 4 and 5 (day 7, 10, 15 and 20 for set 1 of station WG only) for inorganic nutrients, DOC and DON

concentrations. Results of nutrient concentrations in all treatments during the incubation period are shown in Appendix 4.1. Additionally, before the start and after the finish of the incubation, samples were collected for chlorophyll *a* determination. Table 4.1 presents details of the sampling site and initial properties of water at each station. Temperature during incubation was controlled by continuous flow of the online supply water onboard, imitating the natural ambient seawater temperature at the time of collection. The temperature was regularly measured during the incubation and varied between 16-19 °C.

Table 4.1 Sampling sites for incubation experiments in summer and temperature and salinity of water at the time of collection.

Station	Latitude	Longitude	Date	Temperature (°C)	Salinity	Sample depth (m)	Water column depth (m)
WG	51.59.197 N	02.04.897 E	02 Aug 12	16.5	34.8	3	25
9	53.49.800 N	02.39.583 E	10 Aug 12	15.8	34.7	3	68
24	55.49.580 N	01.14.731 E	16 Aug 12	17.6	34.8	4	86

The abbreviations used in figures i.e. T1-T6 represent samples treated in different ways and with different chemicals as described in chapter 2 section 2.3.2. To aid the reader, Table 2.5 (in chapter 2) is repeated here.

Table 2.5 Experimental treatments on summer 2012.

Condition	Treatment [a]		Description
Dark	T1	No addition	No photosynthesis
	T2	Add antibiotics	Reduced microbial decomposition
	T3	Add 1 ml of 10 mM NH_4Cl (final concentration 5.0 µM N)	To test for N limited degradation
	T4	Add 1 ml of 1 mM Na_2HPO_4 (final concentration 0.5 µM P)	To test for P limited degradation
Light	T5	No addition	Whole microbial community
	T6	Add antibiotics	Phytoplankton community with reduced microbial decomposition

[a] Water samples were filtered through 200 µm mesh

Initial DOC and DON concentrations on day 0 are shown in Figure 4.1 with no data for antibiotics treated samples (T2 and T6) because of limitations of the analysis as detailed in section 4.1.4. In general, higher DOC and DON

concentrations are present at station 9. Initial mean DOC concentrations ranged from 87.9 to 91.0 (station 9), 80.2 to 85.8 (station 24) and 75.5 to 83.6 (station WG) µM, while initial mean DON concentration ranged from 5.4 to 6.6 (station 9), 5.6 to 6.6 (station 24) and 4.7-5.9 (station WG) µM.

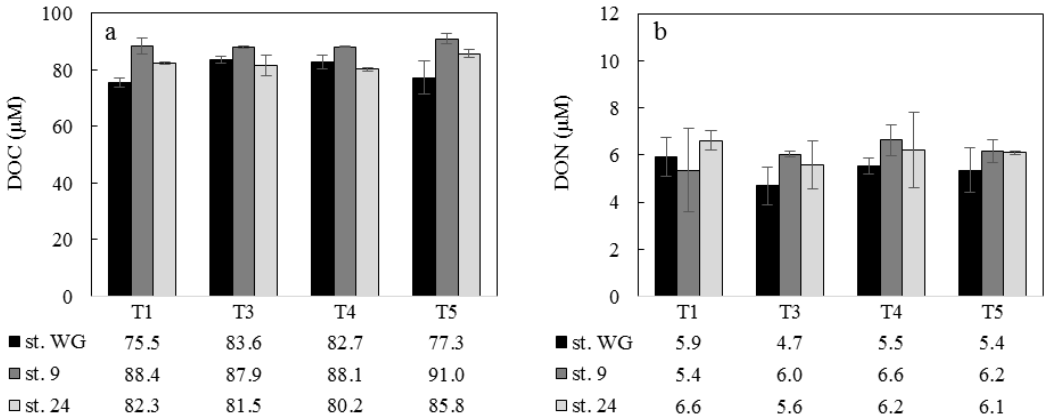


Figure 4.1 Initial DOC (a) and DON (b) concentrations of incubated water in summer 2012 for station WG, station 9 and station 24. The numbers represent the mean concentration and error bars are standard deviation of duplicate incubation bottles. Antibiotic treated bottles (T2 and T6) are not shown in the graph.

Ideally, T1 and T5 treatments should have the same concentration as both had no chemicals added to the seawater used to initiate the experiment, but both presented slightly different concentrations (Figure 4.1). However, the statistical test showed no significant difference in initial DOC concentration between T1 and T5 treatments ($P > 0.05$). Similarly to DOC, for DON there was no significant difference ($P > 0.05$). Thus the differences are within analytical uncertainties. The initial DOM concentrations were similar to those found in the area surrounding Dogger Bank in the North Sea, with northern Dogger Bank contains 89 ± 21 µM DOC (Suratman et al. 2009) and 4.2 ± 1.2 µM DON (Suratman et al. 2008a) in summer. Initial DOC and DON concentrations of incubated water in summer 2012 (Figure 4.1) were also in line with the survey results in summer 2011 in this study (80.3 ± 14.4 µM DOC and 7.2 ± 1.5 µM DON for the whole surface water in the North Sea).

4.1.2 Chlorophyll *a* variation

Samples were collected before and after filtration through 200 µm mesh to investigate the impact of filtration on chlorophyll *a* content. This approach is expected to remove large zooplankton from water samples before the start of the incubation with less effect on phytoplankton. Statistically significant positive correlation was found between concentration in all the sample before and after filtration ($R^2 = 0.97$, $P < 0.05$, $n = 6$) (Figure 4.2). In addition, fluorimetric measurement presented no significant difference ($P > 0.05$) of chlorophyll *a* concentration between unfiltered and 200 µm filtered samples at all stations, but there were significant differences between stations (ANOVA, $P < 0.05$) (Figure 4.3), hence 200 µm filtration appears to not remove phytoplankton. Appendix 4.2 summarises chlorophyll *a* concentrations for the summer 2012 experiment. In six treatments, the light condition (T5 and T6) treatments generally showed higher chrophyll *a* concentration than the dark at the end of the incubation. This was particularly the case for station 24, where chrophyll *a* concentration at the end of the incubation was higher than the initial concentration in both duplicate samples (set 1 and set 2).

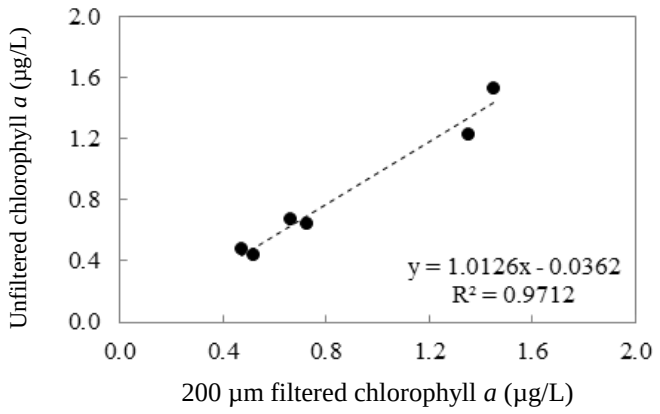


Figure 4.2 Relationship between concentration of chlorophyll *a* before and after filtration with 200 µm mesh in summer experiment for all station.

Chlorophyll *a* was detected in all dark treatments (T1-T4), except station WG set 1 where concentrations generally were below detection limits (0.1 µg/L.) as the incubation was extended to day 20. This indicates 200 µm filtered samples under

dark conditions showed only a slow loss of viable phytoplankton as measured by chlorophyll *a* concentration over 5 days. In the light condition, antibiotic addition (T6) seems not to affect phytoplankton biomass, as no significant difference ($P < 0.05$) of chlorophyll *a* between T5 and T6 was observed.

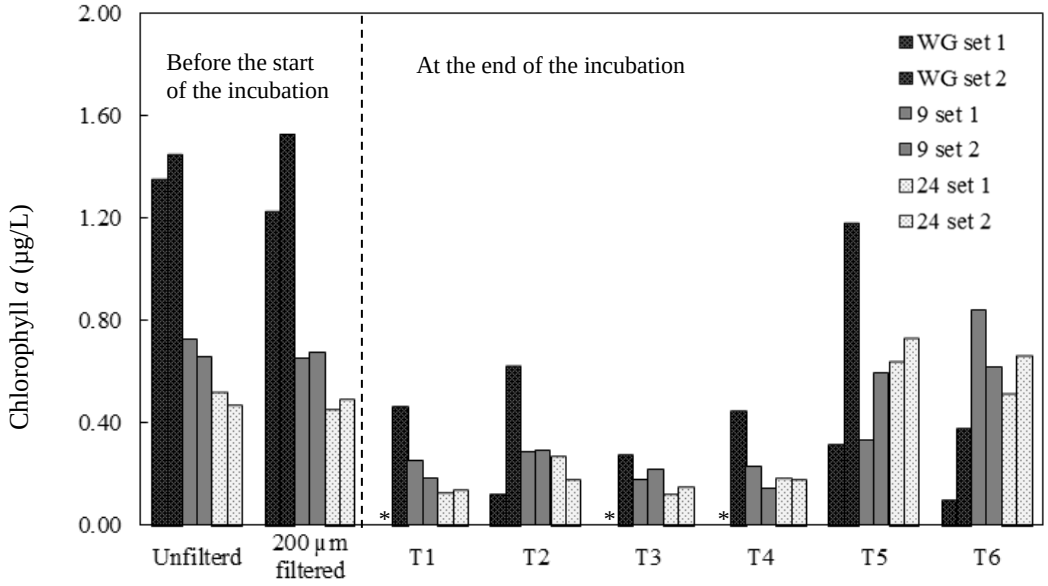


Figure 4.3 Initial concentrations of chlorophyll *a* before the start of the incubation (unfiltered and 200 µm filtered) and the concentration at the end of the incubation on day 5 (on day 20 for WG set 1) in each treatment (T1-T6) for station WG, 9 and 24 in summer. The duplicate bar represents set 1 and set 2. An absent bar (*) of WG set 1 in T1, T3 and T4 represents results below the detection limit (< 0.1 µg/L).

4.1.3 Variation of dissolved inorganic nitrogen

Initial mean concentration of dissolved inorganic nitrogen (DIN) ranged from 0.4 ± 0.1 to 6.2 ± 0.6 (station WG), 0.4 ± 0.1 to 5.9 ± 3.9 (station 9) and 0.3 ± 0.0 to 4.5 ± 0.2 (station 24) µM in the seawater used to initiate experiments at each station (Table 4.2). There was no significant difference in DIN concentration between stations (ANOVA, $P > 0.05$), but the concentration was significantly different between treatment (ANOVA, $P < 0.05$). High concentration was found in T2, T3 and T6 in which chemicals were add to seawater. The cocktail of antibiotics were added to T2 and T6, while ammonium chloride was added to T3, leading to DIN increase compared to original seawater (T1 and T5). Treatments with no chemical addition (T1 and T5) representing the normal sampling site condition showed low DIN

summer water for all three stations (0.4 ± 0.1 to 1.0 ± 0.1 µM) and the DIN concentration was dominated by ammonium concentration.

Table 4.2 Initial mean DIN concentrations (µM) of incubated water in summer for station WG, station 9 and station 24.

Station	DIN concentration (Mean ± SD [a])					
	T1	T2	T3	T4	T5	T6
WG	0.4 ± 0.1	5.8 ± 0.5	6.2 ± 0.6	0.8 ± 0.4	0.4 ± 0.2	4.9 ± 1.9
9	0.4 ± 0.1	5.9 ± 3.9	2.4 ± 0.4	0.7 ± 0.1	0.4 ± 0.1	4.9 ± 1.4
24	0.7 ± 0.5	4.5 ± 0.2	3.6 ± 0.5	0.3 ± 0.0	1.0 ± 0.1	4.0 ± 0.6

[a] SD is standard deviation of duplicate incubation bottles (set 1 and set 2) in each treatments (T1-T6)

The DIN variations (normalized to initial DIN concentrations) over the course of incubation are shown in Figure 4.4. The response of the DIN to the experimental treatment varied between stations. At station 24, there were less than 2 µM change in the DIN pool over the 5 days in all treatments, except in T6. There was evidence of the significant increase ($P < 0.05$) in T6 in all experiments, note changed scale in Figure 4.4 for T6 result. This indicates antibiotic addition to the incubation produced significant changes in the DIN pool under light conditions (T6), approximately 10 times above other treatments. Basically, there are two possible ways to explain why the treatment with light condition and added antibiotics (a treatment designed to look at the action of the phytoplankton community with an expected reduction in microbial decomposition rate) shows a sharper increase in DIN than other treatments in all stations over the incubation time:

1) Light breakdown of antibiotic to DIN
2) Sunlight leads to indirect impacts on DOM removal (Carlson 2002).

When DOM absorbs sunlight, photodegradation leads to the average molecular weight reducing and the formation of various photoproducts (Zepp et al. 1998). Therefore, it is possible that initial DOM and also DOM production by phytoplankton over the incubation time (20 days or 5 days) has been modified by photochemical processes. The photochemical breakdown of DOM can release inorganic compounds (Bushaw-Newton and Moran 1999, Moran and Zepp 1997). Therefore, the treatment condition with light and added antibiotics (T6) may promote phytoplankton growth, and release more DOM by phytoplankton. This DOM is then excited by sunlight and breaks down to form an inorganic compound such as inorganic nitrogen. Also, there are fewer bacteria to take up the inorganic nitrogen

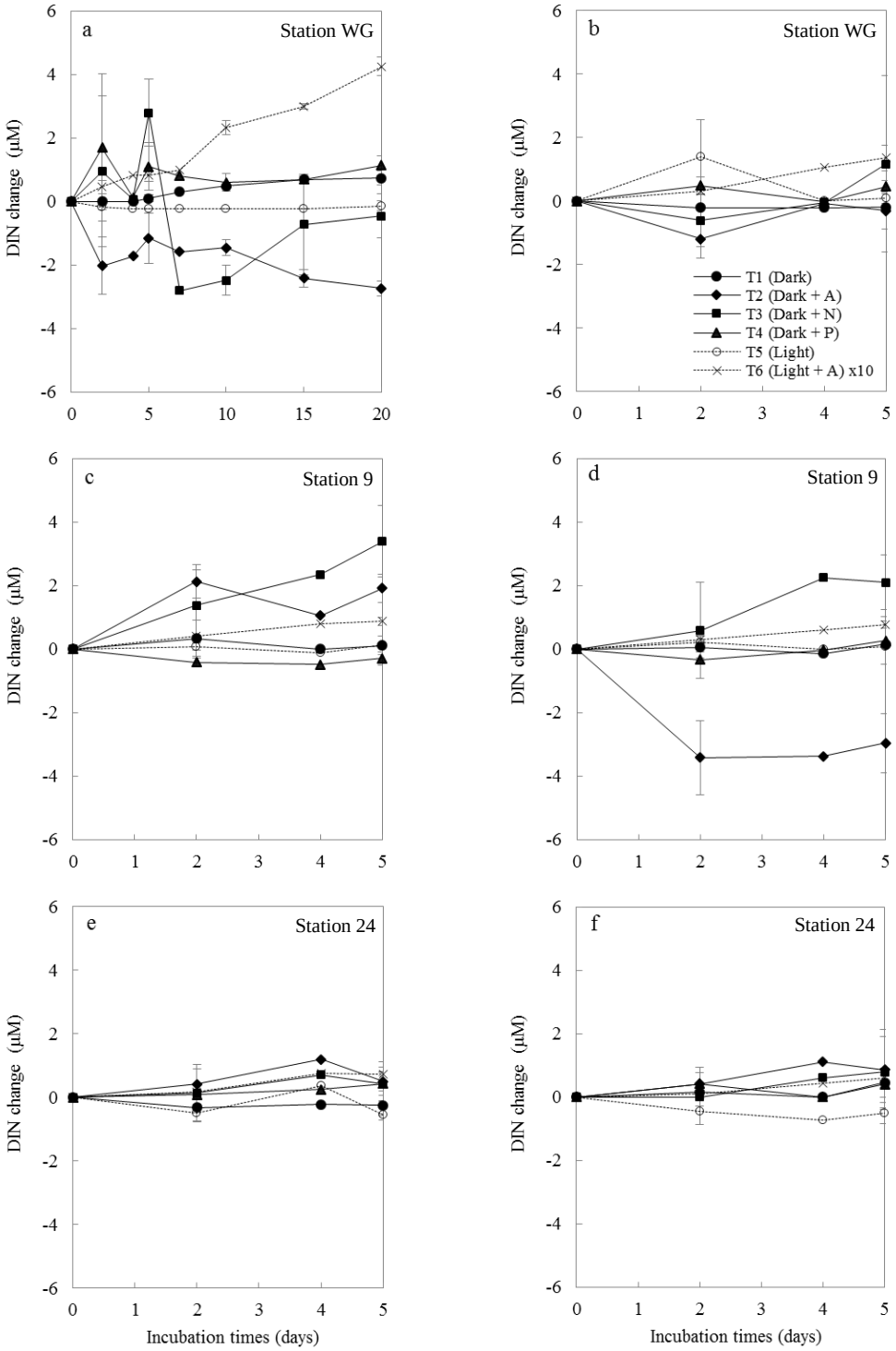


Figure 4.4 Change in DIN of duplicate incubation bottles (set 1 and set 2) at station WG (a, b), station 9 (c, d) and station 24 (e, f) in summer. Error bars are standard deviation of triplicate subsamples on day 2, 5, 10,15 and 20. Note the concentration unit of antibiotic treated bottles under light condition (T6) is multiplied by 10.

(due to added antibiotics), causing the higher DIN concentration over the incubation time.

Therefore, whether light can break down the antibiotic to DIN or not was tested between 25 June – 21 July 2013 (26 days). To do this, artificial seawater (32 g/l NaCl solution) was divided into two bottles (2 liter size, polycarbonate): a control bottle (filled only with artificial seawater) and an antibiotic treated bottle (filled artificial seawater + the cocktail of antibiotics). The use of antibiotics was similar to the incubation experiment on board detailed in chapter 2 (Figure 2.3). The bottles were kept at ambient temperature and natural light condition. The water was incubated for 26 days, sub-samples were collected nine times, on days 0, 2, 4, 5, 7, 10, 15, 20 and 26 to investigate the variation in inorganic nutrient (DIN (nitrate+nitrite and ammonium) and phosphate). Additionally, triplicate sub-samples were collected on day 2, 5, 10, 15, 20, 26.

Results showed that TOxN concentration was lower than the detection limit (< 0.2 µM) in both control and treatment with antibiotics over the incubation times. Thus, most of the DIN pool in Figure 4.5 represents ammonium in the samples. In the control bottles, both DIN and phosphate concentrations were lower than the detection limit (< 0.2, < 0.4 and < 0.1 µM for TOxN, ammonium and phosphate, respectively) over the incubation times. In contrast with the antibiotic treated bottles, DIN increased significantly ($R^2 = 0.98$, $P < 0.05$, $n = 21$) from 2.8 (initial concentration (day 0)) to 15.7 ± 0.1 µM (day 26), while the phosphate concentration appears to be constant, compared to DIN. Therefore, this indicates antibiotic can break down to DIN under light condition, mostly in the form of ammonium as an antibiotic treated bottle showed significantly different ($P < 0.05$) DIN concentration to the control bottles.

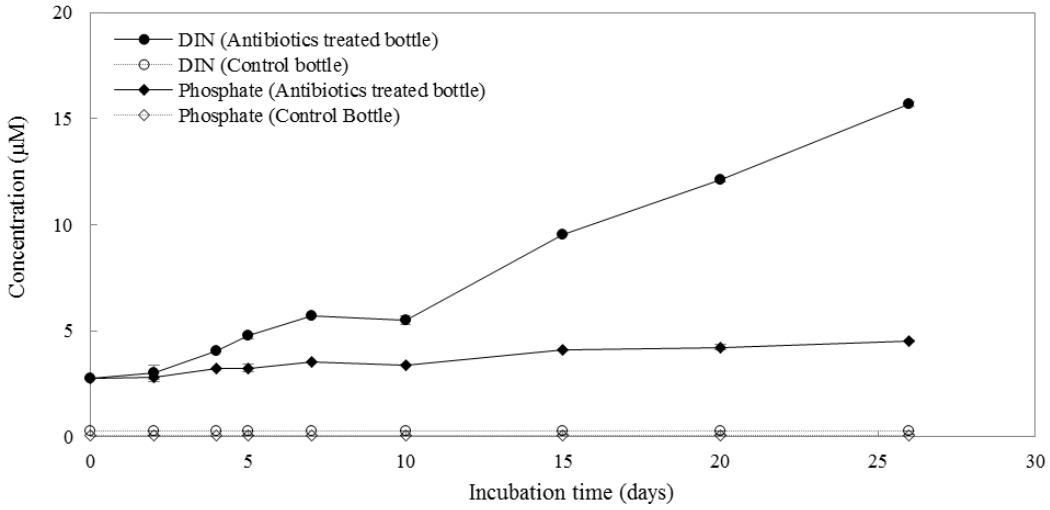


Figure 4.5 DIN and phosphate concentration in control and antibiotic treated bottles in the experiments of light affects antibiotics. The bottles were kept at ambient temperature and natural light condition for 26 days. Error bars are standard deviation of triplicate sub samples on day 2, 5, 10, 15, 20 and 26, an absent error bar indicates standard deviation is 0.0.

4.1.4 DOC and DON variation and limitations of the analysis

DOC and DON variations (normalized to initial concentrations) are shown in Figure 4.6 and Figure 4.7, respectively. Unfortunately for the antibiotic treated samples (T2 and T6), results are not presented in these figures due to a problem during sample analysis. In the sparging step of HTCO-TOC-ND system, all antibiotic treated sample continue to generate foam over the sparging time (240 s). This foam was approximately 3-4 centimeter height and escaped from the sample vials. The leakage of sample result in loss of sample and contamination to other samples. To date, there have been no reports of antibiotic used in DOC and DON analysis, but, it is possible that some type of antibiotic have a detergent like property. Therefore, hereafter the discussion will not consider antibiotic treated samples.

In general, DON concentration did not show a clear pattern over time in the experiment, while a decrease of DOC concentration was observed, notably in samples from WG station and station 9. There seem to be rapid changes within the first five day in both DOC and DON concentration. The N treatments demonstrated the most rapid removal of DOC, compared to all other treatment, and DOC degradation began in the first 2 days of the experiments, notably at station WG and

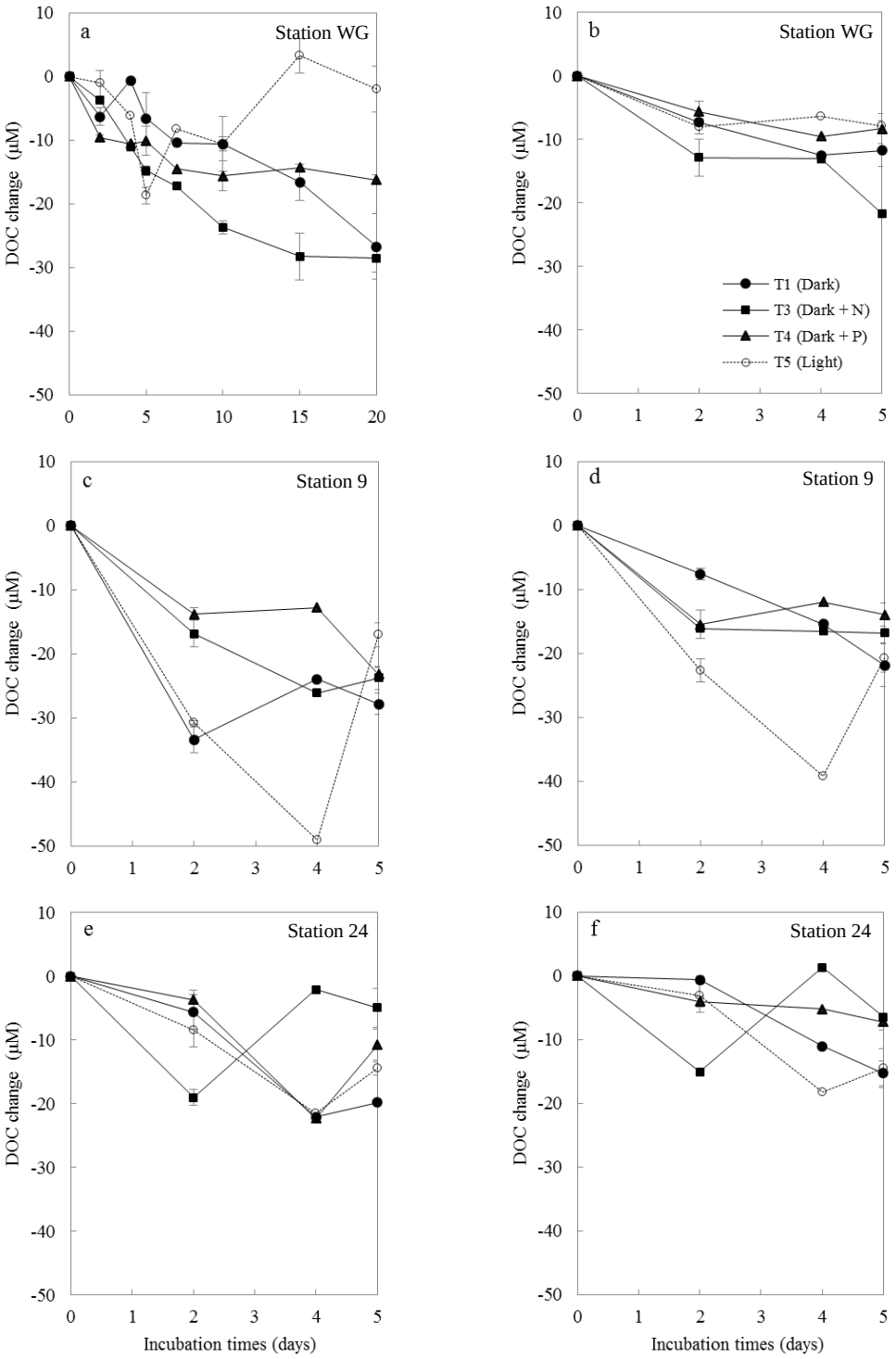


Figure 4.6 Change in DOC of duplicate incubation bottles (set 1 and set 2) at station WG (a, b), station 9 (c, d) and station 24 (e, f) in summer 2012. Error bars are standard deviation of triplicate subsamples on day 2, 5, 10,15 and 20. Antibiotic treated bottles (T2 and T6) are not shown in the graph.

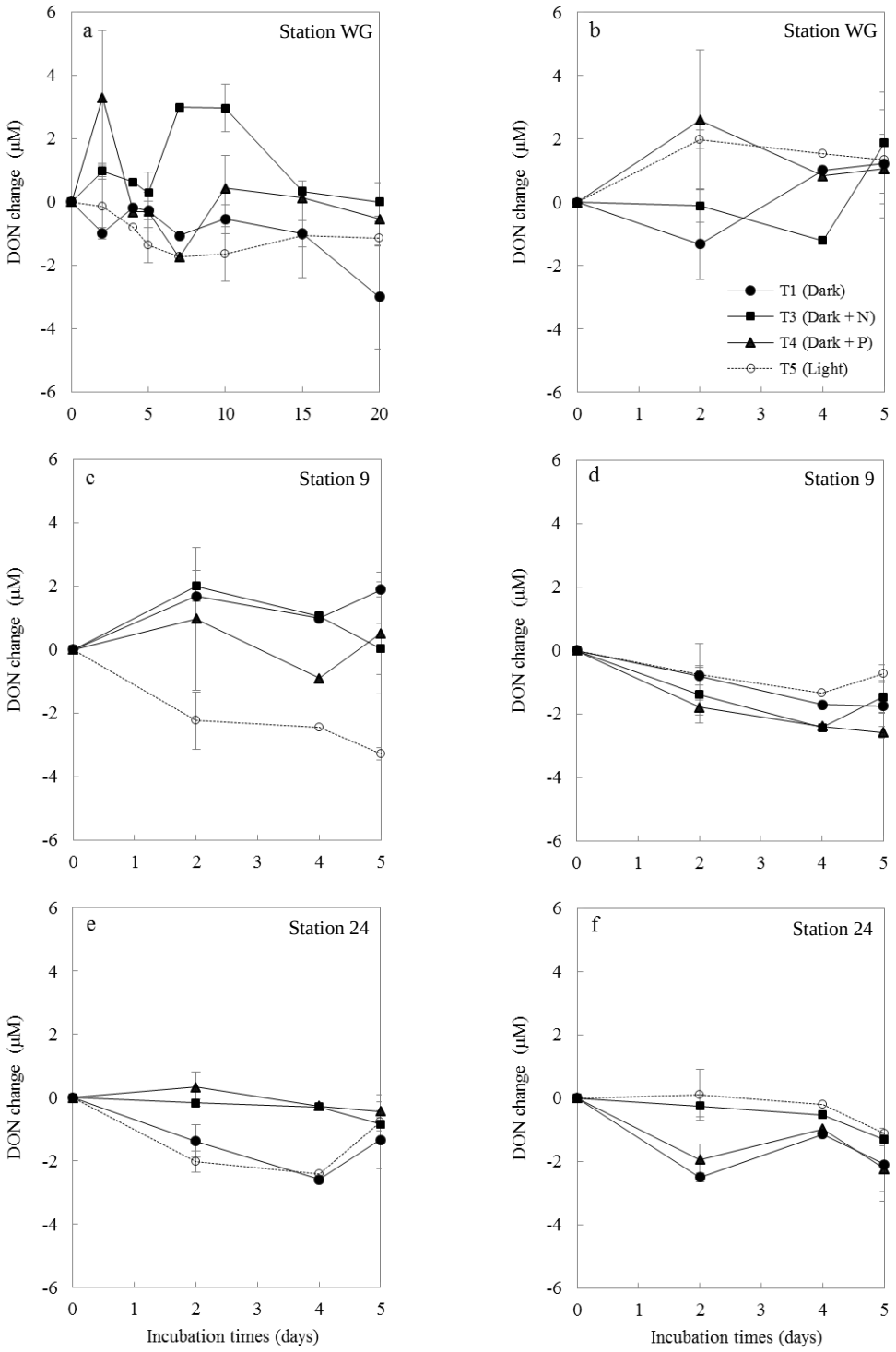


Figure 4.7 Change in DON of duplicate incubation bottles (set 1 and set 2) at station WG (a, b), station 9 (c, d) and station 24 (e, f) in summer 2012. Error bars are standard deviation of triplicate subsamples on day 2, 5, 10,15 and 20. Antibiotic treated bottles (T2 and T6) are not shown in the graph.

station 24. The response of the DON pool to the treatments varied between experiments. Data for degradation rates of DOC and DON in treatments without antibiotics in summer 2012 are compared to later experiments in autumn and winter 2013 and spring 2014 and are discussed further later in this chapter (section 4.2.4.3).

4.1.5 Discussion of the onboard experiment

The general results of the incubation experiment did not indicate a clear trend over the incubation time. Chlorophyll *a* results suggests that phytoplankton still survive in the dark condition. In this approach in which a 200 µm mesh was used to remove most large zooplankton, the overall phytoplankton community was probably not affected by this filter as chlorophyll *a* results in all stations indicate no significant difference between pre- and post-mesh. However, chorophyll *a* is still present at the end of the incubation in all dark treatments. Chorophyll *a* seems to be lost by day 20, but before that period, darkness only slowly affects the phytoplankton biomass as monitored as chlorophyll *a*. In the light condition with non-nutrient treatment (whole microbial community), DOC and DON were little changed during 20 days incubation. This suggests a balance of the production and removal process of these organic compounds. DOC and DON can be released by phytoplankton (Bronk and Glibert 1991, Collos 1992, Bronk et al. 1994, Varela et al. 2005, Suratman et al. 2008b, López-Sandoval et al. 2013), while these compounds are also consumed by bacteria (Zweifel 1993, Kroer 1993, Carlson and Ducklow 1996, Ogawa et al 2001, Cherrier and Bauer 2004). External N addition seems to activate DOC utilization by bacteria in some stations, but not to affect DON utilisation.

In addition, there were some problems when the antibiotic was used during this incubation experiment, particularly in terms of bacteria removal in control treatment and a side effect in sample analysis with TOC/TN analyser. Therefore, experiments in the next three seasons (autumn 2013, winter 2013 and spring 2014) in section 4.2, samples will not be treated with antibiotics because of the following reasons.

1) Light affect antibiotics by breakdown of the antibiotic into DIN, especially in the form of ammonium. This means the experiment with light condition cannot be conducted if the antibiotics are used.

2) Antibiotic blank also provided ammonium 3.6 ± 0.0 µM, phosphate 1.3 ± 0.1 µM and silicate 1.4 ± 0.3 µM to the culture solution, these compounds are additional nutrient sources for phytoplankton, whereas, TOxN concentration was below the limit of detection (< 0.2 µM).
3) An antibiotic blank contains high concentration of organic carbon and nitrogen, approximately 2000 µM DOC and 500 µM TDN, and complicate DOC analysis with NPOC method due to foaming issues when adding acid and sparging.

4.2 Laboratory based incubation experiment

4.2.1 Initial condition of samples

The subsequent 3 seasonal laboratory based experiments to estimate DOC and DON degradation rates were developed from the original experiment (see section 4.1) and specifically to estimate degradation rates without antibiotics but with, in some cases, added nutrients over timescales of about 20 days. In the three seasonal laboratory based experiments, a filtration approach was used instead of antibiotics to try and differentiate between effects on the rates of different phytoplankton and bacterial group. Therefore, seawater used to initiate the experiment was filtered onboard in many steps with gravity methods after filtration through 200 µm mesh. After filtration, incubations were started immediately at sea in the constant temperature room and then when the ship returned to port at Lowestoft (usually after 2-3 days) samples were transported to UEA constant temperature incubators and incubation continued.

Sub-samples of incubated water were analysed on day 0, 2, 4, 5, 7, 10, 15 and 20 for inorganic nutrients, DOC and DON concentrations. The incubations were at constant temperature which varied depending on the season, 15 °C in autumn 2013, 7°C in winter 2013 and 11 °C in spring 2014. All experimental processes are described in detail in chapter 2 (section 2.3.3). During the course of incubations in the three seasons 1,568 incubated water samples were collected for analysis and all inorganic nutrients, DOC and DON concentration data during the incubation period

are summarised in Appendix 4.1. Additionally, before and after the finish of the incubation, 123 samples were collected for chlorophyll *a* determination. Details of sampling sites and initial properties of water in each station are presented in Table 4.3. The highest temperature was in autumn, followed by spring and winter. Initial inorganic nutrient concentration used for DON calculation (day 0) are presented in Table 4.4 and in the case of T7 also represent the nutrient conditions at the sampling site. The results suggest that the spring sampling at WG was after the spring bloom and had depleted most of the nutrients while at DS only partial nutrient depletion had

Table 4.3 Sampling sites for incubation experiments in autumn, winter and spring.

Cruise [a]	Date	Stn [b]	Latitude	Longitude	Temp[c] (°C)	Salinity[d]	Sample depth (m)	Water column depth (m)
CEND 19/13	06 Oct 13	WG	51.58.539 N	02.05.002 E	16.4	34.7	2	33
	08 Oct 13	DS	53.31.708 N	01.04.033 E	13.7	34.4	2	25
CEND 03/14	30 Jan14	DS	53.31.440 N	01.03.350 E	6.5	34.6	4	24
	02 Feb 14	WG	51.58.843 N	02.03.773 E	9.4	35.2	3	32
CEND 08/14	11May14	DS	53.31.447 N	01.03.349 E	10.2	34.6	4	23
	13May14	WG	51.59.010 N	02.06.283 E	12.4	34.8	4	32

[a] CEND: CEFAS Endeavour cruise
[b] Stn: sampling stations (West Gabbard (WG) and Dowsing (DS) station)
[c] Temp: temperature at the time of collection
[d] Salinity at the time of collection

Table 4.4 Initial mean inorganic nitrogen concentrations (µM) of incubated water in autumn, winter and spring.

Nutrients [a]	Station	Season	Concentration (Mean ± SD [b])						
			T1	T2	T3	T4	T5	T6	T7
TOxN	WG	Autumn	8.8 ± 0.0	8.4 ± 1.1	8.0 ± 0.2	6.8 ± 1.3	9.3 ± 0.2	8.8 ± 0.8	8.3 ± .7
		Winter	5.7 ± 1.1	6.4 ± 0.9	6.2 ± 1.3	6.5 ± 0.1	6.5 ± 0.5	6.5 ± 0.3	6.0 ± 1.2
		Spring	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0
	DS	Autumn	1.5 ± 0.1	1.3 ± 0.2	1.5 ± 0.1	1.4 ± 0.1	1.6 ± 0.0	1.5 ±0.0	1.3 ± 0.3
		Winter	4.6 ± 0.9	5.7 ± 0.1	5.4 ± 0.4	5.5 ± 0.2	5.8 ± 0.1	5.0 ± 0.2	4.4 ± 1.1
		Spring	2.7 ± 0.0	2.6 ± 0.0	2.7 ± 0.0	2.6 ± 0.0	2.6 ± 0.0	2.6 ± 0.0	4.0 ± 0.0
Ammonium	WG	Autumn	0.2 ± 0.0	1.0 ± 0.1	4.0 ± 0.1	0.2 ± 0.0	0.9 ± 1.0	0.6 ± 0.6	0.2 ± 0.0
		Winter	0.2 ± 0.0	0.5 ± 0.4	4.5 ± 1.9	0.2 ± 0.0	0.5 ± 0.4	0.2 ± 0.0	0.6 ± 0.6
		Spring	0.2 ± 0.0	0.2 ± 0.0	5.0 ± 0.2	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
	DS	Autumn	0.3 ± 0.0	0.3 ± 0.0	4.1 ± 0.3	0.3 ± 0.0	0.4 ± 0.2	0.3 ± 0.0	0.4 ± 0.2
		Winter	0.4 ± 0.2	0.7 ± 0.2	4.4 ± 1.5	0.6 ± 0.5	1.9 ± 0.4	0.2 ± 0.0	0.2 ± 0.0
		Spring	0.2 ± 0.0	1.2 ± 0.6	5.0 ± 0.0	0.2 ± 0.0	0.4 ± 0.2	1.0 ± 0.4	1.8 ± 0.2

[a] Initial mean phosphate and silicate concentration are presented in Appendix 4.3.
[b] SD is standard deviation of duplicate incubation bottles (set 1 and set 2) in each treatments (T1-T7)

occurred. The autumn sampling at WG took place after at least partial nutrient replenishment while at DS autumn TOxN levels were low, but higher than in summer. During the winter experiment, TOxN concentration was relatively high.

Figure 4.8 shows initial mean DOC and DON concentrations of incubated water collected from station WG and DS. Statistical tests showed significant difference in DOC concentration between the WG and DS station in autumn ($P < 0.05$), whereas in other seasons were no significant difference ($P > 0.05$). DON concentration followed the same pattern. Although DOC and DON concentrations in each station showed some variability in autumn, there was overall no significant difference in initial mean DOC concentration between treatments (ANOVA, $P > 0.05$) as well as the DON concentration. Similarly, statistical tests

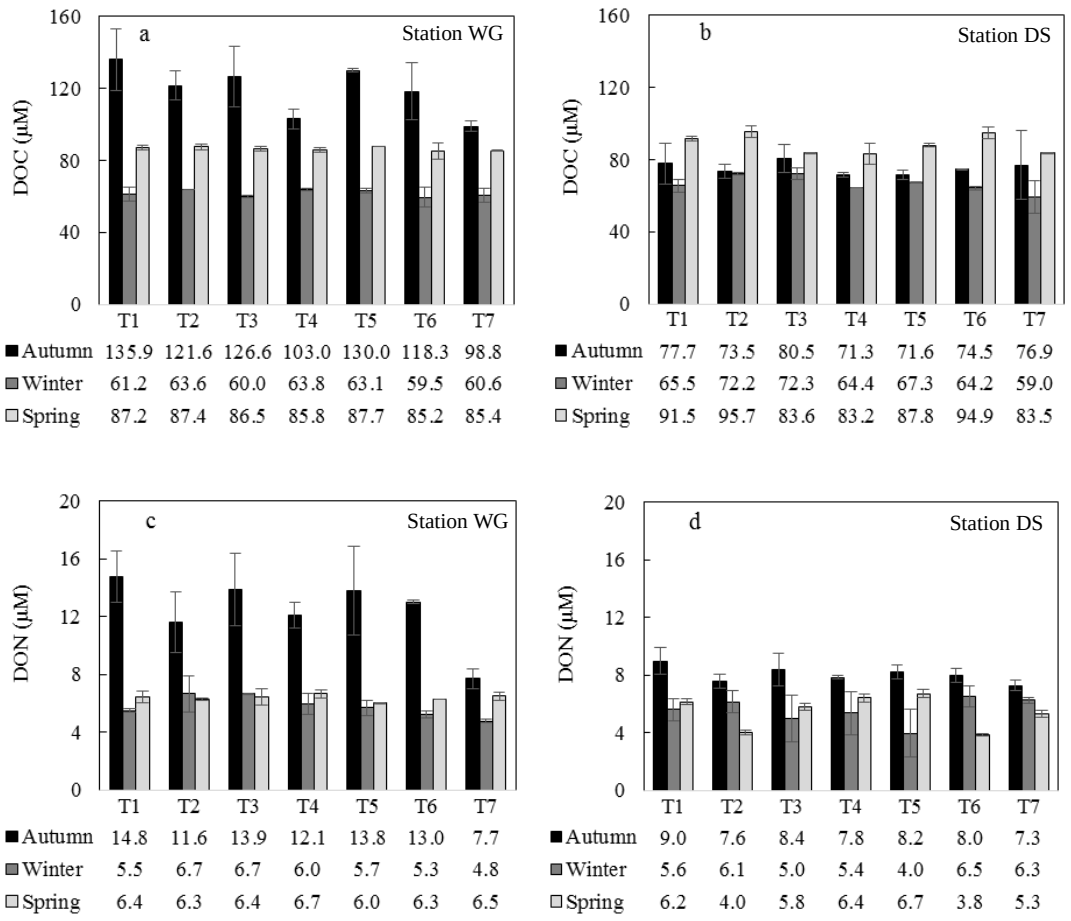


Figure 4.8 Initial mean DOC and DON concentrations of incubated water in autumn, winter and spring for station WG (a, c) and DS (b, d). The number represents the mean concentration, and error bars are standard deviation of duplicate incubation bottles in 7 treatments (T1-T7).

showed no significant difference in initial mean DOC concentration between treatments in winter and spring (ANOVA, $P > 0.05$), the DON concentration showed the same result. In each station, there was significant difference in initial mean DOC concentration between season (ANOVA, $P < 0.05$). Initial DON concentration followed the same pattern.

4.2.2 Chlorophyll *a* variation

For chlorophyll *a* analysis, duplicate samples were collected before and after samples were filtered through a 200 µm mesh. This approach was performed as in the incubation experiment onboard in summer. Additional duplicate samples were collected after the water samples were filtered through a 1.0 µm capsule filter to check if there was any phytoplankton biomass in the filtrate. Finally, chlorophyll *a* samples from all three seasonal experiments were collected in all treatments (T1-T7) on day 20 when most incubations were ended. The spring experiment was extended to 70 days to investigate nutrients only and not chlorophyll *a*. Statistically significant positive correlation was shown between chlorophyll *a* concentration before and after filtration ($R^2 = 0.97$, $P < 0.05$, $n = 12$) (Figure 4.9)

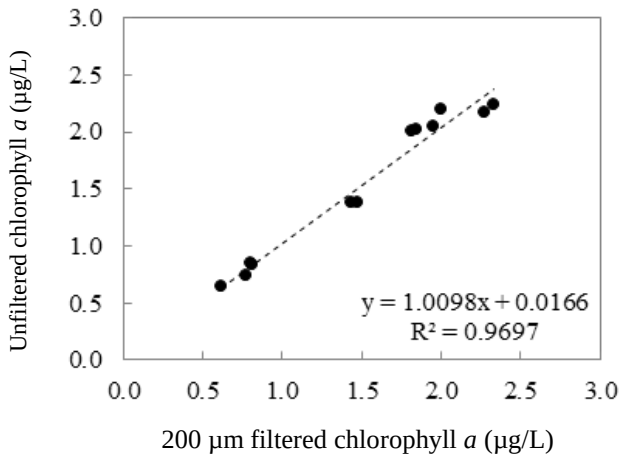


Figure 4.9 Relationship between concentration of chlorophyll *a* before and after filtration with 200 µm mesh in autumn, winter and spring experiments for all station.

Concentration of chlorophyll *a* was relatively high (1-2 µg/L) at both West Gabbard (WG) and Dowsing (DS) sites in autumn and spring but lower (< 1 µg/L) in

winter. Appendix 4.2 summarises chlorophyll *a* concentrations for the autumn 2013, winter 2013 and spring 2014 experiments.

To aid the reader, Table 2.6 (in chapter 2) which describes the different treatments is repeated here.

Table 2.6 Experimental treatments in autumn and winter 2013 and spring 2014.

Condition [a]	Treatment [b]	
Dark	T1	< 1.0 µm
	T2	< 0.1 µm
	T3	< 1.0 µm + Add 1 ml of 10 mM NH_4Cl, final concentration 5.0 µM N
	T4	< 1.0 µm + Add 1 ml of 1 mM Na_2HPO_4, final concentration 0.5 µM P
Light	T5	< 1.0 µm
	T6	< 0.1 µm
	T7	< 200 µm

[a] In bottles in the dark, it is assumed there is no phytoplankton photosynthesing, while this still takes place in the light. The addition of N and P in T3 and T4 was designed to test for N and P limitation of DOC and DON degradation. In T5, T6 and T7 filtration was used to separate the bacterial and phytoplankton community.

[b] Filtration based on general size structure scale (Sieburth et al. 1978, Lalli and Parsons 2006) and available filter size; <200 µm: expect reduced zooplankton, < 1.0 µm: expect reduced zooplankton, phytoplankton and bacterivores, and < 0.1 µm: expect reduced zooplankton, phytoplankton, bacterivores and bacteria.

Figure 4.10 shows chlorophyll *a* concentration before the start and after the finish of the incubation on day 20 for all seasons at WG and DS stations. No chlorophyll *a* was detected in control bottles (T2) with 0.1 µm filtration.

In the autumn season, there was no significant difference ($P > 0.05$) of chlorophyll *a* concentration between before and after 200 µm mesh in both stations. Before the start of the incubation, chlorophyll *a* concentration in < 1.0 µm filtrate at both stations were below the detection limit (0.1 µg/L). However, in the T5 treatment (Light < 1.0 µm) chlorophyll *a* concentration was found in both stations at the end of incubation time. Notably in the T5 treatment at the WG station, chlorophyll *a* concentrations at the end of the course of incubation (8.3 ± 0.9 µg/L) were higher than the initial concentration and T7 (Light < 200 µm) treatment concentration in both duplicate samples. All chlorophyll *a* concentrations in the dark condition (T1-T4) and light condition with < 0.1 µm (T6) were below the detection limit after 20 days.

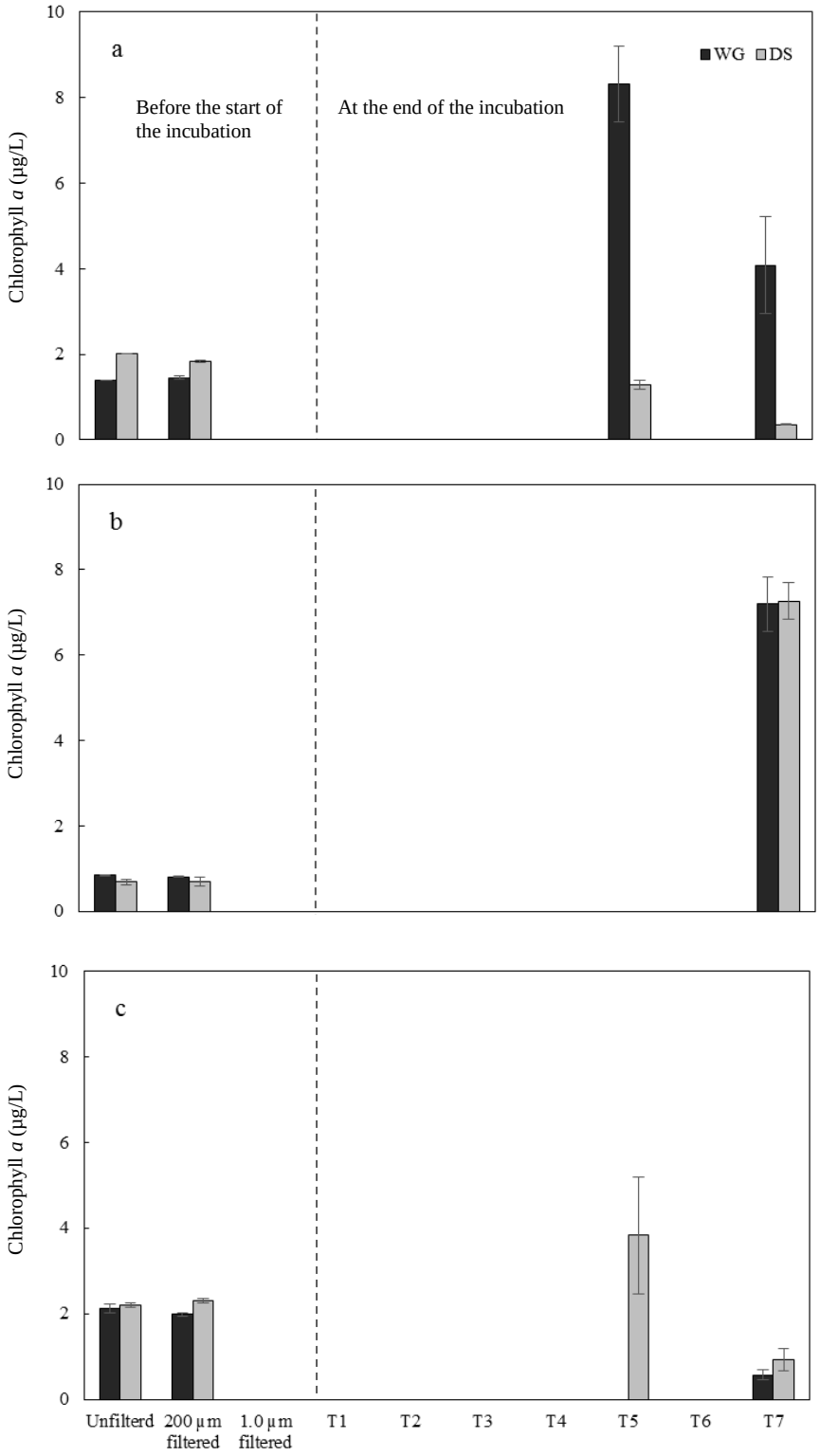


Figure 4.10 Initial concentrations of chlorophyll *a* before the start of the incubation (unfiltered, 200 µm filtered and 1.0 µm filtered) and the concentration at the end of the incubation on day 20 in each treatment (T1-T7) for station WG and DS in autumn (a), winter (b) and spring (c). The absent bar represents results below

detection limit (BDL) values. Error bars are standard deviation of duplicate initial samples and duplicate incubation bottles at the end of the incubation.

In winter, there was no significant difference ($P > 0.05$) of chlorophyll *a* concentration between before and after 200 µm mesh filtration at both stations. After filtration through the 1.0 and 0.1 µm mesh, chlorophyll *a* concentration both before the start and after the finish of the incubation in the dark (T1-T4) and light (T5-T6) condition were below the detection limit. The chlorophyll *a* concentration found in < 200 µm (T7) has approximately sevenfold increased at the end of the course of the light incubation at both stations, suggesting phytoplankton growth, WG 7.2 ± 0.2 µg/L and DS 7.3 ± 0.4 µg/L.

In spring, no significant difference ($P > 0.05$) was shown between chlorophyll *a* before and after 200 µm mesh filtration, similar to autumn and winter. The concentrations were below detection limit after 1.0 µm mesh (before the start of the incubation), all dark condition (T1-T4) and light condition with < 0.1 µm (T6) on day 20. However, chlorophyll *a* was detected in light < 1.0 µm (T5) DS (3.8 ± 1.4 µg/L) with higher concentration than light < 200 µm (T7) DS (0.9 ± 0.3 µg/L). There was no chlorophyll *a* detected in WG T5, but minor concentration was found in T7 (0.6 ± 0.1 µg/L)

In general, we do not expect to detect chlorophyll *a* in T5 treatment as seawater was filtered through a 1.0 µm capsule filter before the experiment which should remove most phytoplankton. However, chlorophyll *a* was present in autumn and spring. This is probably due to water sampled in the autumn and spring seasons containing picophytoplankton whose size is less than 2 or 3 µm (Sieburth et al. 1978, Raven 1998, Vaulot et al. 2008) and hence some may pass through filters. It has been estimated in the central and southern North Sea that picophytoplankton accounted for 7 – 58 % (mean 20 %) of the total phytoplankton chlorophyll *a* biomass (Iriarte and Purdie 1993). Hence, chlorophyll *a* was detected after 20 days growth in the light in T5. In addition to the North Sea (Iriarte and Purdie 1993, Riegman et al. 1993), previous studies reveal that picophytoplankton are important in terms of biomass and primary productivity in shelf waters (Li 1994, Worden et al. 2004) and the global open ocean (Raven 1998, Buitenhuis et al. 2012).

The < 200 µm treatment does not remove phytoplankton, therefore under light incubation (T7) chlorophyll *a* was detected at the end of the incubation as

expected. In all dark treatments (T1-T4) and light treatment with < 0.1 μm (T6), the chlorophyll *a* concentrations were below the detection limit and hence the filtration presumably removed all phytoplankton.

4.2.3 DOC and DON variations and the determination of rate constants

Variations of DOC and DON with time were investigated in order to determine the rate constants of loss during the course of sample incubations. Previous studies have showed higher degradation generally occurred in the first week of incubation (Raymond and Bauer 2000, Hopkinson et al. 2002, Lønborg et al. 2009) consistent with DOM containing a range of compounds of different reactivity. Figure 4.11 and Figure 4.12 show examples of the data obtained in the incubation experiments on DOC and DON variation over the incubation time divided into two sub-stages (day 0-5 and day 5-20) and overall (day 0-20) at the WG station in autumn. The data shown represents a single analysis (on day 0, 4 and 7) and triplicate analysis (on day 2, 5, 10, 15 and 20) of sub-samples from duplicate bottles analysed at the same time. The data is relatively noisy presumably reflecting natural variation in the population of degrading bacteria and possibly different amounts of cell lysis in the different bottles, but overall concentrations do decline with time in almost all cases.

Data for all DOC and DON variation measured during the experiments are summarised in Appendix 4.1. In general, a decrease of DOC and DON concentrations in "control samples" (T2) for each experiment was observed. This suggested that a 0.1 μm filter cannot remove all bacteria from seawater as some microbial DOC and DON consumption process occurred in the "control" sample. Therefore, the sample in T2 is not really a "control" with all bacteria removed, but rather a water sample with a part of the bacteria population removed by filtration, and the results of T2 have not been subtracted from the other treatments (details are discussed in section 4.2.4).

Changes of DOC and DON concentrations on day 0-5 were generally higher than day 5-20 and day 0-20, suggesting most rapid net degradation occurred during this early period after the start of the incubation consistent with previous observations (Lønborg et al. 2009). To obtain the overall data trend in terms of

degradation and production of the substances, these measured concentrations were used to determine rate constants over the time periods of 0-5 days, 5-20 days and 0-20 days (autumn 2013, winter 2013 and spring 2014). An additional time period of 20-70 days was investigated in spring 2014.

To determine the rate constant of DOC and DON loss, first-order or second-order reactions were considered. The reaction (r) is first-order when a reaction rate depends on the concentration of a single reactant ($r = k[A]$, k is the rate constant, [A] is a concentration of substance A, in this case A is the DOM substance), while the second-order reaction rate has the concentration of two components affecting the reaction rate (Lewis and Evans 2011). The second order reaction seems not the most suitable in this case. A previous study (Lønborg et al. 2010) found that the rate is independent of other factors, e.g. initial bacterial biomass, and that the substrate concentration is the only important factor affecting the rate. Thus this process of degradation is not suitable to be described by the second order reaction. Therefore, in this present study the first-order reaction was applied to determine the rate constant of DOC and DON during the course of incubations as applied in previous studies (Hopkinson et al. 1997, Raymond and Bauer 2000, Hopkinson et al. 2002, Lønborg and Søndergaard 2009, Lønborg et al. 2009, Lønborg et al. 2010). The first order decay constant will be calculated by applying the first-order equation as follows:

$$[A]_t = [A]_0 \times e^{-kt} \qquad \text{.....Equation 2}$$

where $[A]_t$ = concentration of DOC or DON at any time

$[A]_0$ = initial DOC or DON concentration

$-k$ = is a rate constant that describes the DOC or DON concentration decrease with incubation time (t) (degradation rate constant or rate constant)

The graphs were plotted and the data fitted to an exponential degradation of DOC and DON concentration (µM) (*y*-axis) with incubation time (days) (*x*-axis) of various treatments as illustrated in Figure 4.11 - Figure 4.12 for the West Gabbard station in autumn (WG1). Figures for other seasons and Dowsing station are presented in Appendix 4.4. The equation presented in each graph was fitted with the Equation 2 (using Microsoft Office Excel 2013) described above and the rate

constant was taken from the k in each equation. Negative rates indicate degradation of DOC or DON, whereas, positive rates indicate production of these substances. The rate constants of duplicate bottles (set 1 and set 2) in each treatment were averaged and the mean rates are discussed in the next section. Note in Figure 4.11, Figure 4.12 and Appendix 4.4, some data points were excluded (shown in filled triangles (set 1) and blank triangles (set 2)) because one replicate differs substantially from the other two which have similar values for the triplicate sub-samples on the collection day (day 2, 5, 10, 15 and 20). Data used to create these graphs are shown in Appendix 4.1 and the excluded data points are shown in italics.

Mean rate constants determined from this equation are summarised in Appendix 4.5. The variation of mean rate constants of DOC (k_{DOC}) in Figure 4.13 - Figure 4.14 and DON (k_{DON}) in Figure 4.15 - Figure 4.16 suggest that faster rates of degradation occurred in the first period (day 0-5) in all seasons, consistent with observations in other studies (Raymond and Bauer 2000, Lønborg et al., 2009).

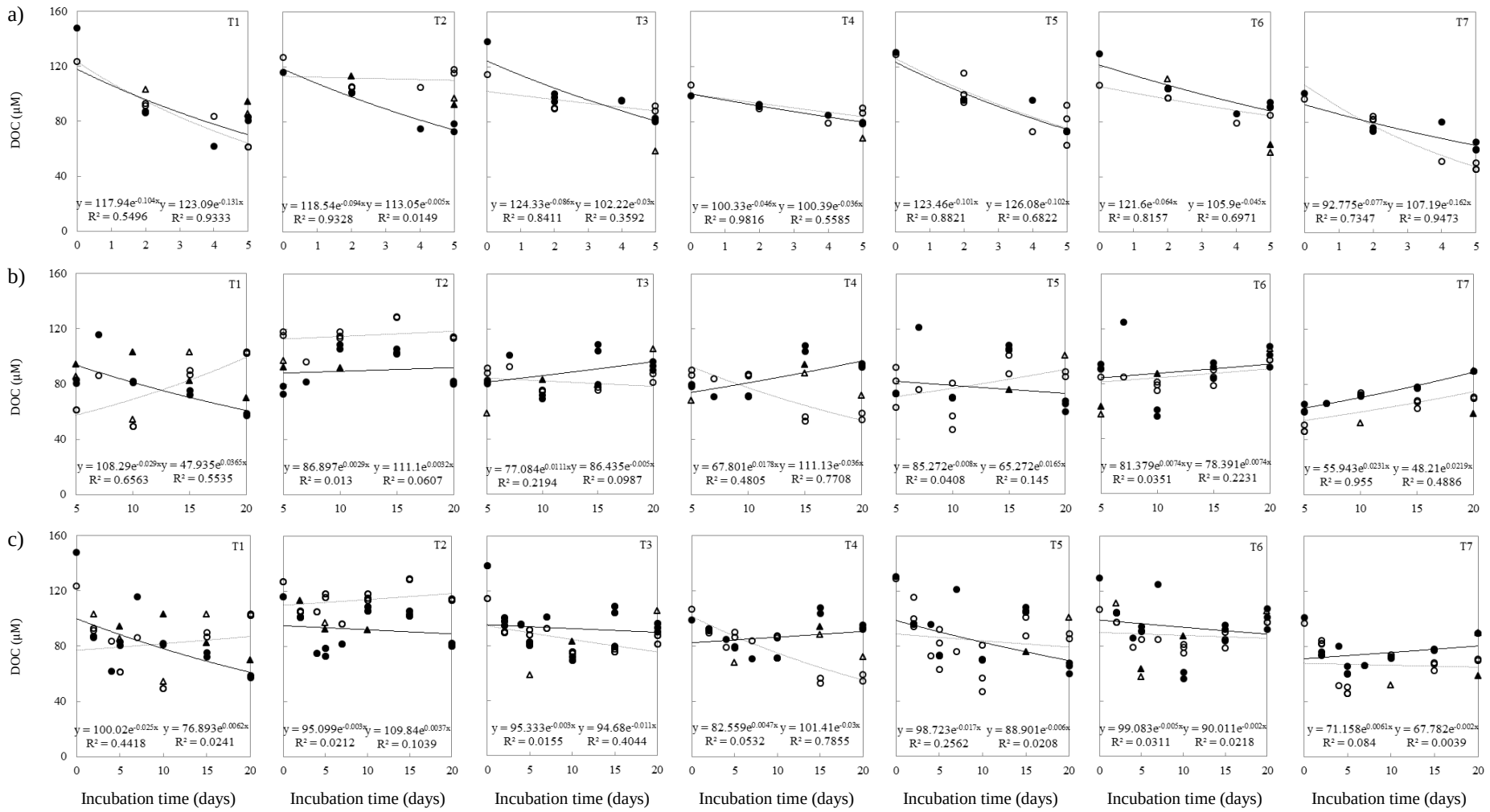


Figure 4.11 Time course of DOC during the incubations with different treatments (T1-T7) sampled at West Gabbard station in autumn 2013 (WG1), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.

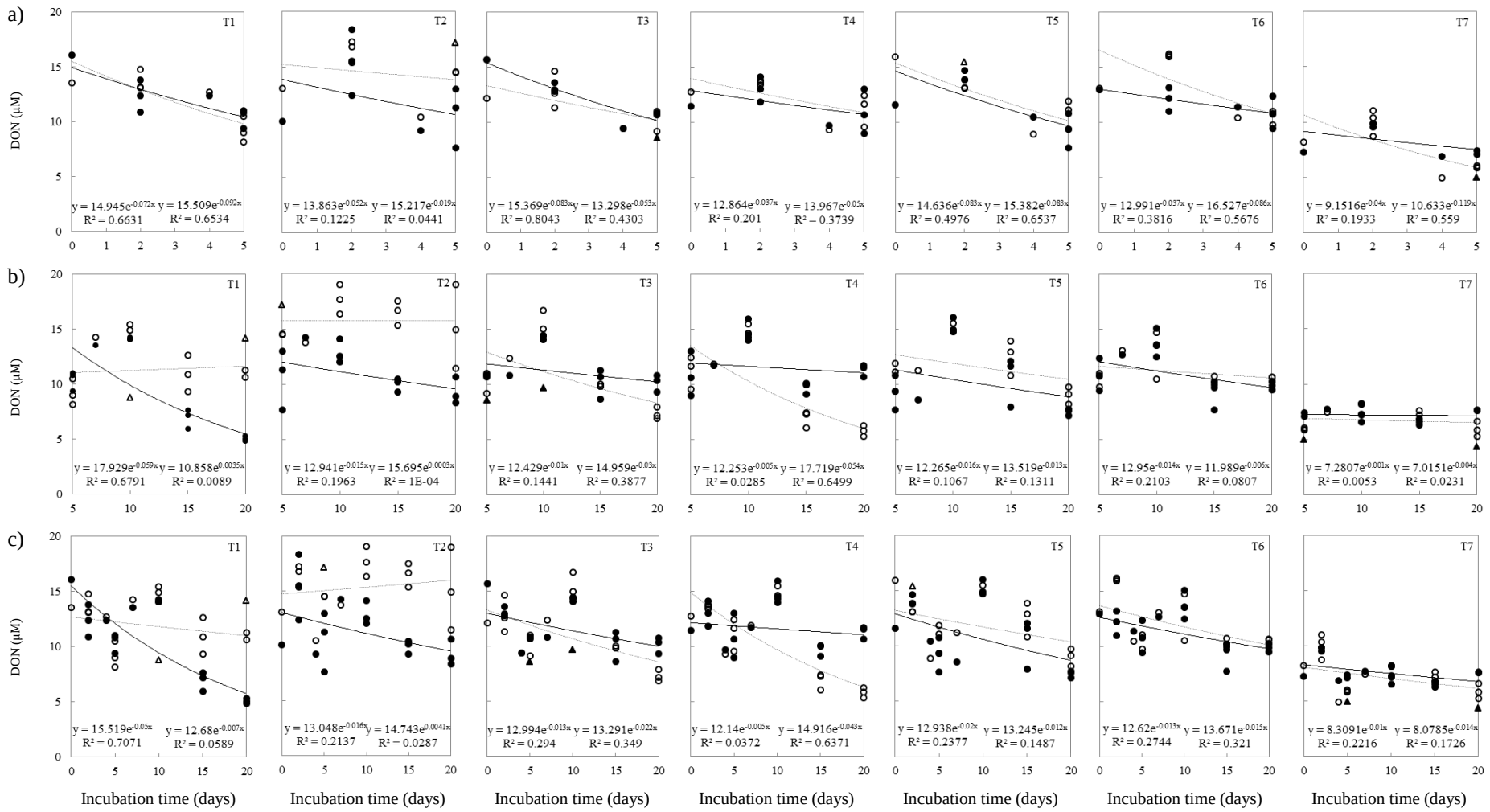


Figure 4.12 Time course of DON during the incubations with different treatments (T1-T7) sampled at West Gabbard station in autumn 2013 (WG1), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model

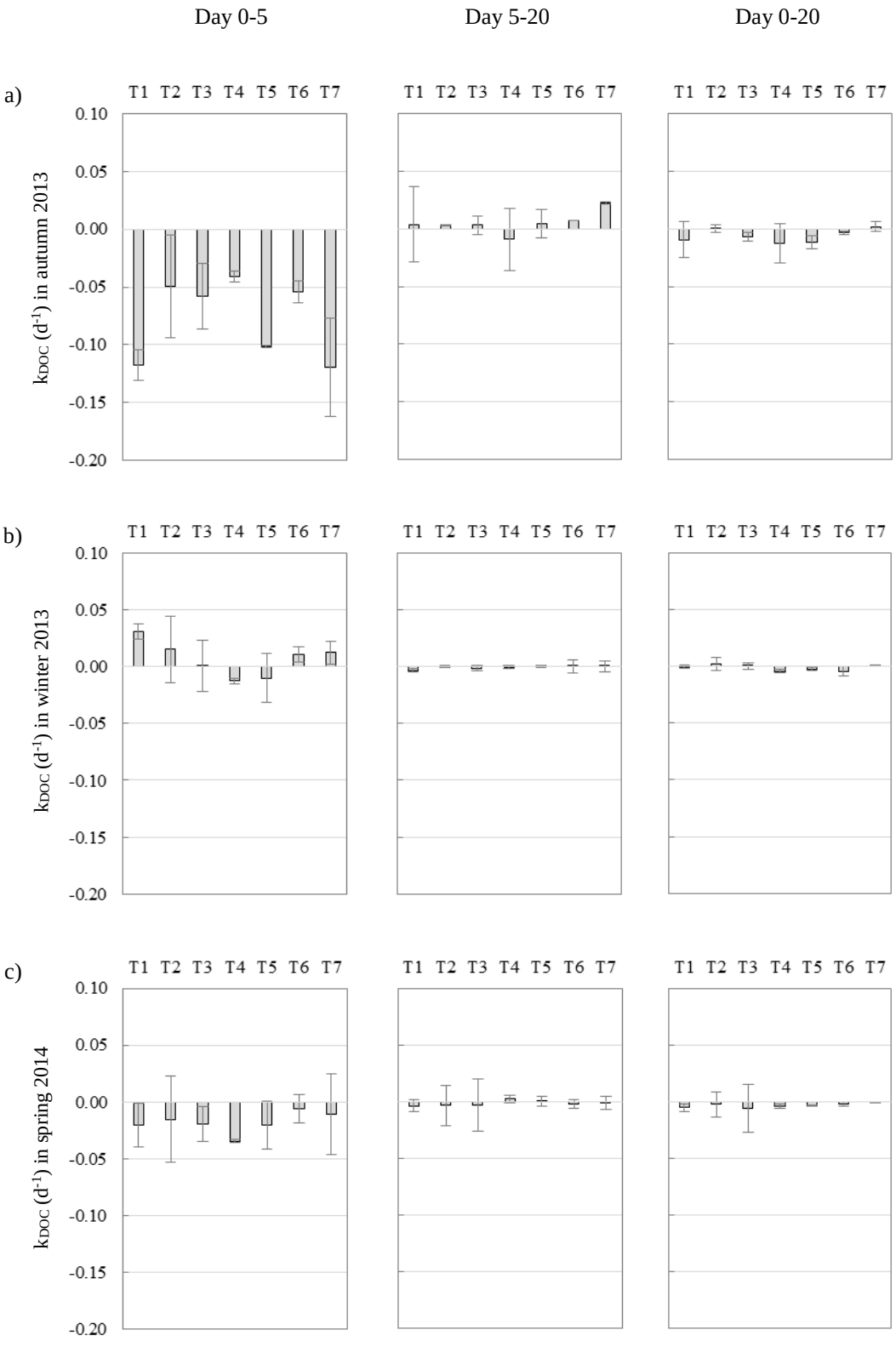


Figure 4.13 Rate constant (d^{-1}) of DOC (k_{DOC}) during the incubations for West Gabbard station conducted in (a) autumn 2013, (b) winter 2013 and (c) spring 2014 with different treatments (T1-T7) on day 0-5, day 5-20 and day 0-20. Positive rates indicate DOC production and negative rates indicate degradation. Error bars are uncertainties in the rate of duplicate incubation bottles

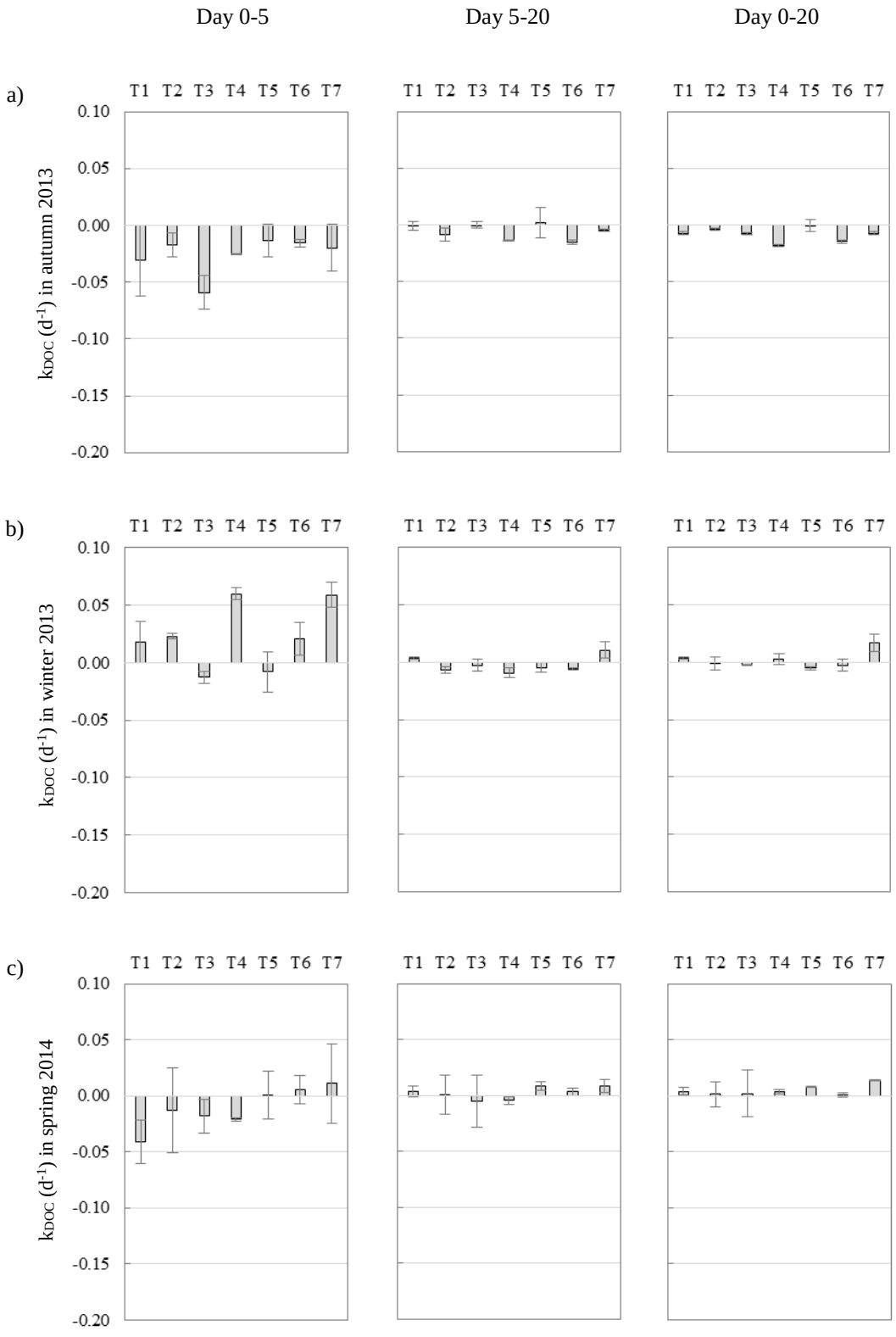


Figure 4.14 Rate constant (d^{-1}) of DOC (k_{DOC}) during the incubations for Dowsing station conducted in (a) autumn 2013, (b) winter 2013 and (c) spring 2014 with different treatments (T1-T7) on day 0-5, day 5-20 and day 0-20. Positive rates indicate DOC production and negative rates indicate degradation. Error bars are uncertainties in the rate of duplicate incubation bottles.

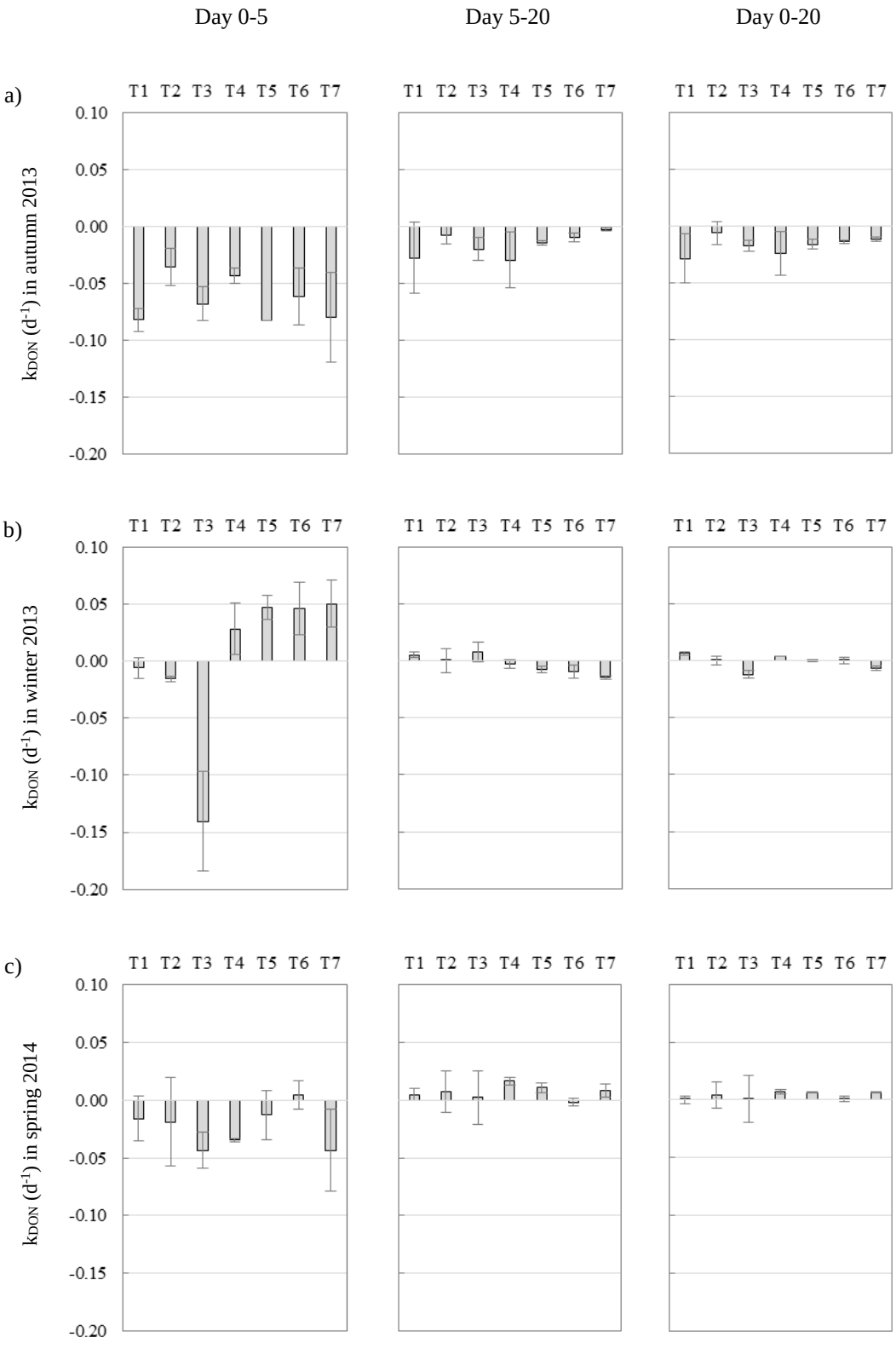


Figure 4.15 Rate constant (d^{-1}) of DON (k_{DON}) during the incubations for West Gabbard station conducted in (a) autumn 2013, (b) winter 2013 and (c) spring 2014 with different treatments (T1-T7) on day 0-5, day 5-20 and day 0-20. Positive rates indicate DON production and negative rates indicate degradation. Error bars are uncertainties in the rate of duplicate incubation bottles.

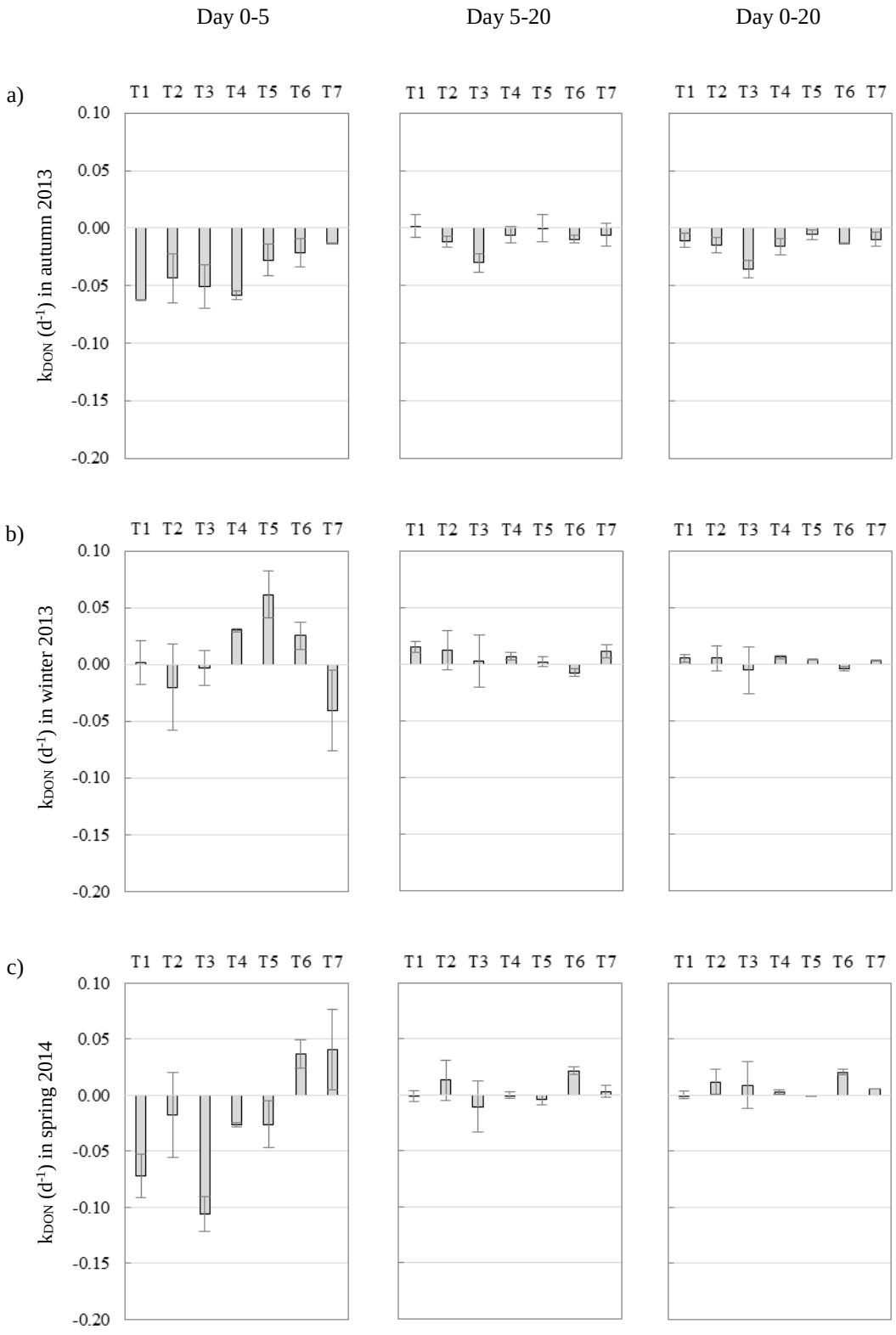


Figure 4.16 Rate constant (d^{-1}) of DON (k_{DON}) during the incubations for Dowsing station conducted in (a) autumn 2013, (b) winter 2013 and (c) spring 2014 with different treatments (T1-T7) on day 0-5, day 5-20 and day 0-20. Positive rates indicate DON production and negative rates indicate degradation. Error bars are uncertainties in the rate of duplicate incubation bottles.

Mean rate constants in Appendix 4.5 and variation of mean rate constants in the different treatments (Figure 4.13 - Figure 4.16) are rate constants determined from the first-order equation 2 which does not consider the limits of detection of rate constants. In order to determine the limits of detection of these rate constants the following procedure were applied:

- Linearized the exponential equations by take the natural logarithm.
- Determine the standard deviation (SD) of the slope (the rate constant) by using a least squares fit with Excel's LINEST function (the natural logarithm of the *y* values (*y* values = DOC or DON concentration) and *x* values (incubation time, day) are used).
- Two times the standard deviation (2*SD) was selected as an estimate of the detection limit for the rate constants, representing approximately 95 % confidence.

Based on conditions in this study, there are eight possible ways to use SD of slope of the best fit i.e. rate constant (k) (before multiplying by 2 (2*SD)) to determine a limit of detection for all of data including:

1) Use SD of the individual slope
2) Use of averaged SD of all individual slope
3) Use of averaged SD by incubation time (Day 0-5, Day 5-20, Day 0-20)
4) Use of averaged SD by incubation time, DOC and DON
5) Use of averaged SD by incubation time and seasons (autumn 2013, winter 2013 and spring 2014)
6) Use of averaged SD by seasons
7) Use of averaged SD by incubation time, DOC, DON and seasons
8) Use of averaged SD by incubation time, DOC, DON, seasons and stations (West Gabbard and Dowsing)

Option 1) provides individual detection limits for each rate constant, while option 2) provides an average detection limit for all rate constants. Option 3) to 8) provide an average detection limit for various subsets of the data.

By considering these eight ways, the first way, 2 times the standard deviation (2*SD) of the 'individual slopes' was chosen to determine the limits of detection in this present study because this provides a simple way to

average across all the data and this is less influenced by differences in season and between sites.

- The limits of detection of the individual rate constants are summarised in Appendix 4.6. When rate constants in Appendix 4.5 considered the absolute value (not considering the negative and positive sign) were below their individual limits of detection (Appendix 4.6), the rate constants were reported as *. The rate constants with identification of * are presented in Table 4.5.

A lot (353 of 504, Table 4.5) of the rate constants were at or below their individual limits of detection illustrating that rates are rather low and difficult to measure by this approach. The variation of mean rate constants of DOC and DON in Figure 4.13 - Figure 4.16 and summarised in Figure 4.17 suggest that faster rates of degradation occurred in the days 0-5. Variability (i.e. SD) is much lower for a longer time period as well as the rate constants themselves. Rate constants were more variable in the first five days and generally too low to measure after five days. Even considering only day 0-5 and more on day 5-20 (Table 4.5), rates of degradation are low and close to detection limit much of the time. This leads to difficulties in how to best handle the data values less than detection limits since they are not necessarily zero, so to treat them as zero will underestimate rates, while to treat them as detection limit will over estimate rates.

Therefore, when duplicate bottles (set 1 and set 2) were identified by * (Table 4.5), the actual measured values were used as a rate constant. The rate constants (day 0-5) of duplicate bottles (set 1 and set 2) in each treatment were averaged and the mean rates are presented in Table 4.6. To average the rate in Table 4.6, the use of measured values were applied to * data in Table 4.5 rather than the use of zero value, half of the limit of detection value or the value of the limit of detection. In Table 4.6, the asterisk code indicates whether one (*) or two (**) of rate constants of duplicate bottles (set 1 and set 2) in each treatment were lower than the limits of detection. The results of mean rate constants in Table 4.6 will be used for the discussion section (section 4.2.4). In addition, these rate constants were transformed to unit % day^{-1} by multiplying by a hundred in Appendix 4.7 in order to compare with other previous studies.

Table 4.5 Rate constants (d^{-1}) obtained by fitting the exponential degradation (-) and production (+) of DOC and DON with incubation time at varying treatment (T1-T7) in two duplicate bottles (set 1 and set 2). Rates constants with lower than limits of detection were indicated by *.

Days	T	Set	k_{DOC} (d^{-1})						k_{DON} (d^{-1})					
			WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
0-5	1	1	-0.10	-0.06	*	*	-0.02	-0.07	-0.07	-0.06	*	*	*	-0.11
	1	2	-0.13	*	*	*	-0.02	*	-0.09	-0.06	*	*	*	*
	2	1	-0.09	*	*	*	*	*	*	-0.07	*	*	*	*
	2	2	*	*	*	*	*	*	*	-0.02	*	*	*	*
	3	1	-0.09	-0.04	*	*	-0.01	-0.06	-0.08	-0.07	-0.18	*	*	*
	3	2	*	-0.07	*	-0.02	-0.03	*	-0.05	*	*	0.13	-0.07	*
	4	1	-0.05	*	-0.01	0.05	-0.03	*	*	*	*	*	*	-0.07
	4	2	-0.04	*	-0.02	*	-0.04	*	*	-0.06	*	*	-0.05	*
	5	1	-0.10	*	-0.03	*	*	*	-0.08	*	*	*	*	-0.06
	5	2	-0.10	*	*	*	-0.03	*	-0.08	*	*	0.04	*	*
	6	1	-0.06	-0.02	*	*	*	*	*	*	*	*	*	*
	6	2	-0.05	*	*	*	*	*	-0.09	-0.03	0.07	*	*	*
	7	1	-0.08	*	*	0.07	-0.02	*	*	*	*	*	*	*
	7	2	-0.16	-0.04	*	*	*	*	-0.12	*	0.07	-0.08	-0.03	*
5-20	1	1	-0.03	*	*	*	0.00	*	-0.06	*	*	*	*	*
	1	2	0.04	*	*	*	*	*	*	*	*	*	*	*
	2	1	*	-0.01	*	-0.01	-0.01	*	*	-0.02	*	*	0.01	*
	2	2	*	*	*	*	*	*	*	-0.01	*	0.03	*	*
	3	1	*	*	*	-0.01	-0.01	*	*	-0.04	*	*	*	*
	3	2	*	*	*	*	0.00	*	-0.03	-0.02	*	*	*	*
	4	1	0.02	-0.01	*	-0.01	*	*	*	-0.01	*	*	0.01	*
	4	2	-0.04	-0.01	*	*	*	*	-0.05	*	*	*	0.02	*
	5	1	*	-0.01	*	*	*	*	*	*	*	*	*	*
	5	2	*	*	*	*	*	0.02	*	*	*	*	0.01	*
	6	1	*	-0.02	*	-0.01	*	*	*	-0.01	*	*	*	*
	6	2	*	-0.01	*	*	*	*	*	*	*	*	*	*
	7	1	0.02	*	*	0.02	*	*	*	-0.02	-0.02	*	*	*
	7	2	0.02	*	*	*	-0.004[a]	0.02	*	*	*	*	*	*
0-20	1	1	-0.02	*	*	*	-0.01	*	-0.05	-0.02	*	*	*	*
	1	2	*	*	*	*	-0.004[a]	*	*	*	*	*	*	*
	2	1	*	*	*	-0.01	-0.01	*	-0.02	-0.02	*	*	0.01	0.01
	2	2	*	*	*	*	*	*	*	-0.01	*	0.02	*	*
	3	1	*	*	*	*	-0.01	*	-0.01	-0.04	*	-0.03	*	*
	3	2	-0.01	*	*	*	*	*	-0.02	-0.03	*	*	*	*
	4	1	*	-0.02	*	*	-0.01	*	*	-0.02	*	*	*	*
	4	2	-0.03	-0.02	*	*	*	*	-0.04	-0.01	*	*	0.01	*
	5	1	-0.02	*	*	-0.01	-0.01	*	-0.02	-0.01	*	*	*	*
	5	2	*	*	*	*	*	0.02	*	*	*	*	0.01	*
	6	1	*	-0.02	-0.01	*	*	*	-0.01	-0.01	*	*	*	0.02
	6	2	*	-0.01	*	-0.01	*	*	-0.02	-0.01	*	*	*	0.02
	7	1	*	*	*	0.02	*	*	*	-0.02	*	*	*	*
	7	2	*	-0.01	*	0.01	*	0.02	*	*	*	*	*	0.01

* The rate constant was below its individual limits of detection. The limits of detection of the individual rate constant are summarised in Appendix 4.6.

[a] When the rate constant was less than 0.005 d^{-1}, it was presented in three decimal digits to be able to indicate a negative or positive value.

WG1, DS1 = West Gabbard and Dowsing station in autumn 2013
WG2, DS2 = West Gabbard and Dowsing station in winter 2013
WG3, DS3 = West Gabbard and Dowsing station in spring 2014

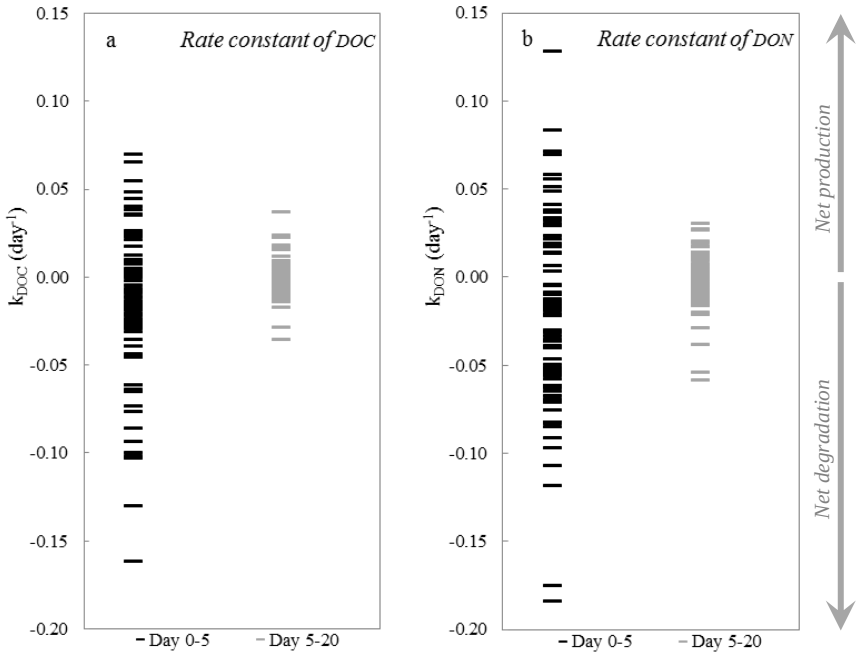


Figure 4.17 Variation of rate constants of (a) DOC (k_{DOC}) and (b) DON (k_{DON}) for time 0 to 5 days and 5 to 20 days of the incubation time for all treatments. Net production (+) and net degradation (–).

Table 4.6 Mean rate constants (d^{-1}) obtained by fitting the exponential degradation (–) and production (+) of DOC and DON with day 0-5 incubation time at varying treatment (T1-T7) in autumn, winter and spring. SE is standard errors.

T	Mean k_{DOC} (d^{-1})						Mean k_{DON} (d^{-1})					
	WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
1	-0.12	-0.03*	0.03**	0.02**	-0.02	-0.04*	-0.08	-0.06	-0.01**	*0.002***	-0.02**	-0.07*
2	-0.05*	-0.02**	0.02**	0.02**	-0.02**	-0.01**	-0.04**	-0.04	-0.02**	-0.02**	-0.02**	-0.02**
3	-0.06*	-0.06	*0.001***	-0.01*	-0.02	-0.02*	-0.07	-0.05*	-0.14*	0.05*	-0.04*	-0.11**
4	-0.04	-0.03**	-0.01	0.06*	-0.03	-0.02**	-0.04**	-0.06*	0.03**	0.03**	-0.03*	-0.03*
5	-0.10	-0.01**	-0.01*	-0.01**	-0.02*	*0.001***	-0.08	-0.03**	0.05**	0.06*	-0.01**	-0.03*
6	-0.05	-0.02*	0.01**	0.02**	-0.01**	0.01**	-0.06*	-0.02*	0.05*	0.03**	*0.004***	0.04**
7	-0.12	-0.02*	0.01**	0.06*	-0.01*	0.01**	-0.08*	-0.01**	0.05*	-0.04*	-0.04*	0.04**
	Mean k_{DOC} (d^{-1}) of all seasons and all stations by treatments (Mean ± SE)						Mean k_{DON} (d^{-1}) of all seasons and all stations by treatments (Mean ± SE)					
1	-0.03 ± 0.02						-0.04 ± 0.02					
2	-0.01 ± 0.01						-0.03 ± 0.00					
3	-0.03 ± 0.01						-0.06 ± 0.03					
4	-0.01 ± 0.01						-0.02 ± 0.02					
5	-0.03 ± 0.02						-0.01 ± 0.02					
6	-0.01 ± 0.01						0.01 ± 0.02					
7	-0.01 ± 0.02						-0.01 ± 0.02					

* One of duplicate bottles (set 1 or set 2) was below its individual limits of detection

** Both two duplicate bottles (set 1 and set 2) were below their individual limits of detection

When the rate constant was less than 0.005 d^{-1} (italicised text), it was presented in three decimal digits to be able to indicate a negative or positive value.

There was no significant difference in mean k_{DOC} between treatments (ANOVA, $P > 0.05$) as well as mean k_{DON}.

k_{DOC} = Rate constants of DOC, k_{DON} = Rate constants of DON

WG1, DS1 = West Gabbard and Dowsing station in autumn 2013
WG2, DS2 = West Gabbard and Dowsing station in winter 2013
WG3, DS3 = West Gabbard and Dowsing station in spring 2014

4.2.4 Discussion of the laboratory based experiment

4.2.4.1 Overall rates

DOM compounds can be taken up by bacteria as has been demonstrated in several studies (Cole et al. 1982, Kroer 1993, Zweifel 1993, Carlson and Ducklow 1996, Kähler et al. 1997, Ogawa et al. 2001, Cherrier and Bauer 2004, Veuger et al. 2004, Bradley et al. 2010, Kanuri et al. 2013). However, much less study has been done on the rate of DOM degradation. The experiment in this present study was therefore designed to determine the rate of DOC and DON loss in seawater modified in some cases by filtration and nutrient addition. The gravity drained seawaters with a screen was used previously to establish a microbial culture (without inoculum) for studying decomposition rate constants (Hopkinson et al. 2002). The filtration by conventional mesh, glass fibre and membrane filters via gentle gravity filtration used in previous studies (Hopkinson et al. 1997, Raymond and Bauer 2000, Wetz et al. 2008) are believed to be suitable to conduct the incubation experiment to study degradation or production rates of DOC and DON in which natural microbial communities are preserved rather than inoculum approach (add bacteria to filtered seawater) used in other studies (Lønborg and Søndergaard 2009, Lønborg et al. 2009, Lønborg et al. 2010). However, there are limitations for example in terms of bacterial removal in control bottles.

The ideal control treatment (T2) for these experiments is the condition with no bacteria and the filtration process not introducing DOC and DON to the treatment. A 0.1 µm capsule filter was used for T2 (details of the capsule filter is presented in section 2.8.2 in chapter 2) because the suggested lower limit of size for cells in the ocean was 0.15 µm (Andersen et al. 2016). However, changes in concentrations of DOC and DON were found (i.e. Figure 4.11 and Figure 4.12 in section 4.2.3) in T2 (dark incubation) and another light incubation which used the same filter (0.1 µm filter). This is taken to suggest that 0.1 µm filtered seawater did not eliminate all bacterial communities. Although, the biggest linear dimension or equivalent cell diameter (typically a spherical shape) has been considered to characterise cell size (Andersen et al. 2016), cells deviating from this or alternatively distorting during the filtration process (Raven 1994) means that bacteria may pass through the filter if they orientate on a smaller dimension than the nominal filter size.

It is known that filtration is not a perfect way to remove bacteria, e. g. using a 0.2 µm polycarbonate filter, 3% of the bacteria in the unfiltered seawater and 2% of the initial bacterial activity still persisted in the filtrate (Gasol and Morán 1999). In addition, it has been proposed by these authors that filtering increases availability of nutrients (e.g. amines and free amino acids) in the filtrate as elevated bacterial activity (leucine uptake method) in the filtrate was observed.

Therefore, based on the above view, the 0.1 µm filtration does not appear to achieve a true control in which bacterial degradation is stopped. Although a substantial decline in bacterial abundance in the filtrate passed through 0.1 µm filter should have occurred, the activities of these bacteria could be raised in the control relative to the treatments because, filtration processes potentially supply DOC and DON to the control filtrate and reduction in bacterivores (generally removed by 0.8 µm filter) increase bacterial abundance over time due to lack of grazing control (Wetz et al. 2008). In this study, the filter blank determination in section 2.8.2 suggested that DOC and DON contamination from new capsule filters were efficiently removed when pre-washed with Milli-Q water. Additionally, at the start of incubation (day 0), the ratio of DOC concentration in 1.0 µm to 0.1 µm filtered seawater was 1.01 ± 0.09 (n = 24), so DOC does not appear to leak from cells during the filtration process. The ratio for DON concentration was 1.11 ± 0.32 (n = 24) suggesting a small amount of DON (~11%) may leak.

Accordingly, in this study, therefore T2 is not considered a true control due to some bacterial cells passing through filters and data of each treatment (T1 and T3-T7) are not corrected by the values derived from the control treatment (T2) (Figure 4.11, Figure 4.12 and Appendix 4.4). However, the filtration approach is more effective than the antibiotic approach performed in summer 2012 (section 4.1), not only in terms of the bacterial removal issues, but also analytical problems described in section 4.1.5.

Rate constant of DOC and DON clearly showed two stages (Figure 4.13 - Figure 4.17). In general, the first stage of day 0-5 showed higher rates than the later second stage on day 5-20 when rates approached zero. In the last incubation experiment in spring 2014, incubation time was extended to day 70. However, there is no significant difference ($P > 0.05$) of the rate constant between this extended stage (day 20-70) and the second stage (day 5-20), implying the time course of

incubation for 20 days was enough to study degradation of labile forms of DOC and DON which change rapidly on an hours – days time frame (Ogawa et al. 2001, Hansell 2013). The faster degradation in the early first stage on day 0-5 suggests most labile forms of DOC and DON were consumed primarily within this period, whereas, semi-labile and refractory forms are resistant to degradation by microbes and persist for months to years and centuries to millennia respectively (Hansell and Carlson 1998, Carlson 2002, Ogawa and Tanoue 2003, Hansell 2013, Repeta 2015).

There is evidence that treatments with light, notably in T7 (< 200 µm filtered) give a positive rate constant implying DOC and DON release in this treatment rather than degradation. As the whole microbial community (bacteria and phytoplankton) in light are presented in T7, the results suggest release of DOM by phytoplankton under light conditions, consistent with other results (Obernosterer and Herndl 1995, Hu and Smith 1998, Suratman et al. 2008b, Cherrier et al. 2015), which is greater than bacterial degradation. Low rates of change were measured in the T7 treatment during the early stage (day 0-5), suggested a balance between degradation and production changes over the incubation time. Marine bacteria can utilise labile compounds of DOM and release refractory DOM by altering the DOM molecular structure (Ogawa et al. 2001), while phytoplankton can release DOM (Bronk et al. 1994, Varela et al. 2005, López-Sandoval et al. 2013).

During the first five days (Table 4.6), the highest degradation rate constant of DOC (k_{DOC}) at West Gabbard station ranged from – 0.12 to – 0.04 day^{-1} in autumn, followed by – 0.03 to – 0.01 day^{-1} in spring and – 0.01 day^{-1} in winter. Dowsing station followed the same patterns in which k_{DOC} were between – 0.06 and – 0.01 day^{-1} in autumn, – 0.04 and – 0.01 day^{-1} in spring and – 0.01 day^{-1} in winter. Higher degradation rate constants of DON (k_{DON}) at West Gabbard station were recorded during winter (– 0.14 to – 0.01 day^{-1}) compared to autumn (– 0.08 to – 0.04 day^{-1}) and spring (– 0.04 to – 0.01 day^{-1}). However, in contrast to the West Gabbard station, highest k_{DON} at Dowsing station ranged from – 0.11 to – 0.02 day^{-1} in spring, followed by – 0.06 to – 0.01 day^{-1} in autumn and – 0.04 to – 0.02 day^{-1} in winter, respectively. Therefore, in comparison with autumn and spring, winter generally presented lower degradation rate constants for DOM (Figure 4.13 - Figure 4.16 and Table 4.6).

Bacteria are potentially controlled in part by nutrient limitation of DOM degradation (Zweifel 1993, Puddu et al. 2000, Church 2008). The experiments here

overall showed no evidence of nutrient limitation as both N and P treatment (T3 and T4) were not significantly different ($p > 0.05$) to T1 (no added nutrients). This suggests sufficient inorganic nutrients are present to support bacteria to degrade organic matter, as nutrient addition has no significant effect on DOC and DON degradation, and hence that they can get enough N and P from the DOM degradation for growth. So given no evidence of impacts of N and P on degradation, to simplify the discussion and comparison with other studies, all k_{DOC} and k_{DON} measured in the experimental treatments for samples in each of the three different seasons and two stations were treated as one sample and the mean rate constants calculated (Table 4.6). Mean rate constants on day 0 – 5 in Table 4.6 show higher degradation of DON than DOC. The k_{DON} ranged between $– 0.06 \pm 0.03$ and $– 0.01 \pm 0.02$ day $^{-1}$ and k_{DOC} ranged between $– 0.03 \pm 0.02$ and $– 0.01 \pm 0.02$ day $^{-1}$.

In previous studies, the decomposition rate constants were generally reported based on different experimental (e.g. inoculum and filtration procedure) and calculation (e.g. calculation based on different DOM pools and decay model) approaches. The comparison of rate constants derived from different model assumptions is inappropriate as suggested by Hopkinson et al. (2002). The approach used for rate constant calculation is therefore noted when previous studies are reported and wherever possible, the same units are displayed.

Table 4.7 summarises the ranges of the first order rate constants for DOC and DON in this present study and other previous studies with as noted earlier, results here converted to % day $^{-1}$. For experiments without inoculum, the decay rates in this study are comparable to the continental shelf waters (the Mid-Atlantic Bight) for labile pools (Hopkinson et al. 2002). In comparison with other studies which used an inoculum approach, the DOC and DON degradation rates in this study yielded lower rates than other studies (Lønborg and Søndergaard 2009, Lønborg et al. 2009, Lønborg et al. 2010). Degradation rates are influenced by many factors, for instance, DOM composition, initial DOM concentrations (Hopkinson et al. 1997), seasons and temperatures (Raymond and Bauer 2000), bacterial abundance and presence of bacterial grazers (Wetz et al. 2008). A previous study in the North Sea used time series of SmartBuoy samples to calculate degradation rates from the gradient of linear regression analysis of in situ collected sample shows a rate of approximately 0.5 to 0.9 % day^{-1} of DON degradation (Johnson et al. 2013).

Table 4.7 Rate constants (% day^{-1}) of DOC (k_{DOC}) and DON (k_{DON}) from different areas, degradation (-) and production (+).

Sampling area	Rate constant (% day^{-1})		Water column depth (m)	Water sample depth (m)	Sampling date	Study method	Rate calculation	Reference
	k_{DOC}	k_{DON}						
Georges Bank, the northeastern US coast	-0.03 to -0.24	-0.03 to -0.06	na	Surface	Apr 1993 Jul 1994	Following the degradation by the natural population after filtration through 0.7 µm, kept in the dark at room temperature (20 °C) for 129 days (Apr 1993) and 299 days (Jul 1994)	A first order exponential decay model	Hopkinson et al. 1997
York River estuary, Chesapeake Bay	-0.48 ± 0.45 (0-5 days) -0.22 ± 0.14 (5-28 days)	na	na	Surface	Sep 1996 to Sep 1997	Following the degradation by the natural population after filtration through 0.7 µm, kept in the dark at *in* situ temperatures for 28 days	A first order decay model	Raymond and Bauer 2000
South of Georges Bank to Cape Hatteras, the Mid-Atlantic Bight	Shelf waters: very labile pools mean -21.9, labile pools mean -1.8 Shelf slope waters: no change, rate constants were report as zero Note: There were reported by authors that decay rates were not statistically significant differences between DOC and DON, as well as between two years.		na na	Surface 1660	Mar, Aug 1996	Following the degradation by the natural population after filtration through 208 µm, kept in the dark at room temperature (19–20 °C) for 180 days	A multi-G model with a first order exponential decay	Hopkinson et al. 2002
Oregon continental shelf	August: -10 in 3 µm filtrate, -16 in 0.8 µm filtrate September: no net decay in 3 µm filtrate, -9 in 0.8 µm filtrate	August: -3 in 3 µm filtrate, -1 in 0.8 µm filtrate September: -9 in 3 µm filtrate, -14 in 0.8 µm filtrate	na	Surface	Aug, Sep 2005	Following the degradation by the natural population after filtration through 0.8 and 3 µm, kept in the dark at 12 °C for 3 days	Changes of DOM concentration over time	Wetz et al. 2008 [a]
Coastal sites in Denmark - Horsens Fjord (an estuary in the east coast)	-4 ± 1 to -11 ± 3 (mean -6.9 ± 2.0)	-1 ± 0 to -20 ± 4 (mean -7.5 ± 4.9)	2.9	1	Sep 2004 – Jul 2005	Establish a microbial inoculum culture by adding an inoculum of 1.2 µm filtered sample water to 0.7 µm filtrate, kept in the dark at room temperature (18 – 20 °C) for 150 days	A first order exponential decay model	Lønborg and Søndergaard 2009
- Darss Sill (in Hjelm Bight south of the island Møn dominated by the Baltic Sea water)	-2 ± 1 to -11 ± 6 (mean -5.9 ± 3.2)	-3 ± 1 to -33 ± 7 (mean -12.0 ± 10.0)	23.2	1				

Table 4.7 (Continued).

Sampling area	Rate constants (% day^{-1})		Water column depth (m)	Water sample depth (m)	Sampling date	Study method	Rate calculation	Reference
	k_{DOC}	k_{DON}						
The fjord Loch Creran, West Scotland	-3 ± 1 to -6 ± 2 at 8 °C -2 ± 1 to -12 ± 3 at 14 °C -9 ± 5 to -16 ± 2 at 18 °C	-4 ± 1 to -8 ± 2 at 8 °C -4 ± 1 to -17 ± 3 at 14 °C -11 ± 0 to -21 ±4 at 18 °C	13	5	Jul 2006 – May 2007	Establish a microbial inoculum culture by adding an inoculum of 1.2 µm filtered sample water to 0.7 µm filtrate, kept in the dark at 8, 14 and 18 °C for 150 days	A first order exponential decay model	Lønborg et al. 2009
The Ria de Vigo, Spain (the coastal upwelling area, NW Iberian Peninsula)	-18 ± 3 to -35 ±4 (Aut) -11 ± 2 to -20 ± 1 (Win) -20 ± 2 (Spr) -19 ± 5 to -30 ± 8 (Sum)	-27 ± 1 to -41 ± 1 (Aut) -20 ± 1 to -22 ± 2 (Win) -26 ± 4 to -28 ± 9 (Spr) -35 ± 1 to -39 ± 3 (Sum)	na	5	Sep 2007 – Jul 2008	Establish a microbial inoculum culture by adding an inoculum of 1.2 µm filtered sample water to 0.2 µm filtrate, kept in the dark at 15 °C for 53 days (70 days for summer)	A first order exponential decay model	Lønborg et al. 2010
The southern North Sea, Dowsing SmartBuoy site (~ 40 miles east of the Humber Estuary)	na	-0.5 (late Spr to Sum) -0.9 (late Sum to Aut)	22	1	Jan – Sep 2010	SmartBuoy time-series sampls under natural condition	The gradient of linear regression analysis	Johnson et al. 2013
The southern North Sea [b]	T1-Dark, T5-Light	T1-Dark, T5-Light			Oct 2013 – May 2014	Following the degradation by the natural population after filtration through 0.1, 1 and 200 µm, kept in the dark and light at 15, 7, 11 °C (autumn, winter, spring) for 20 days	A first order exponential decay model [c]	This study
- Dowsing SmartBuoy site (DS) (~ 40 miles east of the Humber Estuary)	-3.1 ± 4.4, -1.4 ± 2.1 (Aut) 1.7 ± 2.5, -0.8 ± 2.5 (Win) -4.1 ± 3.6, 0.1 ± 3.1 (Spr)	-6.3 ± 0.1, -2.7 ± 1.9 (Aut) 0.2 ± 2.7, 6.2 ± 3.0 (Win) -7.2 ± 5.0, -2.6 ± 4.1 (Spr)	24	2 – 4				
- West Gabbard SmartBuoy site (WG) (~ 40 miles east of the Thames Estuary)	-11.7 ± 1.9, -10.1 ± 0.1(Aut) 3.1 ± 1.0, -1.0 ± 3.1 (Win) -2.0 ± 0.2, -2.1 ± 0.8 (Spr)	-8.2 ± 1.4, -8.3 ± 0.0 (Aut) -0.6 ± 1.3, 4.7 ± 1.5 (Win) -1.6 ± 1.2, -1.3 ± 0.3 (Spr)	32	2 – 4				

Data in the table are obtained from tables, text or graph estimation in the references and is reported in term of the range and/or mean ± standard deviation (SD).
na: Data is not available
Spr, Sum, Aut and Win are spring summer autumn and winter, respectively.
[a] Values are obtained from graph estimation on non-nutrient addition treatments.
[b] In this study, T1 and T5 were 1.0 µm filtered under light and dark condition with no chemical treatments. The value is the mean rate constants on day 0-5 ± SD, SD is standard deviation of samples from duplicate incubation bottles.
[c] Rate constants obtained by fitting the exponential model to the concentration of DOC and DON over incubation times.

This rate was in the range of this present study. The agreement provides confidence in the rates given the different methods used.

In addition, the decay rates in SmartBuoy samples (chapter 3, section 3.7) can also be compared to incubated samples by adjusting the rate calculation method carried out in the incubated samples. In order to compare data sets to investigate how SmartBuoy rates compare to rates obtained by incubation experiments carried out with water samples collected from the same sites in this study, the rates of incubation experiments were recalculated since the incubation rates derived from proper kinetic analysis with the first-order reaction rate are not directly related to the SmartBuoy sample. Thus, the rates obtained by incubation experiments were recalculated by the linear regression analysis with time (as the best fit line with the gradient yielded decay rate, zero-order reaction) as carried out in the Smartbuoy data sets.

To recalculate decay rates of incubation experiments, the data of treatment 7 (T7, < 200 µm filtrate) in autumn 2013 experiments (constant temperature at 15 °C with a day/night light cycle) incubated for 0-5 day was chosen in order to provide most similar conditions to the SmartBuoy samples among other treatments (T1-T6) . In addition to treatment 7, the data of treatment 1 (T1, < 1.0 µm filtrate) in autumn 2013 experiments (constant temperature at 15 °C with dark condition) incubated for 0-5 day was also chosen to allow considering the role of production and consumption on decay rates. Basically, rates determined from T7 indicate both production and consumption processes, whereas T1 provides rates mainly influenced by the consumption process. The plots of incubation data sets (T1 and T7) is shown in Appendix 4.8.

The decay rate of DOC and DON at two SmartBuoy sites in Phase I differed from the rate obtained by incubation experiments carried out with water samples collected from the same sites in this study when using a similar model of rates as a decay function. Results of DOC and DON degradation rates obtained from the SmartBuoy time series and the incubation experiments are summarised in Table 4.8. The SmartBuoy samples demonstrated lower decay rates than incubated samples for DOC although T7 and the SmartBuoy rates were comparable at Dowsing. Many factors may contribute to the lower decay rate. For instance, the Smartbuoy samples

Table 4.8 Summary of DOC and DON decay rates (k_{DOC} and k_{DON}) in autumn 2013 derived Smartbuoy samples and incubation experiments.

Variables	Sites	Decay rates of SmartBuoy samples [a] (μM d^{-1})	Decay rates of incubation experiments [b] (μM d^{-1})	
			T1 (< 1.0 μm filtrate) dark condition	T7 (< 200 μm filtrate) light on daytime and dark on night time
k_{DOC}	West Gabbard	1.77	11.06	8.37
	Dowsing	0.29	2.30	1.60
k_{DON}	West Gabbard	0.06	0.97	0.61
	Dowsing	0.05	0.48	0.09

[a] Rates were determined by the linear regression analysis with time (as the best fit line with the gradient yielded decay rate) in Phase I. Ambient temperatures were 16.4 – 18.3 °C (mean 17.3 ± 0.7 °C, 28 days from 07/09/13 to 05/10/13) at West Gabbard and 8.1 – 15.4 °C (mean 12.0 ± 2.4 °C, 115 days from 27/08/13 to 20/12/13) at Dowsing sites.

[b] Rates were determined by the linear regression analysis with time (as the best fit line with the gradient yielded decay rate) using treatment 1 (T1) and treatment 7 (T7) of autumn 2013 incubation experiments (day 0 – 5), constant temperature at 15 °C.

included the actual water column which included grazing processes by zooplankton that were mostly removed before the start of incubations. This directly affects release by cell breakage and also alters the bacterial and phytoplankton community (Gilbert et al. 1991, Hygum et al. 1997, Puddu et al. 2000, Møller 2005, Møller 2007, Saba et al. 2011). Higher decay rates showed in T1 of incubated samples as most of zooplankton and phytoplankton was removed before the start of incubations under the dark condition. This represented the role of bacterial consumption process only and should therefore yield the higher decay rate in T1, whereas T7 condition allowed both consumption and production processes occurring under the light condition. In addition, the difference between rates of SmartBuoy and incubation experiment is probably a result of the incubation study being carried out at constant temperature and the substance cycling within the system, while temperature and other additional source/sink of dissolved organic pools as well as environmental conditions varied in the natural environment, while the incubation were closed to new external inputs. DOC and DON decay rates generally increased under higher temperatures (Lønborg et al. 2009), while at low temperatures, growth rates of marine bacteria are limited as low rates of extracellular enzymatic hydrolysis (Kirchman and Rich 1997).

The seasonal patterns of decay rates in SmartBouy samples can also be compared to incubated samples. The West Gabbard SmartBouy site provided higher net decay rates of DOC and DON in autumn than in spring, similar to the pattern seen in the degradation rate results of incubation experiments conducted on seawater from West Gabbard site. The Dowsing site showed different patterns between DOC

and DON. The DOC at the Dowsing SmartBuoy site had decay rates in autumn higher than in spring similar to the incubation experiment and to West Gabbard. In contrast, DON in the incubation experiment conducted on seawater from Dowsing site showed higher decay rate in spring than autumn. These differences may reflect temperature or the DOC and DON composition.

4.2.4.2 Stoichiometry of DOC and DON

The relationship of DOC and DON concentration over the course of incubation in different seasons are presented in Figure 4.18 (DOC = mDON + c, where m = gradient and c = intercept). The relationship is estimated from the whole data sets at each station from day 0 to day 20 incubation period. Statistically significant positive correlation was shown between DOC and DON in all seasons: autumn WG ($R^2 = 0.26$, $P < 0.05$, $n = 252$) and DS ($R^2 = 0.34$, $P < 0.05$, $n = 252$), spring WG ($R^2 = 0.11$, $P < 0.05$, $n = 252$) and DS ($R^2 = 0.21$, $P < 0.05$, $n = 252$), and winter WG ($R^2 = 0.02$, $P < 0.05$, $n = 252$) and DS ($R^2 = 0.08$, $P < 0.05$, $n = 252$). WG station showed significant positive correlation between DOC and DON than DS station for the whole incubation dataset in all three seasons (Figure 4.19). The relationship between DOC and DON in Figure 4.18 and Figure 4.19 provide low and variable slope C:N ratio of 0.8 – 5.2 but in these cases degradation rates are low leading to little change in concentration and low R^2 values.

The slope C:N ratios obtained from the regression analysis of DOC-DON plots and the bulk DOC:DON molar ratios are summarised in Table 4.9 for the West Gabbard and Dowsing stations. The two different ways to get C:N ratios of DOM are discussed in chapter 1 (section 1.5). During time courses of incubations for all treatments (Table 4.9), there were no measurable systematic changes in C:N molar ratios throughout the measurement period (0-20 days). This suggests no preferential remineralisation pattern of C or N was observed during the course of the incubations. In comparison to the C:N molar ratios, the slope C:N ratios exhibit considerably lower ratios than the C:N molar ratio (Table 4.9) consistent with the report in other observations (Hopkinson et al. 1997, Hopkinson and Vallino 2005, Lønborg et al. 2010). There were substantially higher bulk C:N molar ratios in this study than the Redfield ratio of 6.6, implying that the DOM is C-rich. This deviation from the Redfield ratio of the C:N molar ratio in this study was consistent over the time

courses of incubation and in accordance with Hopkinson and Vallino (2005) study. The reported bulk C:N molar ratios in this present study were generally similar to previous surface water measurements in the North Sea (12.5 ± 1.5) during 1995-2005 (Van Engeland et al. 2010) and surrounding areas in the east coast of Denmark (11.4 ± 3.8) and Darss Still dominated by the Baltic Sea water (10.6 ± 1.7) (Lønborg

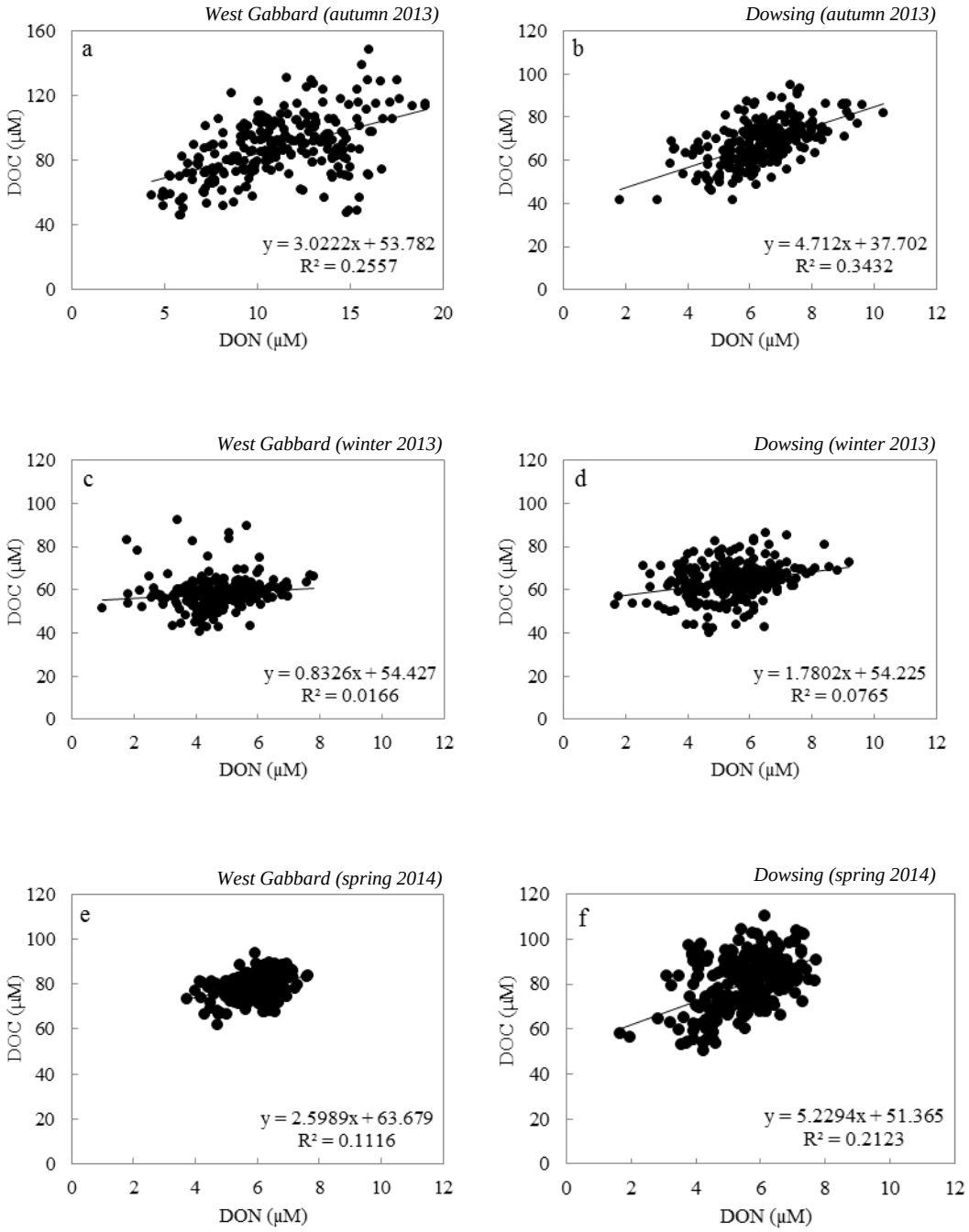


Figure 4.18 Relationship between DOC and DON of the whole incubation data sets (day 0-20) for West Gabbard (a, c and e) and Dowsing (b, d and f) station conducted in autumm (a-b) 2013, winter 2013 (c-d) and spring 2014 (e-f). Note different scale in *y*-axis.

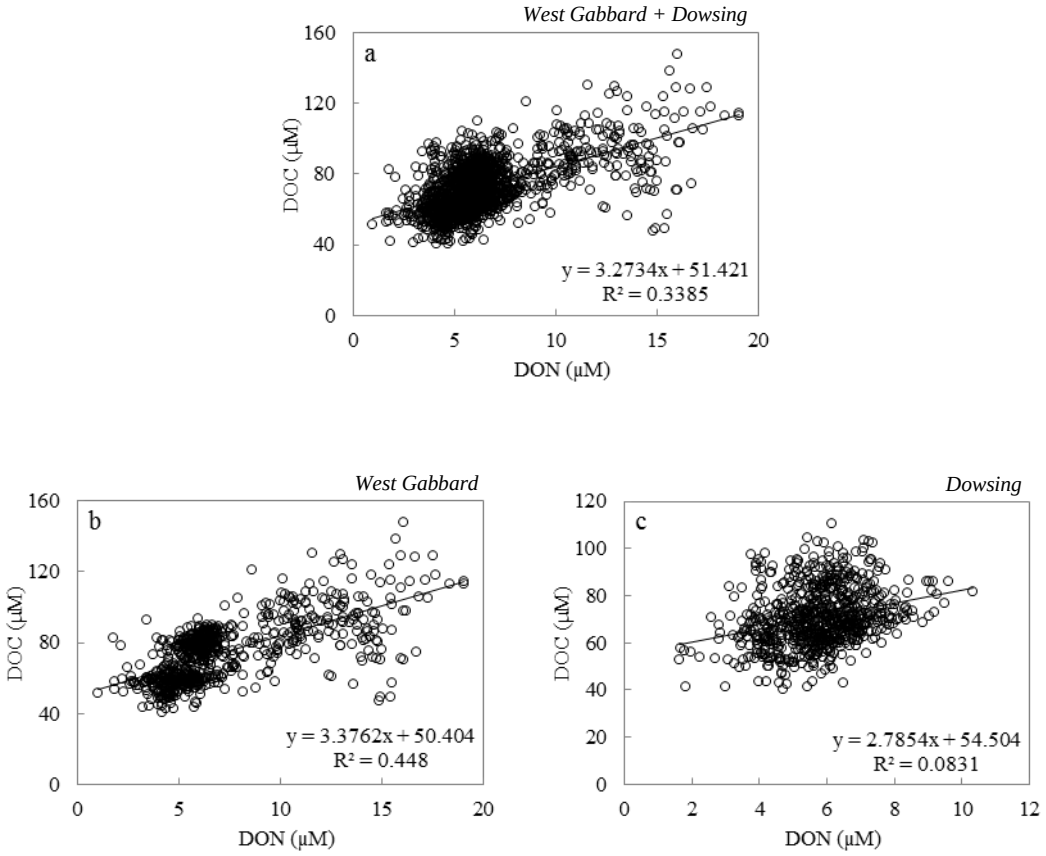


Figure 4.19 Relationship between DOC and DON of the whole incubation data sets (day 0-20) in three seasons for all stations (a) and for separated station at West Gabbard (b) and Dowsing (c) station. Note different scale in *y*-axis.

Table 4.9 Slope of DOC:DON ratios and bulk DOC:DON molar ratios for incubation data sets at the West Gabbard (WG) and (DS) Dowsing stations.

Season	Station	Slope C:N ratio [a]	Bulk C:N molar ratio				
			Mean initial ratio [b] ± SD	Mean ratio [c] ± SD			
				Day 0	Day 0-5	Day 5-20	Day 0-20
Autumn 2013	WG	3.0	12.8 ± 1.5	9.9 ± 1.7	8.0 ± 1.5	8.2 ± 2.1	8.1 ± 2.0
	DS	4.7	10.5 ± 2.1	9.4 ± 0.9	10.1 ± 1.3	11.2 ± 1.9	10.8 ± 1.9
Winter 2013	WG	0.8	12.7 ± 1.1	10.8 ± 1.4	12.8 ± 4.3	12.8 ± 4.4	13.0 ± 4.5
	DS	1.8	9.4 ± 1.2	12.7 ± 4.1	11.7 ± 2.7	12.8 ± 3.9	12.4 ± 3.6
Spring 2014	WG	2.6	13.2 ± 0.5	13.6 ± 0.7	14.1 ± 1.5	13.1 ± 1.5	13.5 ± 1.6
	DS	5.2	15.7 ± 0.8	17.1 ± 4.8	15.8 ± 4.3	14.9 ± 2.7	15.2 ± 3.4
all seasons	WG	3.4	12.7 ± 0.9	11.4 ± 2.1	11.7 ± 3.8	11.4 ± 3.8	11.6 ± 3.8
all seasons	DS	2.8	11.9 ± 3.2	13.1 ± 4.8	12.6 ± 3.9	12.9 ± 3.3	12.8 ± 3.6
all seasons	WG+DS	3.3	12.4 ± 2.3	12.2 ± 3.8	12.1 ± 3.8	12.1 ± 3.6	12.2 ± 3.7

[a] Data sets of day 0-20 in Figure 4.18 and Figure 4.19.
[b] Initial ratio of treatment 7 in two duplicate incubation bottles (T7, < 200 µm) on day 0 represents initial C:N ratio of seawater before a filtration process by capsule filters.
[c] Mean ratios of all treatments (T1-T7)

and Søndergaard 2009), and other measurements in continental shelf waters (Hopkinson et al. 1997, Hopkinson et al. 2002, Ducklow et al 2007, Ribas-Ribas et al. 2011) and open ocean waters (Loh and Bauer 2000, Aminot and Kérouel 2004, Pujo-Pay et al. 2011, Santinelli et al. 2012, Kim and Kim 2013)

In conclusion of the stoichiometry of DOC and DON, preferential remineralisation of N or C over the time courses of the incubation was not seen in the experiments. Low and variable slope C:N ratios of 0.8 – 5.2 in this study differs from other observations (slope C:N ratios ~10-11, higher than the Redfield ratio of 6.6) (Hopkinson and Vallino 2005). In this study, the slope C:N ratios of 0.8 – 2.8 (Figure 4.18 (c,d,e) and Figure 4.19c) are not reasonable to use as the data points are not well distributed (Figure 4.18e) and derived from very low correlation (R^2 = 0.1 and below, $P < 0.05$). However, the slope C:N ratio of 3.0 – 5.2 (R^2 = 0.26 to 0.45, $P < 0.05$) in this study (Figure 4.18 (a,b,f) and Figure 4.19 (a,b)) is close to a C:N molar ratio of 4.9 – 5.0 for bacteria (Goldman et al. 1987, Zimmerman et al. 2014) and is lower than the Redfield ratio, suggesting that the stoichiometry of the degradable DOM (as derived from the slope of DOC-DON plots) was similar by the bacteria. This material could then be directly utilized by bacteria without additional nutrients. This slope C:N ratio was lower than the bulk C:N molar ratios. The substantially higher bulk C:N molar ratios than the Redfield ratio of 6.6 was observed in this study, implying that the DOM is C-rich.

4.2.4.3 Seasonality and controls on degradation

These experiments in section 4.2 cover autumn, winter and spring. To consider the rates in all seasons, DOC and DON data from onboard experiments (section 4.1) without the antibiotic treatment were used to calculate the rate constants for the summer season using a similar approach to that used for the autumn, winter and spring laboratory based data sets. Details of rate constants and limits of detection of the individual rate constant for the summer 2012 are summarised in Appendix 4.9, the mean result is shown in Table 4.10. T1 treatment (no chemical addition under the dark < 200 μm) and T5 treatment (no chemical addition under the light < 200 μm) from summer 2012 onboard experiment (Table 4.10) were chosen in order to compare with other three seasons in laboratory based experiments. These were chosen because summer T1 treatment was closest to T1 in the autumn winter and

spring laboratory based experiments, while, summer T5 was the same treatment as the later T7 laboratory based experiment. Therefore, results from Table 4.6 and Table 4.10 were rearranged to consider all seasons with this additional data as presented in Table 4.11. Initial DOC and DON concentration are also included. Table 4.11 showed autumn and spring have higher net degradation rates than winter as well as higher initial DOC and DON concentration. For the onboard experiment in summer, a net degradation rate and initial DOC and DON concentrations was comparable to the spring for both DOC and DON.

Table 4.10 Mean rate constant (d^{-1}) obtained by fitting the exponential degradation (-) and production (+) of DOC and DON with incubation time to varying treatment (T) without antibiotics in summer 2012, SE is standard errors.

Days	T	Mean k_{DOC} (d^{-1})			Mean k_{DON} (d^{-1})			Mean k_{DOC} (d^{-1})	SE	Mean k_{DON} (d^{-1})	SE
		WG	9	24	WG	9	24				
0-5	1	-0.02*	-0.05*	-0.06	0.05**	-0.01	-0.04**	-0.04	0.01	*0.002*	*0.025*
	3	-0.05	-0.04	0.01**	0.03**	-0.04**	-0.05	-0.03	0.02	-0.02	0.02
	4	-0.02	-0.03*	-0.03	-0.04**	-0.04*	-0.04**	-0.03	0.00	-0.04	0.00
	5	-0.04*	-0.03**	-0.04	-0.02*	-0.07*	-0.02*	-0.04	0.00	-0.04	0.02
5-20 [a]	1	-0.02			-0.04						
	3	-0.02			-0.01*						
	4	-0.01			*0.001**						
	5	0.02			0.01*						
0-20 [a]	1	-0.02			-0.03						
	3	-0.02			-0.01*						
	4	-0.01			-0.01*						
	5	0.01*			-0.01*						

Remark:
WG = West Gabbard station
9 = Station 9
24 = Station 24

When the rate constant was less than 0.005 d^{-1} (italicised text), it was presented in three decimal digits to be able to indicate a negative or positive value.
[a] The experiment was extended to day 20 at station WG set 1 only (see Figure 2.4 in chapter 2 for details).
* One of duplicate bottles (set 1 or set 2) was below its individual limits of detection.
** Both two duplicate bottles (set 1 and set 2) were below their individual limits of detection.
The limits of detection of the individual rate constant are summarised in Appendix 4.9.

In summary for the laboratory based experiment, the rate of DOC and DON in terms of degradation or production can be divided into two stages, the fastest rate occurred within the first 5 days and slowed after day 5. The hypothesis that seasonal rate of DOC and DON net degradation will increase with initial supply concentration of DOC and DON has been tested by plotting the relationship between rate constant and initial concentration for the laboratory based experiment in autumn winter and spring (Figure 4.20). The summer onboard incubation experiment was not included in the figure as they are derived from different experiments and sampling stations, although the results are broadly consistent with the other seasons. Autumn and spring have higher net degradation rates than winter as well as higher initial DOC and DON concentration (Figure 4.20). There is a significant negative correlation ($P <$

0.05) between DOM rate constant and their initial concentration in Figure 4.20. This implies that higher degradation rate is obtained when the incubation started with higher DOC and DON concentration, consistent with a previous study (Hopkinson et al. 1997). The highest significant correlation ($R^2 = 0.71$, $P < 0.05$, $n = 21$) was shown between DOC rate constant and their initial concentration at West Gabbard station (Figure 4.20a), with lower correlation for other sites and parameter, for example, DOC at Dowsing station ($R^2 = 0.26$, $P < 0.05$, $n = 21$), DON at West Gabbard station

Table 4.11 Seasonal rate constant [a] of DOC and DON (k_{DOC} and k_{DON}, d^{-1} ± SE) and related parameters (incubation temperature (°C) and mean initial concentration (µM ± SE, averaged all stations in each season)), the time period of incubation on day 0-5.

Treatments	Parameters		Summer 2012 (17 °C [b])	Autumn 2013 (15 °C [c])	Winter 2013 (7 °C [c])	Spring 2014 (11 °C [c])
T1 (Dark)	DOC	k_{DOC}	-0.04 ± 0.01	-0.07 ± 0.04	0.02 ± 0.01	-0.03 ± 0.01
		Initial concentration	82.1 ± 3.7	106.8 ± 29.1	63.4 ± 2.1	89.3 ± 2.2
	DON	k_{DON}	0.002 [d] ± 0.025	-0.07 ± 0.01	-0.002 [d] ± 0.004	-0.04 ± 0.03
		Initial concentration	6.0 ± 0.4	11.9 ± 2.9	5.6 ± 0.0	6.3 ± 0.1
T3 (Dark + N)	DOC	k_{DOC}	-0.03 ± 0.02	-0.06 ± 0.00	-0.01 ± 0.01	-0.02 ± 0.00
		Initial concentration	84.3 ± 1.9	103.6 ± 23.0	66.2 ± 6.1	85.1 ± 1.5
	DON	k_{DON}	-0.02 ± 0.02	-0.06 ± 0.01	-0.04 ± 0.10	-0.07 ± 0.03
		Initial concentration	5.4 ± 0.4	11.1 ± 2.8	5.8 ± 0.8	6.1 ± 0.3
T4 (Dark + P)	DOC	k_{DOC}	-0.03 ± 0.00	-0.03 ± 0.01	0.02 ± 0.04	-0.03 ± 0.01
		Initial concentration	83.7 ± 2.3	87.1 ± 15.8	64.1 ± 0.3	84.5 ± 1.3
	DON	k_{DON}	-0.04 ± 0.00	-0.05 ± 0.01	0.03 ± 0.00	-0.03 ± 0.00
		Initial concentration	6.1 ± 0.3	10.0 ± 2.1	5.7 ± 0.3	6.5 ± 0.1
T7 (T5 summer) (Light)	DOC	k_{DOC}	-0.04 ± 0.00	-0.07 ± 0.05	0.04 ± 0.02	0.001 [d] ± 0.011
		Initial concentration	84.7 ± 4.0	87.8 ± 10.9	59.8 ± 0.8	84.4 ± 0.9
	DON	k_{DON}	-0.04 ± 0.02	-0.05 ± 0.03	0.01 ± 0.05	-0.001 [d] ± 0.042
		Initial concentration	5.9 ± 0.3	7.5 ± 0.2	5.5 ± 0.7	5.9 ± 0.6

Rate constants in the unit of % d^{-1} are presented in Appendix 4.10. SE =Standard errors

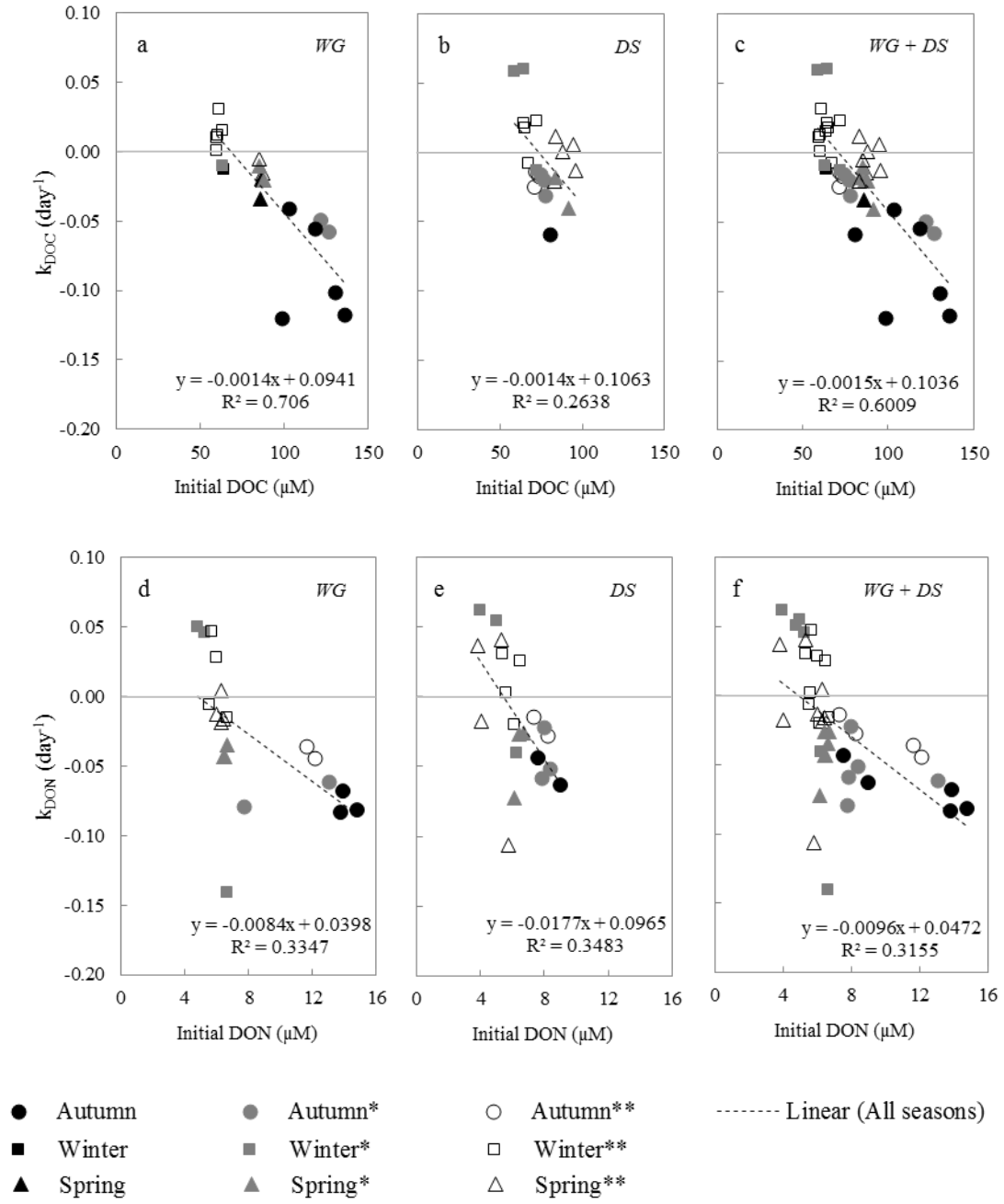
The rate constant with a negative value is net degradation, while a positive value is net production.

[a] Rate constants was averaged all stations in each season based on each treatment: treatment T1, T3 and T4 in summer 2012 was comparable to treatment T1, T3 and T4 in autumn 2013, winter 2013 and spring 2014,respectively; and treatment T5 in summer 2012 was similar to treatment T7 in autumn 2013, winter 2013, spring 2014. Note the experimental treatment details in chapter 2, section 2.3.2 and section 2.3.3.

[b] Average temperature of temperature range 16-19 °C onboard controlled by continuous flow of the online supply water.

[c] Constant temperature controlled by the control temperature room onboard and then the incubator at the UEA based laboratory.

[d] When the rate constant was less than 0.005 d^{-1}, it was presented in three decimal digits.



* One of duplicate bottles (set 1 or set 2) provides rate constant lower than its individual limit of detection.
** Both two duplicate bottles (set 1 and set 2) provide rate constants lower than their individual limits of detection.

Figure 4.20 Relationship between rate constant (first five days) and initial concentration of DOC (at West Gabbard (a), Dowsing (b) and all station (c)) and DON (at West Gabbard (d), Dowsing (e) and all station (f)) in all treatment (T1-T7) using data from Appendix 4.11.

(R^2 = 0.33, P < 0.05, n = 21), and DON at Dowsing station (R^2 = 0.32, P < 0.05, n = 21). The general pattern of laboratory based experiments in Figure 4.20 is that in autumn 2013 samples exhibit net consumption when there were high initial DOC and DON concentrations, whereas winter 2013 samples present net production when there were low DOC and DON concentrations. Both net production and net consumption was observed in spring 2014 samples. The high net production of DOC and DON recorded during winter and spring were particularly found in treatment 7 (T7, < 200 µm, light condition) in which there were also observed high chlorophyll *a* concentration in winter samples (7.2 ± 0.2 µg/L at West Gabbard and 7.3 ± 0.4 µg/L at Dowsing) and lower in spring (0.6 ± 0.1 µg/L at West Gabbard and 0.9 ± 0.3 µg/L at Dowsing), after the finish of the incubation. This suggests higher phytoplankton biomass in treatment 7 supported DOC and DON release during the incubation under light conditions. High net production of DOC and DON during winter was also found in samples treated under dark condition (e.g. treatment 1 (T1, < 1.0 µm), suggesting bacteria release DOM into water by egestion and excretion processes (Nagata et al. 2000, Kujawinski 2011). The viral infection of bacteria can also release viral lysate as DOM (as DFAA and DCAA) from infected cells (Middelboe and Jørgensen 2006).

There is therefore a seasonal component to the degradation rates. As the rates vary seasonally, the possible causes driving these difference are temperature and DOM concentrations. Figure 4.20 suggests DOM concentration may be a controlling factor. Nevertheless, it is not possible to conclude here whether initial concentration or temperature have more influence on degradation rate because both show somewhat similar seasonality. However, it is possible that higher temperature during autumn and spring incubation stimulate the microbial activity, as previous studies suggest temperature influences the decay rate (Lønborg et al. 2009). The Arrhenius equation (which describes the temperature dependence of the reaction rate), was used to test the hypothesis that the seasonal rate of DOC and DON net degradation increases with temperature. The natural logarithm of the *y* value (*y* value = rate constant of DOC and DON (k_{DOC} and k_{DON})) was plotted against 1/*x* value (*x* value = temperature (in kelvin (K)) based on the Arrhenius equation (Figure 4.21). The plot in Figure 4.21 suggests temperature influences the decay rate, with DOM degraded faster under higher temperature. The data suggest decay rates vary seasonally but do

not allow the relative importance of temperature or DOM concentration to be determined. The type of DOC and DON can also effect rates as the labile form is generally easier to consume by microbes in a short period, whereas, the less-labile form takes a long time to degrade and the concentration and lability may vary with season.

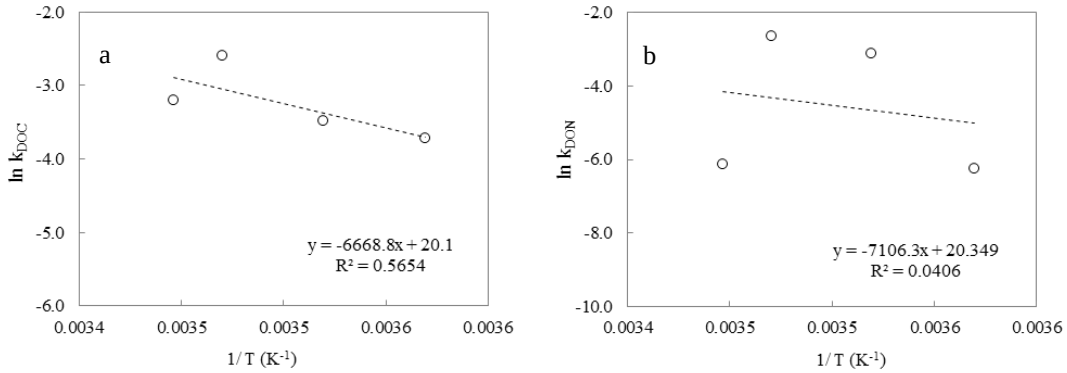


Figure 4.21 Relationship between log rate constant (first five days) of DOC (a) and DON (b) and 1/temperature using data from treatment 1 in Table 4.10.

4.2.4.4 Summary discussion

In conclusion, although rates are low, the rate of DOC and DON in terms of degradation or production can be divided into two stages, the fastest rate occurred within the first 5 days and slower after day 5, implying that labile DOM is primarily consumed within 5 days and semi-labile/ refractory DOM persisted and degraded after day 5. There is no evidence of nutrient limitation (N and P) in DOC and DON degradation observed in this study. Preferential remineralisation of N or C over time courses of the incubation is not observed. In general, high net degradation rates are observed in the dark treatments, whereas low net degradation rates and high net production rates are observed in the light treatments, particularly treatment 7 (T7, < 200 µm). This suggests that bacteria dominate the DOM degradation process and phytoplankton dominate DOM production. The rate is seasonally variable. Summer, autumn and spring generally have higher net degradation rates than winter as well as higher initial DOC and DON concentration. These differences may reflect the influence of both seasonal temperature and initial concentration on the decay rate. The DOC and DON rate results will be combined with the DOC and DON survey results in chapter 3 to consider the overall DOC and DON cycling in chapter 5.

5 CONCLUSION

5.1 Conclusion

In this research, the cruise surveys and SmartBuoy time series were combined with the incubation experiment to investigate the biogeochemical cycling of DOC and DON in coastal waters of the North Sea. The main findings of the research based on specific objectives on page 59 are described below and then linked together in a conceptual model of DOM cycling.

5.1.1 Surface and bottom concentrations of DOC and DON

Determinations in surface and bottom waters of samples in the whole North Sea demonstrate that overall both DOC and DON concentrations were not significantly different between surface and bottom waters in summer and winter. The exception was only DOC in summer 2012 when surface mean concentration was significantly higher than the bottom water. This surface maximum may be associated with the river runoff or net production from autotrophs increasing concentration in the surface water. DOC and DON showed a different vertical pattern to inorganic nutrients which had high accumulation in the bottom water during summer stratification.

5.1.2 Spatial and temporal variation of DOC and DON concentrations

The North Sea water was characterised into three regions during the stratified season including the stratified northern surface water, the northern bottom surface and the well-mixed southern water. Most of the dissolved inorganic nutrients in this study were found in high concentration in the northern bottom waters as dead organisms sink to the bottom and bacterioplankton breaks down the tissues in the process of decay. This leads to high inorganic nutrient concentrations in the bottom water due to release from bottom regeneration process and inflow from offshore waters. In contrast to the inorganic nutrients, dissolved (DOC and DON) and particulate (POC and PON) forms of organic nutrients and chlorophyll *a* generally

exhibited the highest level in the southern well-mixed water. The high concentration was mainly near the coast where there was more influence by river plumes from continental Europe, the coastal area near Skagerrak and the eastern coast of the UK. During seasonal stratification, DON was the dominant form of nitrogen compounds (DIN, DON and PON) in the stratified northern surface water and the southern well-mixed water, whereas in northern bottom water the dominant form of nitrogen was DIN as found in well-mixed water sampled over the winter period. PON made a smaller contribution to nitrogen compounds, particularly in northern bottom water.

This study has shown seasonal variations of nutrients over summer and winter. Riverine runoff was an important source to support inorganic nutrient entering via the coast in winter as enrichment of inorganic nutrients in winter were strongly negatively correlated with salinity, whereas no evidence of this was observed in summer. Although mean DOC and DON concentration show different levels between two summer surveys, their distribution pattern showed a significant influence of riverine input. DOC and DON concentrations plotted against salinity provided evidence that freshwater inputs are important sources of DOC and DON over the summer period and DOC over winter, while this was not so evident for DON in winter.

In summer, DOC and DON has a significant positive correlation with each other. Graphs of DOC versus DON in the northern surface and southern well-mixed waters have slope C:N ratios of 5.7 to 8.1 with a clear non zero intercept of DOC ~ 30 µM. In contrast to summer, there was an absence of any significant correlation between DOC and DON observed during winter. The slope C:N ratio in summer was close to the Redfield ratio of 6.6 suggesting a direct association with phytoplankton in the water column during the summer period but not in winter. However, the phytoplankton biomass (as measured by chlorophyll *a*) measured in winter and summer does not show any correlation with DOC and DON, chlorophyll *a* was strongly positively correlated with POC and PON in summer. The positive relationship between DOC and POC as well as DON with PON was only found in the southern well-mixed water in summer suggesting a relationship between POM particle concentration and DOM as an important process in this water mass. Higher POM may indicate higher recent productivity which can then be a source of DOM.

Eventually, the degradation of POM will produce DOM and in a closed system will produce a reverse relationship.

In addition to the freshwater input, microbial processes also contributed to DOC and DON cycling as revealed in the SmartBuoy samples. Phytoplankton biomass provided a net source of DOC and DON over the spring bloom period at the Dowsing site, whereas this pattern was not shown at the West Gabbard site possibly because the higher turbidity observed and hence less light for phytoplankton and less growth, or that the spring bloom at the West Gabbard was later and hence the spring bloom effect was not seen in the samples analysed.

5.1.3 Influence of bacteria and phytoplankton on the DOC and DON concentration over time

The incubation method used was able to measure DOM cycling rates although they were often low and close to their detection limit. In the incubation experiments, the DOC and DON degradation was faster in the early first stage, day 0-5, suggesting more labile forms of DOC and DON were consumed primarily within this period, whereas, the semi-labile and refractory form is resistant to degradation by bacteria and persists for a longer period of the incubation courses and beyond. In comparison with autumn and spring, winter generally presented lower degradation rate constants on day 0-5. Autumn and spring have higher rates than winter probably because there is more DOC and DON and higher temperature during autumn and spring incubation. The first order net decay rate constants for DOC (k_{DOC}) and DON (k_{DON}) determined by the incubation technique were consistent with previous studies in other areas. This study provides mean net decay of k_{DOC} 4 ± 8 and 2 ± 3 % d^{-1}, while k_{DON} was 3 ± 4, and 4 ± 4 % d^{-1} at the West Gabbard and Dowsing stations respectively, for dark condition treatment containing predominantly bacteria (T1) averaged over the three seasons (autumn, winter and spring).

In general, no evidence of N and P limitation in the incubation experiment was seen, suggesting sufficient inorganic nutrients to support bacteria to degrade organic matter. Under light conditions and in the presence of the whole microbial community (bacteria and phytoplankton), there is a generally balance between

degradation and production changes during the early stage (day 0-5), implying DOC and DON release by phytoplankton under light condition balanced with degradation process during this period. Therefore, there is net DOM degradation in the dark but there can be production in the light. Comparisons of degradation rates between incubation experiment and SmartBuoy samples suggested that the presence of grazers influences DOC and DON decay rates. When the grazers were mostly removed before the start of incubations, higher net decay resulted compared to those determined from SmartBuoy samples. This is interpreted as being due to release of DOM by cell breakage during zooplankton grazing which balances some of the bacterial DOM consumption.

5.1.4 Processes controlling DOC and DON cycling and distribution

The study of incubation experiments, survey cruise and SmartBuoys generally showed a variety of C:N ratio of DOM (both C:N molar ratio and slope C:N ratio). The stoichiometry of DOM net change due to decomposition and production indicated by the slope C:N ratio is taken to suggest that the cruise surveys in summer (the slope C:N ratio was 5.7 to 8.1 in stratified northern surface and southern well-mixed water) generally agree with the Redfield ratio. The slope C:N ratio with close to the Redfield ratio of 6.6 suggesting a dominant role of phytoplankton in the water column, plus a high C:N background (the y-intercept value indicates a background level of DOC which still persists when DON reaches zero). In consideration of the bulk C:N molar ratio which yielded 11.1 to 17.3 in the northern surface and southern well-mixed water, the cumulative DOM in water columns during summer and winter C:N molar ratio was enriched in carbon relative to nitrogen, compared to the Redfield ratio of 6.6. In addition or instead of the DOM composing high C:N background material with the additional Redfield proportion DOM in the shelf sea, there is an alternative interpretation of the bulk C:N molar ratio. Mixing between freshwater (higher DOM concentration and C:N molar ratio) and the seawater (lower DOM concentration and C:N molar ratio) may influence DOM concentration and the C:N molar ratio presence in the shelf sea, or a combination of both processes.

For the incubation experiment, a slope C:N ratio was ~3 for the whole incubation data sets (day 0-20), whereas the C:N molar ratio was ~12. In the SmartBuoy samples, C:N molar ratio was ~11 to 16 while a slope C:N ratio is not available as a significant relationship between DOC and DON was not found in each season. However, the whole data set (all seasons) has a significant correlation between DOC and DON with the slope C:N ratio of 5.6 and 6.8 for the West Gabbard and Dowsing sites respectively. This slope C:N ratio was close to the Redfield ratio of 6.6 suggesting an important role of phytoplankton in the water column at both sites. Higher slope C:N ratios probably reflect preferential N remineralisation, lower slope C:N ratios may reflect preferential C remineralization or an implied role of bacteria since they have a lower C:N ratio compared to the Redfield of 6.6.

The variation of the C:N ratio of DOM within this study reflects the analytical approach used (determination of C:N molar ratio or slope C:N ratio) with the slope C:N ratio generally lower than the ratio of the bulk pools (C:N molar ratio) as also observed in previous studies (Hopkinson et al. 1997, Hung et al. 2003, Hopkinson and Vallino 2005, Suratman et al. 2009, Lønborg et al. 2010). In addition, the different sampling approaches (incubation experiments, survey cruises and SmartBuoys) give somewhat different C:N ratio of DOM which may reflect a different dominant microbial community.

Bacteria play an important role in DOC and DON cycling as bacteria are the main pathway to remineralise DOM by degradation process, while phytoplankton play a role in the release of DOM. These two processes affect the balance of DOM cycling and the DOM concentration in coastal water. During winter when high turbidity and low light is available, phytoplankton productivity is probably low and light limited, leading to low DOM concentration in the water columns (initial concentration) and then slower degradation rates in the incubated samples compared to other seasons. The presence of grazers in the water column contributed to DOM production by zooplankton grazing processes and lead to slower net degradation rates of SmartBuoy samples in autumn compared to incubated samples. In addition to the phytoplankton and bacteria, the freshwater inputs are also important processes influencing DOC and DON cycling and distribution in the North Sea in summer, particularly near the coast receiving the riverine runoff and Baltic outflow.

A conceptual model of DOM cycling in the North Sea

DOM has a seasonal cycle in a dynamic North Sea system illustrated in a conceptual model (Figure 5.1). In addition to processes of DOM cycling in a general shelf sea system (Figure 1.5 in chapter 1), this conceptual model (Figure 5.1) combines together the main findings of this study obtained from cruise surveys, seasonal incubation experiments and SmartBuoy time series samples.

Over the summer surveys (2011 and 2012), the riverine input contributes DOM and POM in the southern well-mixed water (SM), whereas the Baltic Sea input contributes DOM in the stratified northern surface water (NS). The cumulative DOM in water columns during summer was enriched in carbon relative to nitrogen, compared to the Redfield ratio of 6.6. In summer 2011, there was a significant difference ($P < 0.05$) between the C:N molar ratio of DOM which was higher in the stratified northern bottom water (NB) than surface water masses (SM and NS). This suggests either high C:N molar ratio materials input from offshore or preferential remineralisation. Since the mean C:N molar ratio of NB (13.4 ± 3.6) is similar to the mean value of the North Atlantic (~13-14) (Aminot and Kérouel 2004), this suggests deep outer shelf water inputs of high C:N molar ratio materials to the NB. Another possible process is a preferential remineralisation of nitrogen relative to carbon in the NB. Nevertherless, high C:N molar ratio of NB in summer 2011 may be influenced by a combination of both processes. The different pattern found in summer 2012 (the significant lower C:N molar ratio in NB than SM and NS) was because this observation did not include the area above 58°N which generally showed substantially higher C:N molar ratios in summer 2011. The deep outer shelf water also supplies inorganic nutrients to the NB as well as that supplied by bottom regeneration processes, particularly for DIN. In addition, phytoplankton biomass contributes to the POM pool (only investigated in summer 2012). POM later contributes to the DOM pool by degradation and also accumulates in bottom sediment. Incubation experiments conducted in summer 2012 (note different condition with later experiment in autumn and winter 2013 and spring 2014) yields a net degradation rate constant for DOC (k_{DOC}) of $– 0.04 \pm 0.01$ d^{-1}, whereas DON (k_{DON}) yields < 0.005 d^{-1} (Figure 5.1 (purple)).

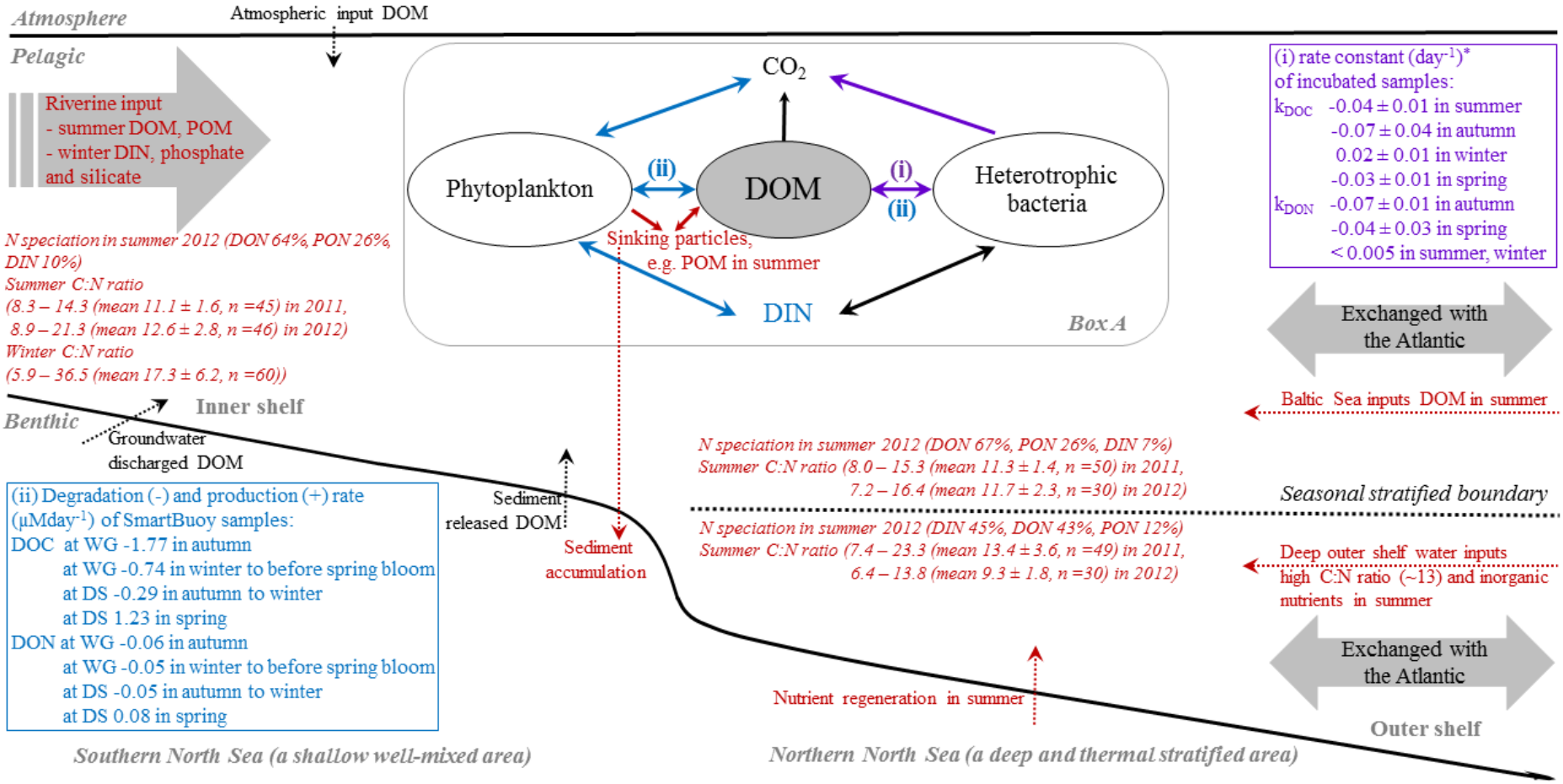


Figure 5.1 A conceptual model of DOM cycling in the North Sea. Results from cruise surveys (red), seasonal incubation experiments on day 0-5 (purple) and seasonal SmartBuoy samples (blue) are indicated in different colour. WG and DS are the West Gabbard and Dowsing station, respectively. C:N ratio is DOC:DON molar ratio (range, mean ± SD). (i) Rate constant (k) of treatment 1 (T1 is dark < 1.0 μm, except summer < 200 μm) which represents net degradation (-) condition, k is averaged value of all stations in each season (summer 2012, autumn and winter 2013 and spring 2014), k < 0.005 indicates mean rate constant was less than 0.005. (ii) SmartBuoy samples are investigated in autumn and winter 2013 and spring 2014, presented season is partly overlapped as the rate calculation based on trends of degradation and production over timescale in natural condition. Box A is internal cycling of DOM. * Unit % day^{-1} in Appendix 4.10

In autumn 2013, the highest degradation rates, k_{DOC} (– 0.07 ± 0.04 d^{-1}) and k_{DON} (– 0.07 ± 0.01 d^{-1}), were observed, consistent with the highest mean initial concentration 106.8 ± 29.1µM for DOC and 11.9 ± 2.9 µM for DON in this season. Similarly, SmartBuoy samples yield high net degradation of DOC (– 1.77 µM d^{-1}) and DON (– 0.06 µM d^{-1}) in autumn at the West Gabbard site, while net degradation pattern continued in winter 2013 at the Dowsing site (DOC – 0.29 µM d^{-1} and DON – 0.05 µM d^{-1}). The cruise survey in winter 2011 (the southern North Sea) indicates inorganic nutrients (DIN, phosphate and silicate) via riverine input, are important input processes. In comparison with summer surveys, observation in winter shows significantly ($P < 0.05$) higher C:N molar ratio of DOM (17.3 ± 6.2) supplied by high C:N ratio material via riverine runoff. There was a small net production rate constant of DOC (k_{DOC}) of 0.02 ± 0.01 d^{-1} in winter 2013 consistent with low initial concentration at the start of the incubation experiment. Conversely, the net degradation rate of SmartBuoy samples yields – 0.74 µM d^{-1} for DOC and – 0.05 µM d^{-1} for DON over winter before the spring bloom period at the West Gabbard site but the signal of phytoplankton bloom was relatively less clear compared to the Dowsing site.

In spring 2014, the high chlorophyll fluorescence during the spring was only recorded at the SmartBuoy Dowsing site. This represents the spring bloom with increasing chlorophyll, declines in inorganic nutrients, and the production of DOC and DON associated with the bloom. The Dowsing site yielded net production rates of DOC and DON of 1.23 µM d^{-1} and 0.08 µM d^{-1}, respectively, during the period. It has been estimated here that the concentration of DOC increased ~50 % and DON increased ~40 % during spring bloom period (compared to previous spring bloom). A strong significant positive relationship between oxygen concentration and chlorophyll fluorescence, as well as oxygen saturation and the fluorescence reflecting net oxygen production during the spring bloom.

The DOC concentration increased from 150.7 µM on 15 March 2014 to the maximum 224.0 µM on 20 April 2014 (four days after the fluorescence reached its highest level), the DOC then slightly decreased to 211.6 µM on 28 April 2014. There was a small increase in concentration of the DON from 12.2 µM to the final 16.9 µM in the same period. Thus it seems that the spring bloom represents with increasing

chlorophyll, declines in inorganic nutrients, and the production of DOC and DON associated with the bloom as was seen by Johnson et al. (2013). There is no evidence of a lag between the bloom and DOC production, suggesting DOC is released during the growth phase and not just the bloom decline. The DOC was consumed at a rate of approximately 2 μMd^{-1} in summer (a net decay rate derived from the gradient of the best fit line of the linear regression analysis of the summer incubation onboard, treatment 1), therefore, the increase of DOC (~ 70 µM) during the spring bloom could be consumed over time scales of a month. Thus, the relationship between DOC and chlorophyll *a* seen during the spring bloom period, may not be seen during the summer survey.

It has been indicated that shelf sea regions have the potential to export DOC from the continental shelf water to the open ocean (Barrón and Duarte 2015). Higher DOM concentrations are observed in inner shelf rather than the outer shelf and both areas this study having higher than average surface DOC concentrations in the North Atlantic Ocean (~ 60-80 µM) (Aminot and Kérouel 2004, Carlson et al. 2010, Kähler et al. 2010). This is taken to suggest that DOC in the North Sea is potentially exported to the North Atlantic Ocean over the summer period. However, further research to quantity the export is required i.e. a mathematical modelling. There was less evidence for C:N ratio change driven DOM export. Although, a significance ($P < 0.05$) higher C:N molar ratios was found in the NB than other water masses in the summer 2011 survey, and this is taken to suggest a preferential remineralisation of nitrogen relative to carbon. There appears to be no preferential remineralisation during incubation experiments as C:N molar ratios did not show systematic changes over time. Therefore, the northern bottom water where there is a high C:N molar ratio of DOM in this study requires further research on what causes this phenomena in water to get a better understanding of DOM cycling in the North Sea .

In summary, DOM cycling in the North Sea is influenced by riverine inputs (an external source) over the summer period, while relevant internal processes within water columns dominate other seasons i.e. bacterial degradation of DOM in autumn and phytoplankton production of DOM in spring. This study suggests high C:N background material compared with the Redfield proportion DOM cycled in water columns in all seasons. However, the mixing between freshwater and the ocean water may also influence DOM concentrations and the C:N molar ratio presence in

this study, but information is not sufficient (i.e. DON in rivers draining to the North Sea) to confirm this.

5.2 Further research

To improve our understanding of DOC and DON cycling in coastal waters in the North Sea, further research in DOC and DON biogeochemistry could include the following:

- Improvement of incubation experiments including the determination of DOM chemical composition during the course of incubation. Variability of the chemical composition (e.g. amino acids, fatty acids, polysaccharides and urea) over time is an additional factor in the interaction between DOM and microbes, for instance, providing information on bacterial selection of individual molecule or compound classes during DOM utilisation. The molecular-level analysis can be achieved with techniques such as chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy.

- Improvement of the understanding of DOM lability, particularly the labile and semi-labile DOM that contributes most to the surface waters biological availability. The amount of labile and semi-labile DOM present in water columns indicates the availability of DOM to organisms. Incubation experiments coinciding with the study on molecular weight distribution of DOM in the incubated waters (using untrafiltration techniques) would allow different molecular weight to be determined. The low molecular weight (<1 kDa) and fast turnover rate possibly indicate the labile pool, while the high molecular weight (>1 kDa) and lower turnover rate possibly indicate the semi-labile pool.

- Identify the main source of riverine DOC and DON discharge to coastal zone which contributes to high concentration in coastal water, particularly in the coastal European waters and the eastern UK coast. A previous study in the UK suggests that peatland catchments are a significant source of DOC and DON discharged to the fluvial systems (Edokpa et al. 2015). The effluent of wastewater treatment plants is also a potential DON source (Pehlivanoglu-Mantas and Sedlak 2006). However, this should be considered in other areas covering the main fluvial discharge to the

southern North Sea. This can be possibly be achieved by sampling of more rivers and at high flow.

- DOM and POM monitoring along with the inorganic nutrients at SmartBuoy sites or more frequent sampling (e.g. monthly) at the fixed stations to investigate their variation. This present study did not include POM investigation at SmartBuoy sites. Additional investigation on POM concentration would allow better understanding on how POM seasonal cycling links to DOM and inorganic nutrients in the North Sea region.

- Investigation of factors which influence the high C:N molar ratio of DOM in the deep outer shelf water. In this present study, the high C:N molar ratio of DOM observed in the northern bottom water is similar to the North Atlantic, suggesting deep outer shelf water inputs of high C:N molar ratio material to the northern bottom water. The preferential remineralization of nitrogen relative to carbon is another possible process inducing high C:N molar ratio in the northern bottom water that can be further investigated via incubation experiment of the northern bottom water.

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Appendix for chapter 1

Appendix 1.1: Comparison of model I and model II regression

Both model I (ordinary least squares) and model II (Major Axis or Semi-Major Axis) regressions require data that is normally distributed. Where data is not normally distributed, log transformation can be tested as a way to force normality. Normality of the DOC/N datasets was tested in the R statistical programming language. Raw data failed the normality test, where log-transformed data was 'weakly' normal ($0.05 < p < 0.1$). Therefore log-transformation was tested as a method of applying more statistically robust regressions, although having a not constant slope.

Legendre and Legendre (1998) suggest that where the errors in both variables are similar, units are the same and data is normally distributed, that major axis type II regression is most appropriate. As an example, Figure 1 shows the results of MA (model II) and OLS (model I) regressions on not transformed and log-transformed data for summer 2011 data. This demonstrates that the OLS regression in non-transformed space is a better approximation (in terms of slope and intercept) to the very similar OLS and MA regressions in log-transformed space, than the MA regression in untransformed data. Therefore, the ordinary least square method (the model I regression) was chosen as the best approximation of the linear slope and used throughout this study as in other previous studies to determine the slope C:N and slope N:P ratios (Krom et al. 1991, Fanning 1992, Sanders and Jickells 2000, Kress and Herut 2001, Hung et al. 2003, Schroeder et al. 2010, Pujo-Pay et al. 2011). However, it is important to note that as the data used for the regressions is not bivariate normal and it is therefore difficult to accurately calculate uncertainties on the derived slopes (Legrande and Legrande 1998).

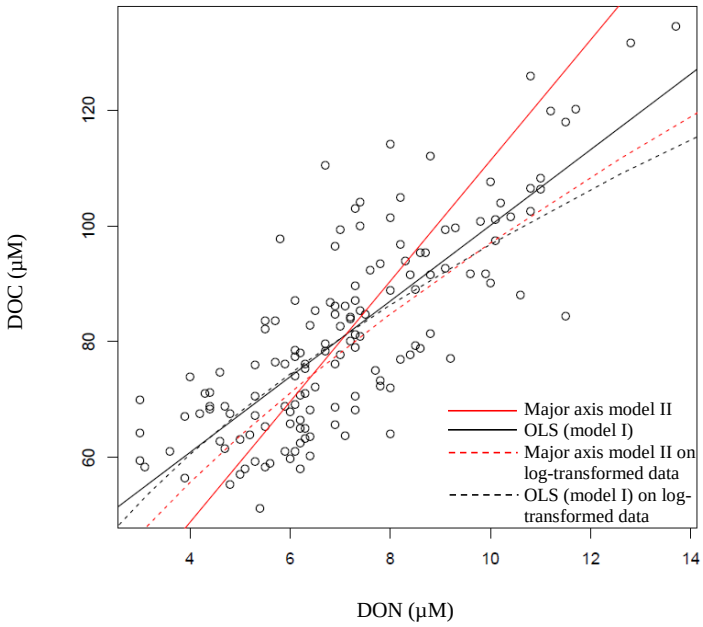


Figure 1 Scatter diagram of the example data (the whole summer 2011 data) showing regression lines derived from the major axis model II method, ordinary least square (OLS (model I)) method on untransformed and log-transformed data.

Appendix for chapter 2

Appendix 2.1: Preparation of stock and standard solution for DOC analysis.

Preparation of potassium hydrogen phthalate (KHP) standard:

A 1,000 mg C/l of stock solution was prepared by dissolving 2.128 g of analytical grade potassium hydrogen phthalate (Sigma-Aldrich, USA) in 1,000 ml of de-ionised water (Milli-Q water) (18.2 MΩ.cm, Purelab Ultra, ELGA Process Water, England). The stock solution was diluted to give a secondary stock solution with the concentration of 10,000 µM C. From the secondary stock solution, working standards of 0, 25, 50, 100, 200, and 300 µM was prepared.

Appendix 2.2: Preparation of stock and standard solution for TDN analysis.

Preparation of a mix standard of ammonium sulphate and potassium nitrate:

A 1,000 mg N/l of stock solution was prepared by

- dissolving 4.717 g of analytical grade ammonium sulphate (Sigma-Aldrich, USA) in 1,000 ml of de-ionised water (Milli-Q water) (18.2 MΩ.cm, Purelab Ultra, ELGA Process Water, England)
- dissolving 7.219 g of analytical grade potassium nitrate (Sigma-Aldrich, USA) in 1,000 ml of the de-ionised water
- Mix equal volumes of the above solutions to produce a mix standard solution

The stock solution (1,000 mg N/l) was diluted to give a secondary stock solution with the concentration of 2,000 µM C. From the secondary stock solution, working standards of 0, 5, 10, 20, 30, and 50 µM was prepared.

Appendix 2.3: Precision results for the same batch for DOC analysis.

Standard number	Concentration (µM)		Mean concentration (µM)
1	100.5	99.8	100.1
2	99.4	99.5	99.4
3	101.2	101.9	101.5
4	99.6	99.7	99.6
5	96.9	98.6	97.7
6	105.3	106.5	105.9
7	102.8	103.5	103.2
8	99.1	99.9	99.5
9	102.4	101.1	101.8
10	101.0	101.2	101.1
11	98.5	98.8	98.6
12	100.4	99.8	100.1
13	102.2	101.3	101.8
14	104.5	106.5	105.5
15	101.0	101.4	101.2
16	102.1	105.3	103.7
17	98.4	99.9	99.2
18	103.0	104.7	103.9
19	101.9	101.2	101.5
20	101.8	102.8	102.3
21	106.0	106.6	106.3
22	105.6	107.9	106.8
23	97.0	99.5	98.2
24	105.3	101.9	103.6
25	101.6	98.1	99.9
26	96.9	99.1	98.0
27	103.5	102.7	103.1
28	102.6	103.1	102.8
29	104.0	103.8	103.9
30	101.7	102.2	102.0
31	102.6	106.8	104.7
32	102.2	99.0	100.6
33	99.5	102.4	101.0
34	100.4	99.8	100.1
35	104.9	105.3	105.1
36	103.1	102.5	102.8
37	104.0	102.5	103.3
38	106.0	105.5	105.8
39	100.0	100.0	100.0
40	101.0	105.0	103.0
		Mean	102.0
		SD	2.4
		%CV	2

Appendix 2.4: Duplicate analysis of DOC and TDN concentration (frozen samples reanalysis).

Analysis	Sample	Prime Station	Sample depth (m)	Concentration (µM) Analysed on 28 Jun 2013	Concentration (µM) Analysed on 28 Nov 2014
DOC	1	2	2	73.6	70.1
	2	5	4	66.2	64.2
	3	39	32	63.0	61.1
	4	25	62	62.1	62.4
	5	25	4	74.4	73.8
	6	58	4	94.8	101.5
	7	32	74	55.8	56.9
TDN	1	1	2	6.5	6.5
	2	2	28	5.0	5.0
	3	5	24	5.5	5.8
	4	39	32	4.1	4.2
	5	25	62	8.1	8.6
	6	58	146	12.8	12.4
	7	58	4	5.1	5.6

Samples were collected during summer 2012 cruise (CEND 13/12) and kept frozen at -20 °C. The frozen samples were reanalyzed after 17 months storage in the PP tubes.

Appendix 2.5: Precision results for the same batch for TDN analysis.

Standard number	Concentration (µM)		Mean concentration (µM)
1	10.1	10.0	10.0
2	9.9	10.1	10.0
3	11.1	11.2	11.1
4	9.9	10.0	9.9
5	10.6	10.6	10.6
6	10.8	10.4	10.6
7	9.9	10.5	10.2
8	9.9	10.1	10.0
9	9.5	9.6	9.5
10	9.9	10.3	10.1
11	9.4	10.9	10.2
12	10.0	10.1	10.0
13	9.2	9.8	9.5
14	10.6	10.5	10.6
15	10.5	10.5	10.5
16	10.7	10.7	10.7
17	10.4	10.5	10.5
18	10.1	10.3	10.2
19	11.2	11.1	11.1
20	10.2	9.9	10.0
21	9.7	9.3	9.5
22	9.9	9.9	9.9
23	10.8	10.5	10.6
24	10.9	10.8	10.8
25	9.5	9.3	9.4
26	10.3	10.1	10.2
27	11.1	10.6	10.9
28	10.4	10.5	10.5
29	10.7	10.1	10.4
30	10.3	10.5	10.4
31	10.5	10.9	10.7
32	10.0	10.1	10.1
33	10.0	10.2	10.1
34	11.1	10.4	10.7
35	9.8	9.8	9.8
36	10.1	10.4	10.2
37	10.1	10.1	10.1
38	10.4	10.4	10.4
39	11.0	11.3	11.1
40	10.0	10.2	10.1
		Mean	10.3
		SD	0.4
		%CV	4

Appendix for chapter 3

Appendix 3.1: Results of surface samples from CEND 14/11 cruise (summer 2011).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
1	1	4	33	09/08/2011	09:50	51.7775	1.7763	17.5	34.8	1.5	2.7	0.4	2.0	103.0	7.3	11.5	4.2
2	2	4	34	09/08/2011	15:30	51.5727	2.7722	na	34.6	0.6	< 0.2	0.2	1.1	101.1	10.1	10.8	0.7
3	5	3	18	09/08/2011	20:45	51.8503	3.6528	17.8	33.0	0.8	3.9	0.1	0.4	93.5	7.8	12.5	4.7
4	6	6	27	10/08/2011	04:09	52.6752	4.1895	17.2	33.3	0.7	0.4	0.2	1.0	118.0	11.5	12.5	1.1
5	8	4	31	10/08/2011	09:00	52.6833	3.4028	16.7	34.9	0.6	< 0.2	0.2	1.1	92.4	7.6	8.3	0.7
6	10	4	40	10/08/2011	14:30	52.8250	2.7312	16.4	34.6	0.6	0.5	0.2	1.3	105.0	8.2	9.2	1.0
7	12	4	45	11/08/2011	03:45	53.9570	1.3038	13.4	34.4	0.6	0.8	0.2	1.5	100.0	7.4	8.8	1.3
8	14	3	53	11/08/2011	08:15	53.9833	0.2528	13.8	34.3	1.2	0.8	0.3	2.1	89.1	8.5	10.5	2.0
9	17	4	76	11/08/2011	17:00	54.8978	-0.2865	na	34.6	0.6	0.5	0.2	1.3	104.2	7.4	8.6	1.1
10	19	3	80	11/08/2011	21:00	54.8045	0.1903	14.3	34.7	4.6	< 0.2	0.5	3.7	78.4	6.7	11.4	4.7
11	20	4	41	12/08/2011	0.15	54.7895	1.2793	14.3	34.5	0.4	< 0.2	0.2	1.5	80.2	7.2	7.7	0.5
12	22	3	25	12/08/2011	11:40	54.5527	2.6542	15.2	34.6	0.5	< 0.2	0.2	1.8	79.7	6.7	7.4	0.7
13	26	4	42	12/08/2011	18:10	54.6105	3.3102	15.8	34.9	0.4	< 0.2	0.2	1.9	85.4	6.5	7.0	0.5
14	27	2	62	13/08/2011	03:20	53.8505	2.5827	15.2	34.6	0.4	< 0.2	0.2	1.8	84.7	7.5	8.0	0.5
15	29	4	39	13/08/2011	07:20	53.7715	3.5308	15.9	34.5	0.5	< 0.2	0.2	2.5	91.8	9.6	10.2	0.6
16	31	4	41	13/08/2011	12:05	53.7868	4.4712	16.7	34.6	0.6	1.5	0.3	3.7	93.9	8.3	10.4	2.2
17	34	2	32	13/08/2011	18:30	53.7495	5.3640	16.6	34.2	0.4	< 0.2	0.2	1.8	101.6	10.4	10.9	0.5
18	35	5	45	14/08/2011	03:30	54.7630	4.8327	15.7	34.6	0.4	< 0.2	0.2	3.4	87.1	7.3	7.8	0.5
19	37	2	44	14/08/2011	07:10	54.6373	5.5920	16.2	34.4	0.2	< 0.2	0.2	3.8	83.9	7.2	7.6	0.4
20	39	2	42	14/08/2011	10:43	54.5622	6.3307	16.7	34.4	0.3	< 0.2	0.3	6.6	91.5	8.8	9.3	0.5
21	42	3	33	14/08/2011	18:00	54.9452	7.1003	17.1	33.6	0.1	< 0.2	0.2	1.2	102.6	10.8	11.1	0.2
22	46	2	31	15/08/2011	05:10	55.5888	7.2037	16.3	33.3	0.8	2.2	0.2	2.1	88.0	10.6	13.6	3.0
23	47	3	36	15/08/2011	07:00	55.6633	6.8237	16.8	33.5	0.3	< 0.2	0.2	1.0	106.5	10.8	11.3	0.5
24	50	3	39	15/08/2011	15:35	56.6023	6.9152	16.1	34.0	0.1	< 0.2	0.2	2.3	90.1	10.0	10.2	0.2
25	51	4	55	16/08/2011	03:25	55.7903	5.2410	16.0	34.3	0.3	< 0.2	0.2	2.4	91.5	8.4	8.8	0.4
26	53	3	34	16/08/2011	07:10	55.5158	4.5888	15.5	34.7	0.3	< 0.2	0.2	1.3	96.5	6.9	7.3	0.4
27	55	3	36	16/08/2011	11:25	55.5607	3.7632	15.1	34.8	0.2	< 0.2	0.2	1.5	87.1	6.1	6.5	0.4
28	58	3	78	16/08/2011	18:00	55.7450	2.7758	14.8	34.9	0.1	< 0.2	0.2	1.4	83.7	5.5	5.7	0.2

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, na = data is not available, < 0.2 = less than the detection limit of CEFAS instrument

Appendix 3.1: (continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
29	61	3	86	17/08/2011	03:45	55.8087	1.2013	14.0	34.8	0.4	< 0.2	0.1	1.7	89.7	7.3	7.7	0.5
30	63	4	87	17/08/2011	09:25	55.9303	0.0293	14.1	34.8	0.1	< 0.2	0.2	1.5	78.5	6.1	6.3	0.2
31	66	4	102	17/08/2011	17:00	55.5893	-0.8505	14.4	34.8	0.2	< 0.2	0.2	2.2	82.7	7.0	7.4	0.4
32	67	3	67	17/08/2011	03:50	56.5033	-1.3453	13.8	34.5	0.1	< 0.2	0.3	2.3	73.3	7.8	8.1	0.2
33	69	3	76	18/08/2011	07:50	56.6243	-0.4433	14.1	34.9	0.1	< 0.2	0.2	1.6	76.1	6.3	6.5	0.2
34	71	3	84	18/08/2011	11:45	56.8087	0.3573	14.6	35.0	0.1	< 0.2	0.1	1.3	77.7	7.0	7.2	0.2
35	75	3	99	18/08/2011	18:15	56.8002	1.4352	14.8	35.0	0.1	< 0.2	0.2	1.3	68.2	6.4	6.6	0.2
36	76	3	98	19/08/2011	03:30	57.0977	1.5568	14.6	35.0	0.1	< 0.2	0.2	1.3	76.2	6.9	7.2	0.2
37	78	5	81	19/08/2011	07:50	57.3652	2.4298	14.9	33.9	0.1	< 0.2	0.1	0.9	75.4	6.3	6.6	0.2
38	83	3	74	19/08/2011	15:15	56.6948	2.4462	14.6	35.0	0.1	< 0.2	0.1	1.5	74.1	6.1	6.3	0.2
39	85	4	69	20/08/2011	03:20	57.1043	3.2535	15.1	34.1	0.1	< 0.2	0.1	0.5	76.2	5.9	6.1	0.2
40	87	4	62	20/08/2011	07:40	56.7393	3.5272	15.0	34.5	0.1	< 0.2	0.2	0.7	71.1	6.3	6.6	0.2
41	91	4	55	20/08/2011	15:00	56.7300	4.5642	15.5	34.2	0.1	< 0.2	0.1	0.6	72.3	7.8	8.1	0.2
42	94	3	58	20/08/2011	19:30	56.7740	5.7668	15.9	34.0	0.1	< 0.2	0.2	0.7	81.2	7.3	7.6	0.2
43	95	3	107	21/08/2011	03:30	57.6958	5.1528	15.6	31.8	0.1	< 0.2	0.1	0.6	95.4	8.6	8.8	0.2
44	97	4	87	21/08/2011	07:10	57.6532	4.7435	15.5	32.3	0.1	< 0.2	0.1	0.5	86.2	6.9	7.2	0.2
45	100	5	147	21/08/2011	11:45	58.0750	4.8283	15.5	31.8	0.1	< 0.2	0.1	0.8	96.8	8.2	8.4	0.2
46	103	3	193	21/08/2011	18:20	58.5055	3.9158	15.5	31.9	0.1	< 0.2	0.2	0.7	95.4	8.7	9.0	0.2
47	105	4	65	22/08/2011	03:50	57.7438	3.5440	15.5	32.3	3.7	0.9	0.5	2.5	58.4	5.5	10.1	4.6
48	108	3	73	22/08/2011	10:25	58.2275	2.6983	15.1	34.1	0.1	< 0.2	0.2	1.0	79.0	7.3	7.6	0.2
49	110	5	112	22/08/2011	18:00	58.2785	1.4642	14.5	35.2	0.1	< 0.2	0.2	1.4	76.4	5.7	6.0	0.2
50	111	2	148	23/08/2011	03:50	58.3768	0.7010	14.6	35.1	0.1	< 0.2	0.2	1.1	65.1	6.3	6.5	0.2
51	114	4	91	23/08/2011	12:00	57.7808	1.5015	14.9	34.7	0.1	< 0.2	0.2	1.2	67.6	4.8	5.1	0.2
52	116	3	90	23/08/2011	18:15	57.5390	0.5063	14.5	35.2	0.1	< 0.2	0.2	1.2	60.2	6.4	6.7	0.2
53	120	3	103	25/08/2011	03:45	57.0765	-1.7215	13.8	34.6	0.1	< 0.2	0.2	1.2	65.8	6.0	6.3	0.2
54	123	6	110	27/08/2011	12:00	58.0488	-1.2513	13.7	35.2	0.1	0.6	0.2	1.1	68.9	5.9	6.6	0.7
55	125	5	65	29/08/2011	16:45	58.4773	-2.5555	12.2	35.1	2.5	0.6	0.4	1.7	58.1	5.1	8.1	3.0
56	126	4	99	30/08/2011	04:10	57.8857	-0.2802	12.9	35.2	1.2	< 0.2	0.2	1.2	57.1	5.0	6.3	1.3

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.2 = less than the detection limit of CEFAS instrument

Appendix 3.1: (continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
57	128	4	112	30/08/2011	07:20	58.2030	-0.5095	12.9	35.2	0.6	< 0.2	0.2	1.1	63.8	7.1	7.8	0.7
58	131	4	91	30/08/2011	17:00	59.1393	-2.1702	12.2	35.2	2.9	0.5	0.4	1.9	64.1	8.0	11.3	3.3
59	132	6	111	31/08/2011	05:10	59.2830	-1.2583	13.5	34.7	0.1	< 0.2	0.1	1.0	63.9	5.2	5.4	0.2
60	134	3	143	31/08/2011	08:20	59.1795	-0.5033	13.7	34.3	0.1	< 0.2	0.1	1.0	66.4	6.2	6.4	0.2
61	138	5	130	31/08/2011	17:50	60.5075	-0.4945	13.4	34.9	0.5	< 0.2	0.2	1.2	68.2	7.3	8.0	0.7
62	139	3	137	01/09/2011	04:10	59.2633	0.8358	13.8	34.3	0.1	< 0.2	0.1	1.1	70.6	5.3	5.6	0.2
63	141	6	116	01/09/2011	08:00	59.3367	1.6193	13.5	34.4	1.9	< 0.2	0.3	1.6	51.2	5.4	7.4	2.0
64	143	5	124	01/09/2011	10:35	59.2958	2.0907	13.5	34.1	0.1	< 0.2	0.1	1.2	62.5	6.2	6.5	0.2
65	149	3	166	01/09/2011	20:00	59.1897	3.3540	14.8	31.9	0.2	< 0.2	0.1	1.0	84.2	7.2	7.5	0.4
66	150	5	130	02/09/2011	04:10	60.1527	3.0885	14.4	32.2	0.1	< 0.2	0.1	1.0	85.3	7.4	7.6	0.2
67	152	3	114	02/09/2011	08:30	60.3012	2.1275	13.9	33.5	0.1	< 0.2	0.1	1.0	72.2	6.5	6.7	0.2
68	155	4	141	02/09/2011	13:00	60.3968	1.2360	13.8	33.8	0.1	< 0.2	0.1	1.0	86.2	7.1	7.3	0.2
69	157	4	127	02/09/2011	18:30	60.3285	0.5733	13.7	35.4	0.1	< 0.2	0.2	1.0	70.7	6.2	6.4	0.2
70	159	6	205	03/09/2011	10:30	61.0515	2.5883	13.7	33.7	0.2	< 0.2	0.1	1.1	67.9	6.0	6.3	0.4
71	162	3	157	03/09/2011	18:15	61.2515	1.2420	13.0	34.9	0.1	< 0.2	0.2	1.5	61.1	6.1	6.4	0.2
72	163	4	172	04/09/2011	04:00	61.2972	0.4935	13.3	35.1	0.1	< 0.2	0.2	1.5	59.8	6.0	6.2	0.2
73	165	3	150	04/09/2011	08:00	61.1808	0.2368	12.7	35.3	1.9	0.4	0.2	1.9	61.1	5.9	8.2	2.4
74	168	3	134	04/09/2011	13:50	61.0232	-0.9987	12.5	35.2	0.3	< 0.2	0.2	1.5	68.7	6.9	7.4	0.5

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.2 = less than the detection limit of CEFAS instrument

Appendix 3.2: Results of bottom samples from CEND 14/11 cruise (summer 2011).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
1	5	15	18	09/08/2011	20:45	51.8503	3.6528	17.8	33.0	0.2	1.0	0.2	0.4	131.6	12.8	14.0	1.2
2	6	25	27	10/08/2011	04:09	52.6752	4.1895	17.3	34.0	0.2	1.2	0.1	0.6	134.5	13.7	15.1	1.3
3	8	24	31	10/08/2011	09:00	52.6833	3.4028	16.7	34.9	0.1	1.5	0.1	0.4	108.3	11.0	12.6	1.6
4	10	35	40	10/08/2011	14:30	52.8250	2.7312	16.4	34.6	0.1	1.6	0.1	0.8	99.4	9.1	10.8	1.6
5	12	39	45	11/08/2011	03:45	53.9570	1.3038	13.4	34.4	0.2	1.4	0.2	1.6	101.4	8.0	9.6	1.6
6	14	49	53	11/08/2011	08:15	53.9833	0.2528	13.5	34.4	0.7	2.4	0.3	1.7	107.7	10.0	13.0	3.0
7	19	75	80	11/08/2011	21:00	54.8045	0.1903	8.3	34.6	4.7	1.3	0.6	4.0	99.3	7.0	12.9	6.0
8	20	37	41	12/08/2011	03:30	54.7895	1.2793	12.0	34.6	0.1	1.5	0.2	2.9	99.7	9.3	10.9	1.6
9	22	22	25	12/08/2011	11:40	54.5527	2.6542	15.0	34.6	0.1	0.3	0.2	0.9	114.2	8.0	8.5	0.5
10	26	40	42	12/08/2011	18:10	54.6105	3.3102	15.2	34.9	0.1	1.2	0.3	1.9	84.7	6.9	8.3	1.4
11	27	58	62	13/08/2011	0.14	53.8505	2.5827	15.0	34.6	0.2	1.9	0.3	2.0	103.9	10.2	12.3	2.1
12	29	36	39	13/08/2011	07:20	53.7715	3.5308	15.8	34.5	0.1	2.4	0.3	2.5	81.0	7.4	9.9	2.6
13	31	38	41	13/08/2011	12:05	53.7868	4.4712	16.4	34.6	0.2	1.8	0.4	3.9	125.9	10.8	12.8	2.1
14	34	29	32	13/08/2011	18:30	53.7495	5.3640	16.6	34.2	0.1	1.5	0.3	2.1	106.4	11.0	12.6	1.6
15	35	43	45	14/08/2011	03:30	54.7630	4.8327	14.2	34.6	0.5	2.3	0.5	5.0	88.8	8.0	10.7	2.7
16	37	41	44	14/08/2011	07:10	54.6373	5.5920	15.7	34.4	0.1	1.9	0.3	4.1	100.8	9.8	11.8	2.0
17	39	37	42	14/08/2011	10:43	54.5622	6.3307	16.1	34.4	0.2	2.3	0.5	7.7	86.8	6.8	9.3	2.4
18	42	31	33	14/08/2011	18:00	54.9452	7.1003	16.5	33.6	0.5	2.0	0.4	1.2	119.8	11.2	13.7	2.5
19	47	33	36	15/08/2011	07:00	55.6633	6.8237	16.3	34.0	0.4	1.8	0.4	2.4	92.7	9.1	11.2	2.1
20	50	35	39	15/08/2011	15:35	56.6023	6.9152	15.3	34.0	0.4	2.9	0.3	3.9	91.7	9.9	13.2	3.3
21	51	51	55	16/08/2011	03:25	55.7903	5.2410	8.2	34.7	1.0	2.8	0.6	6.8	75.0	7.7	11.5	3.8
22	53	30	34	16/08/2011	07:10	55.5158	4.5888	10.5	34.9	0.3	1.9	0.4	2.3	78.8	8.6	10.8	2.2
23	55	35	36	16/08/2011	11:25	55.5607	3.7632	10.4	34.8	0.8	1.6	0.5	2.5	77.1	9.2	11.6	2.4
24	58	75	78	16/08/2011	18:00	55.7450	2.7758	7.1	34.9	7.0	0.8	0.8	4.5	67.3	5.3	13.1	7.7
25	61	84	86	17/08/2011	03:45	55.8087	1.2013	7.3	34.9	3.7	4.6	0.9	3.9	65.0	6.2	14.5	8.3
26	63	85	87	17/08/2011	09:25	55.9303	0.0293	8.7	34.8	1.9	3.8	0.7	4.0	63.6	6.4	12.1	5.7
27	66	98	102	17/08/2011	17:00	55.5893	-0.8505	8.4	34.7	5.6	1.6	0.7	4.2	69.1	6.1	13.4	7.3
28	67	65	67	17/08/2011	03:50	56.5033	-1.3453	11.9	34.8	1.3	2.9	0.5	2.6	97.5	10.1	14.3	4.2
29	69	74	76	18/08/2011	07:50	56.6243	-0.4433	10.2	34.9	3.5	2.6	0.7	3.4	65.3	5.5	11.6	6.1
30	71	82	84	18/08/2011	11:45	56.8087	0.3573	7.3	35.0	6.0	3.3	0.9	4.0	84.5	11.5	20.8	9.3

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth

Appendix 3.2: (continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
31	75	97	99	18/08/2011	18:15	56.8002	1.4352	6.7	35.0	6.9	2.2	0.9	3.8	63.1	5.0	14.1	9.1
32	76	96	98	19/08/2011	03:30	57.0977	1.5568	6.7	35.1	6.3	2.9	0.8	4.5	77.0	8.2	17.4	9.1
33	78	74	81	19/08/2011	07:50	57.3652	2.4298	6.8	35.1	3.4	4.5	0.7	3.6	70.6	7.3	15.2	7.9
34	83	72	74	19/08/2011	15:15	56.6948	2.4462	6.7	35.0	6.8	1.5	0.8	4.9	79.4	8.5	16.8	8.3
35	85	65	69	20/08/2011	03:20	57.1043	3.2535	7.1	35.1	3.5	4.3	0.7	3.8	63.3	6.3	14.0	7.7
36	87	57	62	20/08/2011	07:40	56.7393	3.5272	7.0	35.0	0.1	0.8	0.1	0.8	72.0	8.0	8.9	0.9
37	91	54	55	20/08/2011	15:00	56.7300	4.5642	7.2	35.1	1.7	3.9	0.7	4.1	59.0	5.6	11.2	5.7
38	94	54	58	20/08/2011	19:30	56.7740	5.7668	7.0	34.9	0.6	2.7	0.5	5.2	120.1	11.7	15.0	3.4
39	95	101	107	21/08/2011	03:30	54.6958	5.1528	7.1	35.2	0.2	0.7	0.2	0.9	58.1	6.2	7.0	0.9
40	97	84	87	21/08/2011	07:10	57.6532	4.7435	7.1	35.1	10.1	1.0	0.9	4.4	55.3	4.8	16.0	11.2
41	100	130	147	21/08/2011	11:45	58.0750	4.8283	7.3	35.3	13.2	0.9	1.0	5.7	59.3	5.3	19.5	14.1
42	103	188	193	21/08/2011	18:20	58.5055	3.9158	7.3	35.3	13.4	0.4	1.1	6.0	77.8	8.4	22.2	13.7
43	105	62	65	22/08/2011	03:50	57.7438	3.5440	7.6	35.1	0.1	0.9	0.1	0.3	112.0	8.8	9.8	1.0
44	108	70	73	22/08/2011	10:25	58.2275	2.6983	7.3	35.1	6.6	3.1	0.8	3.6	68.8	4.7	14.3	9.7
45	110	108	112	22/08/2011	18:00	58.2785	1.4642	8.0	35.2	11.0	0.8	1.0	5.2	74.7	4.6	16.4	11.8
46	111	144	148	23/08/2011	03:50	58.3768	0.7010	6.8	35.2	14.0	1.0	1.1	6.1	74.0	4.0	19.0	15.0
47	114	87	91	23/08/2011	12:00	57.7808	1.5015	6.9	35.1	10.1	0.7	1.0	4.7	76.0	5.3	16.1	10.9
48	116	85	90	23/08/2011	18:15	57.5390	0.5063	9.3	35.2	9.4	0.8	0.8	4.3	67.6	4.2	14.3	10.1
49	120	101	103	25/08/2011	03:45	57.0765	-1.7215	12.4	34.7	0.9	3.2	0.5	3.1	81.4	8.8	12.9	4.1
50	123	100	110	27/08/2011	12:00	58.0488	-1.2513	10.1	35.3	8.7	1.2	0.8	4.1	83.7	5.7	15.6	9.9
51	125	62	65	29/08/2011	16:45	58.4773	-2.5555	12.2	35.1	2.3	2.3	0.4	1.4	78.0	6.2	10.8	4.6
52	126	92	99	30/08/2011	04:10	57.8857	-0.2802	9.9	35.3	9.3	0.7	0.8	4.6	56.4	3.9	14.0	10.1
53	128	103	112	30/08/2011	07:20	58.2030	-0.5095	9.3	35.3	11.1	1.5	0.9	5.3	110.5	6.7	19.2	12.6
54	131	86	91	30/08/2011	17:00	59.1393	-2.1702	12.2	35.2	2.7	2.0	0.4	1.6	65.6	6.9	11.6	4.7
55	132	107	111	31/08/2011	05:10	59.2830	-1.2583	9.9	35.4	11.0	1.3	0.8	4.4	61.5	4.7	17.0	12.3
56	134	139	143	31/08/2011	08:20	59.1795	-0.5033	7.2	35.3	13.3	2.1	1.0	5.5	97.7	5.8	21.2	15.4
57	138	126	130	31/08/2011	17:50	60.5075	-0.4945	9.3	35.4	12.7	1.1	1.0	6.4	68.9	4.4	18.1	13.8
58	139	134	137	01/09/2011	04:10	59.2633	0.8358	6.7	35.2	12.9	1.4	1.0	5.1	68.4	4.4	18.7	14.3
59	141	112	116	01/09/2011	08:00	59.3367	1.6193	7.0	35.1	13.5	1.9	1.1	6.3	71.0	4.3	19.6	15.4
60	143	121	124	01/09/2011	10:35	59.2958	2.0907	6.8	35.3	13.2	1.3	1.0	5.6	61.1	3.6	18.1	14.5

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth

Appendix 3.2: (continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
61	149	163	166	01/09/2011	20:00	59.1897	3.3540	8.9	35.4	13.4	1.3	1.0	6.5	77.5	6.1	20.8	14.7
62	150	124	130	02/09/2011	04:10	60.1527	3.0885	9.2	35.4	13.0	1.6	1.0	5.5	70.0	3.0	17.5	14.5
63	152	110	114	02/09/2011	08:30	60.3012	2.1275	7.8	35.4	14.4	1.4	1.1	6.5	71.3	4.4	20.2	15.8
64	155	138	141	02/09/2011	13:00	60.3968	1.2360	7.0	35.3	14.1	1.6	1.1	6.4	64.3	3.0	18.7	15.6
65	157	125	127	02/09/2011	18:30	60.3285	0.5733	8.8	35.4	13.5	0.7	1.0	6.8	59.5	3.0	17.3	14.3
66	159	200	205	03/09/2011	10:30	61.0515	2.5883	9.2	35.4	13.1	3.0	1.0	6.2	82.2	5.5	21.6	16.2
67	162	152	157	03/09/2011	18:15	61.2515	1.2420	9.5	35.4	12.5	1.2	0.9	5.4	82.9	6.4	20.2	13.7
68	163	168	172	04/09/2011	04:00	61.2972	0.4935	9.7	35.4	12.6	0.7	0.9	5.8	58.4	3.1	16.5	13.4
69	165	144	150	04/09/2011	08:00	61.1808	0.2368	9.9	35.4	12.0	0.7	0.9	4.9	62.8	4.6	17.2	12.7
70	168	130	134	04/09/2011	13:50	61.0232	-0.9987	10.1	35.4	11.7	1.0	0.9	5.2	67.1	3.9	16.6	12.7

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth

Appendix 3.3: Results of surface samples from CEND 02/12 cruise (winter 2011).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
1	1	2	22	20/01/2012	08:15	51.5231	1.0262	7.1	35.1	1.3	11.4	0.3	0.8	6.7	76.6	5.9	17.6	11.7
2	8	4	20	20/01/2012	13:08	51.5545	1.0833	na	35.1	1.3	11.4	0.3	0.8	6.8	145.6	4.7	16.4	11.7
3	10	4	17	20/01/2012	14:00	51.6965	1.3422	na	35.1	1.7	13.3	0.3	0.8	7.6	155.7	9.3	22.9	13.6
4	11	4	16	20/01/2012	12:32	51.7768	1.4887	na	35.1	1.1	12.5	0.2	0.8	7.4	118.4	5.8	18.6	12.7
5	12	4	22	20/01/2012	15:08	51.8258	1.6323	na	35.1	1.3	11.3	0.2	0.7	7.0	119.2	5.0	16.5	11.5
6	13	4	24	20/01/2012	15:30	51.8055	1.8023	na	35.3	0.8	8.5	< 0.2	0.6	5.7	118.8	6.1	14.7	8.6
7	25	4	39	20/01/2012	07:12	52.3458	2.0080	na	34.7	0.4	10.9	0.2	0.7	6.9	109.5	5.9	17.0	11.1
8	28	4	29	21/01/2012	01:30	52.7513	1.9112	na	34.3	0.5	10.6	< 0.2	0.7	5.6	109.8	8.6	19.3	10.7
9	29	4	31	21/01/2012	02:31	52.8918	1.6678	na	34.2	0.4	12.6	0.2	0.7	5.9	107.5	7.5	20.3	12.8
10	31	4	27	21/01/2012	04:30	53.1803	1.4234	na	34.7	0.5	6.6	0.2	0.6	5.2	104.5	5.4	12.3	6.9
11	34	4	24	21/01/2012	07:33	53.5340	1.0647	7.0	34.7	0.4	6.4	< 0.2	0.6	4.9	103.2	5.2	11.7	6.5
12	40	4	17	21/01/2012	11:30	53.4050	0.8185	na	34.1	0.4	12.0	< 0.2	0.7	6.3	142.5	7.1	19.1	12.1
13	42	2	39	21/01/2012	13:50	53.0512	0.4685	5.9	34.1	0.4	13.7	0.2	0.8	6.7	224.8	6.8	20.7	14.0
14	43	3	25	21/01/2012	14:47	52.9738	0.3720	5.8	34.1	0.5	14.4	0.7	0.8	6.7	175.1	6.4	21.5	15.1
15	48	4	21	21/01/2012	18:00	53.3751	0.5657	na	33.3	0.4	22.9	< 0.2	0.9	8.9	105.6	4.7	27.7	23.0
16	50	3	16	21/01/2012	19:21	53.5326	0.3379	6.8	34.7	0.4	6.6	0.2	0.6	5.1	131.9	6.0	12.8	6.8
17	51	4	21	21/01/2012	20:00	53.6493	0.3678	na	34.7	0.5	5.4	0.3	0.6	4.7	106.1	5.7	11.3	5.7
18	52	4	23	21/01/2012	20:30	53.7439	0.2889	na	34.7	0.4	5.7	0.2	0.6	4.8	120.1	4.4	10.4	6.0
19	53	4	28	21/01/2012	21:00	53.8418	0.2141	na	34.7	0.5	6.0	0.3	0.6	4.9	89.8	3.7	9.9	6.2
20	54	4	35	21/01/2012	21:30	53.9358	0.1416	na	34.7	0.5	6.4	0.2	0.6	5.1	98.9	4.8	11.4	6.6
21	55	4	45	21/01/2012	22:00	54.0267	0.0718	na	34.5	0.5	7.8	0.2	0.6	5.3	99.4	4.4	12.4	8.0
22	57	4	51	21/01/2012	23:30	54.2457	-0.1743	na	34.5	0.3	8.7	0.3	0.7	5.9	175.5	4.8	13.8	9.0
23	58	4	49	22/01/2012	00:30	54.3694	-0.3537	na	34.5	0.4	8.2	0.2	0.7	5.9	100.1	4.6	13.0	8.4
24	59	4	52	22/01/2012	01:30	54.4958	-0.5375	na	34.4	0.3	8.8	0.2	0.7	6.2	101.4	5.1	14.2	9.1
25	60	4	53	22/01/2012	02:30	54.6303	-0.7332	na	34.6	0.4	6.7	0.3	0.6	5.4	113.7	4.9	11.9	7.0
26	61	2	58	22/01/2012	03:24	54.7353	-0.8830	7.6	34.8	0.4	5.8	0.3	0.6	5.0	113.3	5.0	11.1	6.2
27	62	4	68	22/01/2012	04:30	54.8677	-1.0099	na	34.8	0.3	5.5	0.3	0.6	5.1	92.8	4.4	10.2	5.8
28	63	2	73	22/01/2012	05:32	55.0093	-1.1365	7.9	34.9	0.3	5.7	0.4	0.6	4.7	91.9	4.6	10.6	6.0
29	68	4	75	22/01/2012	08:30	54.9357	-0.9151	na	34.8	0.3	5.5	0.2	0.6	4.9	82.1	6.1	11.7	5.6
30	72	4	66	22/01/2012	16:30	54.7283	-0.4254	na	34.7	0.3	6.4	0.2	0.6	5.4	97.6	9.1	15.6	6.6

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.2 = less than the detection limit of CEFAS instrument

Appendix 3.3: (continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
31	73	4	77	22/01/2012	18:30	54.5173	0.2825	na	34.9	0.4	5.7	0.2	0.6	4.9	56.2	5.7	11.6	5.9
32	74	4	61	22/01/2012	20:30	54.3123	0.9650	na	34.8	0.4	4.9	0.4	0.5	4.6	58.5	9.9	15.2	5.3
33	75	4	75	22/01/2012	22:30	54.1266	1.5819	na	34.9	0.4	5.2	0.3	0.5	4.5	69.3	5.5	11.0	5.5
34	76	5	75	22/01/2012	23:57	54.0008	1.9920	6.7	34.9	0.4	5.5	0.3	0.5	4.3	81.9	7.1	13.0	5.9
35	77	4	30	23/01/2012	02:30	53.6142	2.3039	na	34.8	0.6	5.0	0.4	0.5	4.4	95.7	5.9	11.4	5.4
36	78	4	33	23/01/2012	04:30	53.2422	2.5941	na	34.6	0.6	7.2	0.5	0.6	4.9	99.1	12.3	20.0	7.7
37	79	4	37	23/01/2012	06:30	52.8750	2.8777	na	35.4	0.7	6.9	0.4	0.4	4.3	99.4	6.1	13.3	7.2
38	80	4	45	23/01/2012	08:30	52.7493	2.7664	na	35.4	0.9	7.0	0.4	0.4	4.1	97.7	9.8	17.2	7.4
39	81	4	46	23/01/2012	09:30	52.7463	2.5755	na	35.3	0.9	7.4	0.3	0.5	5.0	91.1	7.7	15.3	7.6
40	84	4	52	23/01/2012	11:30	52.6719	2.4049	na	35.0	0.6	8.4	0.2	0.6	5.7	94.6	9.3	18.0	8.7
41	85	4	44	23/01/2012	12:30	52.4520	2.4384	na	35.2	0.7	8.2	0.3	0.6	5.7	102.2	5.9	14.4	8.5
42	95	3	35	23/01/2012	23:30	51.9769	2.0878	8.4	35.3	0.9	7.9	0.3	0.5	5.2	57.2	5.5	13.7	8.3
43	96	2	36	24/01/2012	00:34	51.9780	2.0875	8.4	35.3	0.9	8.0	0.3	0.5	5.1	143.1	8.0	16.3	8.2
44	99	3	34	24/01/2012	03:31	51.9766	2.0854	8.7	35.3	0.9	8.0	0.3	0.5	4.8	97.3	7.1	15.4	8.3
45	101	3	32	24/01/2012	05:35	51.9762	2.0863	8.7	35.3	0.5	8.0	0.3	0.5	4.9	74.5	5.2	13.5	8.3
46	110	4	47	25/01/2012	06:30	52.1615	2.5048	na	35.3	0.6	8.7	0.3	0.5	4.7	81.6	5.7	14.7	9.0
47	111	4	47	25/01/2012	07:30	51.9871	2.3954	na	35.3	0.6	7.9	0.3	0.5	5.1	105.8	10.3	18.5	8.2
48	112	4	48	25/01/2012	08:30	51.8024	2.1877	na	35.3	0.5	9.0	0.4	0.6	4.6	128.2	9.5	18.9	9.4
49	113	4	55	25/01/2012	09:30	51.5825	2.0249	na	35.3	0.5	9.1	0.3	0.6	4.5	138.9	7.6	17.0	9.4
50	114	4	42	25/01/2012	09:30	51.3612	1.8495	na	35.2	0.7	11.1	0.6	0.7	5.9	87.3	11.7	23.4	11.7
51	115	4	49	25/01/2012	11:30	51.1735	1.6771	na	35.2	0.4	10.5	0.6	0.6	5.3	77.0	6.4	17.5	11.1
52	116	4	52	25/01/2012	12:30	51.0687	1.4582	na	35.3	0.7	6.3	0.4	0.5	4.2	149.7	8.6	15.2	6.6

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth,

Appendix 3.4: Results of bottom samples from CEND 02/12 cruise (winter 2011).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	TDN (µM)	DIN (µM)
1	1	20	22	20/01/2012	08:15	51.5231	1.0262	7.1	35.1	1.1	7.5	0.2	0.5	4.7	87.9	11.0	18.8	7.7
2	34	22	24	21/01/2012	07:33	53.5340	1.0647	7.0	34.7	0.5	6.5	0.2	0.6	4.9	117.5	6.5	13.2	6.7
3	42	34	39	21/01/2012	13:50	53.0512	0.4685	5.9	34.1	0.5	13.8	< 0.2	0.8	6.7	115.1	7.1	21.0	13.9
4	43	25	25	21/01/2012	14:44	52.9738	0.3720	5.7	34.1	0.5	14.5	0.8	0.8	6.7	116.1	7.4	22.7	15.3
5	50	14	16	21/01/2012	19:19	53.5326	0.3379	6.9	34.7	0.4	6.8	0.3	0.6	5.0	85.7	5.9	13.0	7.1
6	61	55	58	22/01/2012	03:24	54.7353	-0.8830	7.6	34.8	0.4	5.9	0.4	0.6	5.0	118.5	6.5	12.7	6.2
7	63	71	73	22/01/2012	05:27	55.0093	-1.1365	7.9	34.9	0.3	5.6	0.2	0.6	4.8	90.4	5.8	11.5	5.8
8	76	71	75	22/01/2012	23:57	54.0008	1.9920	6.7	35.0	0.5	5.5	0.4	0.5	4.3	103.2	8.0	14.0	6.0

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, , < 0.2 = less than the detection limit of CEFAS instrument

Appendix 3.5: Results of surface samples from CEND 13/12 cruise (summer 2012).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	POC (µM)	PON (µM)	TDN (µM)	DIN (µM)
1	1	2	25	08/08/2012	08:20	51.7577	1.7892	17.2	34.9	1.3	0.8	0.9	0.3	1.9	67.6	6.0	20.0	3.2	7.7	1.7
2	2	2	33	08/08/2012	18:25	51.5717	2.7755	17.1	34.6	1.2	1.0	< 0.4	0.2	1.4	68.4	5.8	9.7	1.1	7.0	1.2
3	3	3	24	09/08/2012	03:42	51.8011	3.5891	18.5	33.9	7.0	0.4	< 0.4	0.3	0.7	82.9	7.8	31.2	4.8	8.5	0.6
4	5	4	29	09/08/2012	15:00	52.7020	3.3843	17.2	35.1	1.0	1.1	< 0.4	0.1	0.9	53.9	3.2	7.2	0.6	4.4	1.3
5	4	4	37	09/08/2012	19:30	52.8310	2.7574	17.0	34.9	1.3	0.2	0.9	0.2	1.1	76.8	5.5	15.0	1.2	6.6	1.1
6	9	3	68	10/08/2012	03:40	53.8280	2.6558	15.8	34.7	0.7	0.2	< 0.4	0.2	0.8	62.4	4.6	9.6	1.6	4.9	0.4
7	10	4	39	10/08/2012	08:40	53.7862	3.4065	16.8	34.5	0.4	0.2	< 0.4	0.1	0.5	36.7	4.1	6.6	1.0	4.5	0.4
8	11	3	41	10/08/2012	13:23	53.8089	4.5736	17.5	34.5	0.9	0.2	< 0.4	0.2	2.7	90.6	4.2	19.5	1.5	4.6	0.4
9	12	3	30	10/08/2012	19:08	53.7379	5.3023	18.4	34.1	1.2	0.2	< 0.4	< 0.1	0.3	52.7	4.1	20.5	3.4	4.5	0.4
10	18	5	43	11/08/2012	03:36	54.7722	4.9533	17.1	34.7	0.2	0.2	< 0.4	0.1	0.7	61.3	5.7	5.8	0.7	6.1	0.4
11	19	3	44	11/08/2012	07:17	54.6836	5.4764	16.9	34.4	0.3	0.2	< 0.4	0.2	0.8	58.3	3.8	9.5	1.1	4.2	0.4
12	20	4	40	11/08/2012	11:51	54.5711	6.2836	17.1	34.4	0.6	0.2	< 0.4	0.1	2.0	54.0	4.7	12.1	1.5	5.1	0.4
13	21	4	32	11/08/2012	18:09	54.9298	7.0784	18.2	33.3	2.4	0.2	8.1	0.4	1.2	124.4	6.7	43.8	5.9	15.0	8.3
14	30	2	28	12/08/2012	03:32	55.5800	7.2004	17.0	33.1	1.4	0.2	< 0.4	0.1	0.7	95.2	9.8	15.5	2.5	10.1	0.4
15	29	5	37	12/08/2012	08:50	55.6887	6.7024	16.9	33.9	1.1	0.2	< 0.4	0.1	0.7	72.5	4.8	14.6	2.1	5.2	0.4
16	39	4	35	12/08/2012	14:53	56.5846	6.9799	18.2	34.0	0.3	0.2	< 0.4	0.1	0.7	63.2	5.0	8.6	1.3	5.4	0.4
17	28	4	54	13/08/2012	03:24	55.7810	5.2520	17.1	34.9	0.3	0.2	0.8	0.2	1.6	69.9	4.3	8.3	0.9	5.2	0.9
18	27	4	33	13/08/2012	07:59	55.5543	4.5034	17.3	34.9	0.3	0.2	< 0.4	0.1	0.9	49.9	5.0	8.7	1.3	5.4	0.4
19	26	4	37	13/08/2012	12:04	55.6260	3.6747	17.2	34.8	0.3	0.2	1.0	0.2	1.6	76.1	3.6	9.0	1.0	4.8	1.1
20	25	4	67	13/08/2012	18:26	55.6730	2.7831	17.0	34.8	0.2	0.2	< 0.4	0.1	1.2	61.7	3.9	6.8	0.6	4.2	0.4
21	17	4	43	14/08/2012	03:44	54.5850	3.4035	16.2	34.8	0.4	0.2	< 0.4	0.1	0.8	59.5	5.1	8.5	1.1	5.4	0.4
22	16	4	29	14/08/2012	07:15	54.4898	2.7798	15.2	34.9	0.5	0.2	< 0.4	0.2	1.0	55.0	5.4	8.3	1.5	5.8	0.4
23	15	4	36	14/08/2012	12:38	54.7726	1.3053	17.1	34.5	0.4	0.2	< 0.4	0.1	1.4	56.7	6.0	8.8	0.9	6.4	0.4
24	14	4	76	14/08/2012	18:15	54.7890	0.1740	16.4	34.4	3.6	0.2	< 0.4	0.1	1.0	59.1	5.6	21.8	2.9	6.0	0.4
25	8	4	41	15/08/2012	03:57	53.9215	1.3096	16.1	34.3	0.5	0.2	< 0.4	0.2	1.6	67.7	7.0	8.7	1.4	7.4	0.4
26	7	4	49	15/08/2012	08:22	54.0201	0.2327	15.1	34.1	0.6	0.2	< 0.4	0.2	2.3	66.9	5.1	8.9	1.2	5.5	0.4
27	13	4	81	15/08/2012	16:00	54.9303	0.3074	17.2	34.1	3.1	0.2	< 0.4	0.2	1.6	76.6	7.4	18.7	1.3	7.8	0.4
28	22	4	100	16/08/2012	03:47	55.5546	0.7861	15.3	34.5	1.7	0.2	< 0.4	0.1	1.3	65.2	6.0	14.0	1.1	6.4	0.4
29	23	4	101	16/08/2012	08:35	55.9369	0.0054	16.6	34.7	0.7	0.2	0.8	0.2	1.5	63.6	5.2	9.3	2.4	6.1	0.9
30	24	4	86	16/08/2012	18:18	55.8258	1.2373	17.2	34.8	0.5	0.2	< 0.4	0.1	0.7	54.4	5.8	8.1	0.8	6.2	0.4

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.4 and < 0.1 = less than the detection limit of UEA instrument

Appendix 3.5: (Continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	POC (µM)	PON (µM)	TDN (µM)	DIN (µM)
31	34	4	100	17/08/2012	03:40	56.7362	1.5511	16.2	34.9	0.2	0.6	0.9	0.2	1.4	58.2	4.1	3.1	2.0	5.6	1.5
32	42	4	97	17/08/2012	07:09	57.1084	1.6325	16.1	34.9	0.2	0.2	0.5	0.2	1.1	58.2	4.0	2.7	2.4	4.7	0.6
33	43	4	82	17/08/2012	11:33	57.3735	2.4319	16.1	34.8	0.3	0.2	< 0.4	0.1	0.6	53.9	4.5	10.6	2.5	4.9	0.4
34	35	4	73	17/08/2012	18:14	56.7202	2.5093	16.4	35.1	0.2	0.2	< 0.4	0.1	0.5	45.8	5.1	12.5	2.2	5.5	0.4
35	44	4	69	18/08/2012	03:41	57.0899	3.2327	16.6	34.2	0.3	0.2	< 0.4	< 0.1	0.1	42.7	3.0	10.0	2.3	3.4	0.4
36	36	4	61	18/08/2012	07:42	56.7393	3.4808	16.6	34.6	0.3	0.2	< 0.4	0.1	0.3	53.3	4.3	10.4	2.1	4.7	0.4
37	37	4	58	18/08/2012	12:14	56.7351	4.5504	16.8	34.7	0.4	0.2	< 0.4	0.1	0.7	63.7	4.8	10.0	2.5	5.1	0.4
38	38	4	56	18/08/2012	17:59	56.7858	5.8076	17.4	34.2	0.8	0.2	< 0.4	0.1	1.2	77.5	7.5	15.0	2.7	7.8	0.4
39	50	4	99	19/08/2012	03:35	57.6810	5.1231	16.6	30.9	0.4	0.2	< 0.4	0.1	0.6	99.5	6.4	11.7	2.2	6.8	0.4
40	49	4	84	19/08/2012	07:00	57.7371	4.7522	16.7	32.1	0.3	0.2	< 0.4	< 0.1	0.1	55.9	5.9	8.1	2.8	6.3	0.4
41	58	4	151	19/08/2012	10:32	58.0595	4.8340	16.5	32.4	0.3	0.2	< 0.4	0.1	0.8	79.3	6.8	9.3	2.0	7.2	0.4
42	48	4	66	19/08/2012	17:52	57.7388	3.4785	16.7	33.9	0.2	0.2	< 0.4	0.1	0.2	58.8	6.1	8.2	1.8	6.5	0.4
43	57	4	160	20/08/2012	03:38	58.4253	3.9094	16.1	32.6	0.3	0.2	< 0.4	0.1	0.6	76.1	6.3	9.5	2.5	6.7	0.4
44	56	4	73	20/08/2012	09:02	58.3012	2.8028	16.2	34.0	0.2	0.2	< 0.4	0.1	0.9	62.2	6.1	7.7	1.8	6.4	0.4
45	55	4	107	20/08/2012	13:43	58.1897	1.4543	16.0	35.1	0.2	0.2	< 0.4	< 0.1	0.3	32.7	4.6	8.6	2.0	4.9	0.4
46	47	4	92	20/08/2012	18:55	57.7799	1.5269	16.2	34.9	0.2	0.2	< 0.4	0.1	0.7	54.8	5.1	8.8	2.6	5.5	0.4
47	54	4	150	21/08/2012	03:36	58.3586	0.6767	15.7	35.1	0.2	0.2	< 0.4	0.1	0.9	59.9	4.7	6.4	1.3	5.1	0.4
48	46	4	88	21/08/2012	11:27	57.5004	0.5581	15.9	35.2	0.3	0.2	1.2	0.2	1.2	58.3	5.1	7.9	1.0	6.4	1.3
49	41	4	83	21/08/2012	05:00	57.0825	-0.3094	15.9	35.0	0.2	0.2	1.2	0.2	1.5	63.3	4.8	12.4	2.7	6.1	1.4
50	33	4	121	22/08/2012	03:39	56.7265	0.3255	16.3	35.0	0.3	0.2	< 0.4	0.1	0.5	47.7	5.6	9.9	2.0	6.0	0.4
51	32	4	79	22/08/2012	08:20	56.5568	-0.3361	16.0	34.8	0.6	0.2	< 0.4	0.1	0.8	54.9	6.1	13.3	1.8	6.5	0.4
52	31	4	62	22/08/2012	14:47	56.4843	-1.3753	15.1	34.7	0.5	0.2	0.7	0.2	1.6	70.2	5.4	11.8	2.1	6.3	0.9
53	40	4	113	23/08/2012	04:12	57.0075	-1.7840	13.2	34.9	3.1	0.2	< 0.4	0.1	0.2	43.5	3.9	19.4	2.9	4.3	0.4

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.4 and < 0.1 = less than the detection limit of UEA instrument

Appendix 3.6: Results of bottom samples from CEND 13/12 cruise (summer 2012).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a*(µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	POC (µM)	PON (µM)	TDN (µM)	DIN (µM)
1	1	20	25	08/08/2012	08:20	51.7577	1.7892	17.6	34.8	1.4	1.6	0.9	0.3	2.0	83.3	5.7	30.1	4.9	8.2	2.5
2	2	28	33	08/08/2012	18:25	51.5717	2.7755	17.5	34.7	1.2	0.5	0.2	0.1	0.7	61.0	4.5	11.7	2.2	5.2	0.7
3	3	21	24	09/08/2012	03:42	51.8011	3.5891	18.5	33.9	7.2	0.9	0.2	0.2	0.8	98.4	8.2	39.3	5.6	9.3	1.1
4	5	24	29	09/08/2012	15:00	52.7020	3.3843	17.1	35.1	1.2	0.5	0.2	0.1	0.9	54.2	4.1	10.0	1.3	4.9	0.7
5	4	33	37	09/08/2012	19:30	52.8310	2.7574	16.9	34.9	1.9	0.2	0.2	0.1	0.7	69.3	5.6	18.3	1.7	6.0	0.4
6	9	63	68	10/08/2012	03:40	53.8280	2.6558	14.6	34.8	1.3	0.2	1.0	0.3	2.5	59.7	4.8	14.5	2.1	5.9	1.2
7	10	35	39	10/08/2012	08:40	53.7862	3.4065	16.0	34.6	1.1	0.2	0.2	0.1	0.3	52.7	5.3	11.3	1.7	5.7	0.4
8	11	36	41	10/08/2012	13:23	53.8089	4.5736	16.9	34.5	1.7	0.3	0.2	0.2	3.1	64.1	4.9	14.6	1.9	5.5	0.5
9	12	26	30	10/08/2012	19:08	53.7379	5.3023	17.8	34.6	4.8	0.2	0.2	0.1	0.4	76.0	5.2	22.2	2.8	5.6	0.4
10	18	39	43	11/08/2012	03:36	54.7722	4.9533	14.8	34.6	1.6	0.2	0.2	0.1	0.5	36.3	2.8	12.1	2.2	3.2	0.4
11	19	39	44	11/08/2012	07:17	54.6836	5.4764	15.2	34.5	1.6	0.4	0.2	0.3	2.6	63.8	4.5	10.3	1.2	5.2	0.7
12	20	35	40	11/08/2012	11:51	54.5711	6.2836	16.0	34.5	1.7	0.2	0.5	0.1	2.0	43.1	4.7	10.8	1.7	5.4	0.7
13	21	29	32	11/08/2012	18:09	54.9298	7.0784	16.5	33.5	2.9	1.0	0.9	0.1	2.0	56.9	5.6	15.3	2.0	7.4	1.9
14	30	24	28	12/08/2012	03:32	55.5800	7.2004	16.4	33.8	2.6	0.2	0.2	0.2	1.6	93.1	8.1	13.9	2.3	8.5	0.4
15	29	34	37	12/08/2012	08:50	55.6887	6.7024	15.4	34.0	0.3	0.2	1.8	0.2	5.2	62.2	6.7	9.4	1.9	8.7	2.0
16	39	32	35	12/08/2012	14:53	56.5846	6.9799	14.5	34.4	7.8	0.2	0.2	0.1	2.8	68.6	5.7	33.9	3.8	6.0	0.4
17	28	50	54	13/08/2012	03:24	55.7810	5.2520	10.5	34.7	0.6	0.7	1.0	0.5	5.1	60.4	7.5	16.2	2.4	9.1	1.7
18	27	28	33	13/08/2012	07:59	55.5543	4.5034	14.5	34.9	1.3	0.2	0.2	0.3	2.0	64.3	5.0	12.6	1.8	5.4	0.4
19	26	32	37	13/08/2012	12:04	55.6260	3.6747	15.0	34.9	1.1	0.2	0.2	0.2	1.5	64.3	4.8	14.0	1.6	5.2	0.4
20	25	62	67	13/08/2012	18:26	55.6730	2.7831	10.5	35.0	0.6	0.5	1.2	0.2	1.2	37.2	5.6	10.5	1.3	7.3	1.7
21	17	38	43	14/08/2012	03:44	54.5850	3.4035	12.5	34.9	2.3	0.2	0.2	0.2	4.2	54.3	4.1	20.6	3.0	4.5	0.4
22	16	24	29	14/08/2012	07:15	54.4898	2.7798	11.0	34.9	1.7	0.2	0.2	0.3	1.1	57.9	4.6	12.8	2.4	5.0	0.4
23	15	32	36	14/08/2012	12:38	54.7726	1.3053	14.5	34.6	5.5	0.2	0.2	0.1	0.9	54.7	5.2	30.0	3.6	5.6	0.4
24	14	72	76	14/08/2012	18:15	54.7890	0.1740	9.0	34.9	0.2	3.3	0.2	0.5	2.8	41.3	5.2	4.2	0.4	8.8	3.6
25	8	36	41	15/08/2012	03:57	53.9215	1.3096	13.5	34.7	6.5	0.2	0.2	0.2	1.4	50.2	4.8	36.2	3.8	5.2	0.4
26	7	44	49	15/08/2012	08:22	54.0201	0.2327	12.0	34.3	3.7	0.2	0.2	0.2	2.7	73.0	5.7	24.3	2.5	6.1	0.4
27	13	76	81	15/08/2012	16:00	54.9303	0.3074	10.0	34.8	0.2	4.5	0.2	0.7	3.3	55.3	5.6	5.4	2.7	10.3	4.7
28	22	95	100	16/08/2012	03:47	55.5546	0.7861	8.5	34.8	0.2	3.5	1.2	0.6	3.4	48.4	3.5	5.3	0.3	8.2	4.7
29	23	96	101	16/08/2012	08:35	55.9369	0.0054	8.5	34.8	0.1	4.9	0.2	0.6	3.2	50.6	4.8	5.4	1.4	9.9	5.1
30	24	81	86	16/08/2012	18:18	55.8258	1.2373	8.5	34.7	0.1	4.9	0.2	0.5	2.9	43.2	3.7	2.0	1.6	8.8	5.2

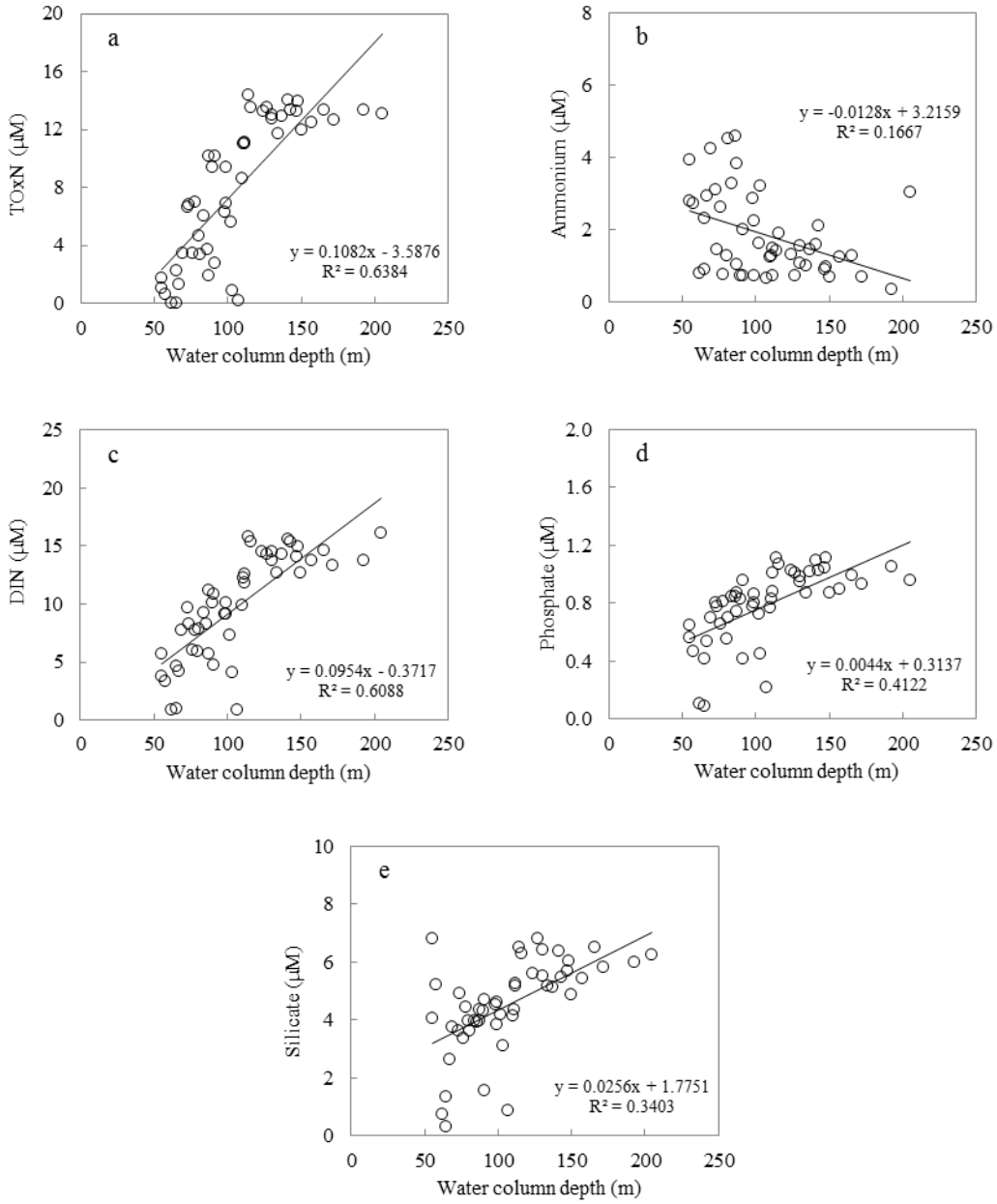
[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth

Appendix 3.6: (Continued).

Sample	Station[a]	Depth[b] (m)	Depth[c] (m)	Date of collection	Time of collection	Latitude	Longitude	Temp (°C)	Salinity	Chl *a* (µg/l)	TOxN (µM)	Ammonium (µM)	Phosphate (µM)	Silicate (µM)	DOC (µM)	DON (µM)	POC (µM)	PON (µM)	TDN (µM)	DIN (µM)
31	34	95	100	17/08/2012	03:40	56.7362	1.5511	8.5	35.0	0.1	5.5	1.8	0.7	3.8	48.6	5.7	4.1	1.5	13.0	7.3
32	42	92	97	17/08/2012	07:09	57.1084	1.6325	8.5	35.0	0.1	4.3	3.2	0.7	3.9	61.0	5.8	1.1	1.6	13.3	7.5
33	43	77	82	17/08/2012	11:33	57.3735	2.4319	8.5	35.1	0.4	1.9	4.0	0.7	3.4	49.7	5.6	1.6	1.6	11.5	5.9
34	35	68	73	17/08/2012	18:14	56.7202	2.5093	8.5	35.1	0.8	4.7	3.9	0.8	3.9	48.8	3.9	12.7	2.0	12.6	8.7
35	44	64	69	18/08/2012	03:41	57.0899	3.2327	9.0	35.1	1.4	0.2	0.2	0.2	2.2	37.4	4.4	12.5	2.3	4.8	0.4
36	36	56	61	18/08/2012	07:42	56.7393	3.4808	8.0	35.1	0.4	2.3	2.2	0.6	3.4	49.6	4.1	10.1	1.5	8.6	4.5
37	37	53	58	18/08/2012	12:14	56.7351	4.5504	8.5	35.1	0.8	0.2	0.5	0.5	3.3	49.1	5.4	11.2	2.2	6.1	0.6
38	38	51	56	18/08/2012	17:59	56.7858	5.8076	8.5	34.6	0.5	1.1	1.5	0.3	3.7	61.2	4.9	9.9	1.9	7.4	2.6
39	50	94	99	19/08/2012	03:35	57.6810	5.1231	8.5	35.2	< 0.1	8.6	0.2	0.7	3.2	43.2	5.5	4.8	1.5	14.4	8.9
40	49	79	84	19/08/2012	07:00	57.7371	4.7522	9.0	35.2	0.1	7.2	0.2	0.6	2.7	38.2	4.6	5.5	1.0	12.0	7.4
41	58	146	151	19/08/2012	10:32	58.0595	4.8340	9.0	35.3	< 0.1	9.7	0.3	0.8	3.9	42.5	6.6	9.5	0.7	16.6	10.0
42	48	62	66	19/08/2012	17:52	57.7388	3.4785	9.0	35.1	0.7	2.7	1.3	0.5	2.6	45.2	4.9	10.1	1.9	8.9	4.0
43	57	155	160	20/08/2012	03:38	58.4253	3.9094	9.0	35.4	< 0.1	10.7	0.5	0.9	4.4	41.9	6.2	7.0	0.5	17.4	11.2
44	56	68	73	20/08/2012	09:02	58.3012	2.8028	8.5	35.1	0.8	5.3	1.6	0.7	3.1	47.2	6.4	7.2	1.4	13.4	7.0
45	55	102	107	20/08/2012	13:43	58.1897	1.4543	8.5	35.3	0.1	6.3	3.2	0.9	4.3	45.8	5.4	6.1	1.6	14.8	9.5
46	47	87	92	20/08/2012	18:55	57.7799	1.5269	9.0	35.2	0.3	5.5	3.9	0.8	3.5	45.5	4.6	4.8	0.4	14.0	9.4
47	54	145	150	21/08/2012	03:36	58.3586	0.6767	8.0	35.3	< 0.1	9.4	0.2	0.8	3.3	50.2	6.4	5.2	0.5	16.0	9.6
48	46	83	88	21/08/2012	11:27	57.5004	0.5581	9.0	35.2	0.1	2.6	3.6	0.6	3.1	46.3	5.0	6.7	1.3	11.1	6.2
49	41	78	83	21/08/2012	05:00	57.0825	-0.3094	9.0	35.1	0.3	1.8	3.4	0.6	2.9	44.0	4.6	9.4	2.2	9.8	5.2
50	33	116	121	22/08/2012	03:39	56.7265	0.3255	8.5	34.9	0.6	3.5	2.5	0.7	2.9	40.2	4.4	7.3	2.7	10.5	6.1
51	32	74	79	22/08/2012	08:20	56.5568	-0.3361	8.5	35.0	0.4	0.8	1.7	0.3	1.8	36.8	3.8	8.5	1.8	6.3	2.5
52	31	57	62	22/08/2012	14:47	56.4843	-1.3753	8.5	34.8	0.3	0.2	1.2	0.3	1.7	42.3	4.9	7.9	1.8	6.2	1.4
53	40	98	113	23/08/2012	04:12	57.0075	-1.7840	7.5	35.1	0.4	0.5	2.1	0.4	2.9	55.6	7.1	6.0	1.1	9.7	2.6

[a] The station based on IBTS cruise track (CEFAS), [b] Sample depth, [c] Water column depth, < 0.1 = less than the detection limit of UEA instrument

Appendix 3.7: Relationship between inorganic nutrient and water column depth in the northern bottom water during summer 2011.



Appendix 3.8: Correlations of DOC and DON with salinity and inorganic nitrogen for three water masses in summer 2011.

Parameters			Correlation coefficient (r)	Confidence level at 95 %
DOC	Stratified northern surface water	Salinity	-0.509*	0.000
		TOxN	-0.296*	0.037
		Ammonium	-0.186	0.196
		DIN	-0.295*	0.037
	Stratified northern bottom water	Salinity	-0.233	0.107
		TOxN	-0.215	0.139
		Ammonium	0.071	0.626
		DIN	-0.219	0.130
	Southern well-mixed water	Salinity	-0.408*	0.005
		TOxN	-0.141	0.357
		Ammonium	0.065	0.673
		DIN	0.020	0.898
DON	Stratified northern surface water	Salinity	-0.444*	0.001
		TOxN	-0.147	0.030
		Ammonium	-0.162	0.260
		DIN	-0.157	0.277
	Stratified northern bottom water	Salinity	-0.549*	0.000
		TOxN	-0.646*	0.000
		Ammonium	0.384*	0.006
		DIN	-0.167*	0.000
	Southern well-mixed water	Salinity	-0.551*	0.000
		TOxN	-0.164	0.281
		Ammonium	0.118	0.441
		DIN	0.061	0.690

* Correlation is significant at the 0.05 confidence level.
The number of samples (n) is 50, 49 and 45 for northern bottom waters, northern surface water and southern mixed water, respectively.

Appendix 3.9: Correlations of DOC and DON with salinity chlorophyll *a* and inorganic nitrogen for the whole water mass in winter 2011.

Parameters		Correlation coefficient (r)	Confidence level at 95 %
DOC	Salinity	-0.288*	0.026
	Chlorophyll *a*	0.109	0.406
	TOxN	0.396*	0.002
	Ammonium	-0.027	0.839
	DIN	0.395*	0.002
DON	Salinity	0.225	0.085
	Chlorophyll *a*	0.225	0.084
	TOxN	0.043	0.746
	Ammonium	0.294*	0.023
	DIN	0.055	0.676

* Correlation is significant at the 0.05 confidence level.
The number of samples is 60 (n = 60) for mixed surface and bottom waters.

Appendix 3.10: Correlations of DOC and DON with salinity, chlorophyll *a* and nutrients for three water masses in summer 2012.

Parameters			Correlation coefficient (r)	Confidence level at 95 %
DOC	Stratified northern surface water	Salinity	-0.637*	0.000
		Chlorophyll *a*	0.042	0.825
		TOxN	-0.037	0.848
		Ammonium	0.083	0.661
		DIN	0.065	0.733
		POC	0.096	0.613
	Stratified northern bottom water	Salinity	-0.342	0.064
		Chlorophyll *a*	-0.050	0.794
		TOxN	-0.131	0.489
		Ammonium	0.188	0.321
		DIN	-0.050	0.795
		POC	-0.023	0.902
	Southern well-mixed water	Salinity	-0.536*	0.000
		Chlorophyll *a*	0.259	0.082
		TOxN	0.140	0.352
		Ammonium	0.537*	0.000
		DIN	0.556*	0.000
		POC	0.541*	0.000
DON	Stratified northern surface water	Salinity	-0.503*	0.005
		Chlorophyll *a*	0.212	0.261
		TOxN	-0.203	0.282
		Ammonium	-0.251	0.182
		DIN	-0.274	0.142
		PON	-0.015	0.939
	Stratified northern bottom water	Salinity	0.220	0.243
		Chlorophyll *a*	-0.070	0.715
		TOxN	0.199	0.293
		Ammonium	-0.159	0.402
		DIN	0.129	0.495
		PON	-0.105	0.581
	Southern well-mixed water	Salinity	-0.636*	0.000
		Chlorophyll *a*	0.330	0.025
		TOxN	0.081	0.593
		Ammonium	0.182	0.226
		DIN	0.197	0.190
		PON	0.428*	0.003

* Correlation is significant at the 0.05 confidence level. The number of samples (n) is 30, 30 and 46 for northern bottom waters, northern surface water and southern mixed water, respectively.

Appendix 3.11: Summary of SmartBuoy data for analysed bag samples and related in situ parameter.

1) West Gabbard SmartBuoy site

Analysed bag samples (unit in µM)

Sample	ID	Bag No.	Date of collection	Time of collection	TOxN	Ammonium	Phosphate	Silicate	DOC	DON	TDN	DIN
1	WG 94	1	07/09/2013	00:00	4.5	1.0	0.3	3.4	178.7	10.1	15.5	5.4
2	WG 94	2	11/09/2013	00:00	4.0	1.2	0.4	3.3	157.3	10.6	15.7	5.1
3	WG 94	4	15/09/2013	00:00	4.0	1.3	0.3	2.9	161.3	8.7	14.0	5.3
4	WG 94	5	19/09/2013	00:00	3.9	0.7	0.4	2.9	129.1	9.3	13.9	4.7
5	WG 94	7	23/09/2013	00:00	4.9	2.2	0.5	5.0	140.6	8.4	15.6	7.2
6	WG 94	8	27/09/2013	00:00	5.7	2.1	0.6	5.2	131.8	9.7	17.5	7.8
7	WG 94	10	01/10/2013	00:00	6.7	0.4	0.5	5.0	119.2	8.2	15.4	7.1
8	WG 94	11	05/10/2013	00:00	10.0	0.6	0.7	6.9	132.0	8.3	18.9	10.6
9	WG 96	1	02/02/2014	23:59	0.3	0.4	0.3	5.1	159.1	13.2	13.9	0.7
10	WG 96	2	06/02/2014	23:59	< 0.2	1.4	0.2	4.9	201.3	15.7	17.2	1.5
11	WG 96	4	10/02/2014	23:59	< 0.2	0.7	0.4	5.1	186.1	15.8	16.6	0.8
12	WG 96	5	14/02/2014	23:59	5.9	0.7	0.5	5.4	141.1	9.5	16.1	6.6
13	WG 96	6	18/02/2014	23:59	0.3	2.6	0.3	6.1	138.7	10.2	13.1	2.9
14	WG 96	7	22/02/2014	23:59	6.5	0.5	0.3	5.5	132.8	11.8	18.8	6.9
15	WG 96	9	26/02/2014	23:59	5.3	0.6	0.4	5.8	144.8	14.5	20.5	6.0
16	WG 96	10	02/03/2014	23:59	1.7	1.1	0.3	4.4	135.5	14.2	16.9	2.8
17	WG 96	11	06/03/2014	23:59	< 0.2	3.3	0.2	4.2	159.7	12.6	16.0	3.4
18	WG 96	12	10/03/2014	23:59	2.9	< 0.4	0.3	4.5	151.5	16.0	19.1	3.1
19	WG 96	14	14/03/2014	23:59	6.5	< 0.4	0.3	6.7	146.7	10.3	17.1	6.7
20	WG 96	15	18/03/2014	23:59	1.8	7.6	0.2	6.3	130.2	11.0	20.5	9.5
21	WG 96	17	22/03/2014	23:59	2.0	0.5	0.2	5.0	152.1	10.4	12.9	2.5
22	WG 96	18	26/03/2014	23:59	2.6	1.9	0.2	3.7	185.0	10.5	15.1	4.6
23	WG 96	20	30/03/2014	23:59	< 0.2	1.3	0.2	4.8	182.7	15.0	16.3	1.4
24	WG 96	21	03/04/2014	23:59	0.5	0.2	0.2	2.9	142.6	12.3	13.0	0.7
25	WG 96	22	07/04/2014	23:59	4.2	1.3	0.2	3.0	101.7	8.0	13.5	5.5
26	WG 96	23	11/04/2014	23:59	< 0.2	< 0.4	0.2	2.8	110.2	9.6	9.9	0.3
27	WG 96	25	15/04/2014	23:59	1.1	0.6	0.3	1.2	109.6	8.9	10.6	1.7
28	WG 96	26	19/04/2014	23:59	< 0.2	< 0.4	0.2	1.3	116.9	15.0	15.3	0.3
29	WG 96	27	23/04/2014	23:59	< 0.2	0.4	0.2	0.7	97.2	9.9	10.4	0.5
30	WG 96	28	27/04/2014	23:59	< 0.2	1.0	0.2	1.0	127.0	10.6	11.7	1.1
31	WG 96	30	01/05/2014	23:59	0.4	0.4	0.2	1.0	95.6	8.3	9.0	0.8

< 0.2 and < 0.4 = less than the detection limit of UEA instrument

In situ measurement at the time of bag sample collection

Sample	Date of collection	Time of collection	Temp (°C)	Salinity (unitless)	Chlorophyll Fluorescence (arbitrary unit)	Oxygen concentration (mg/l)	Oxygen saturation (%)	Turbidity (FTU)	Wave height (m)
1	07/09/2013	00:00	18.3	34.6	1.1	7.5	100.7	5.0	1.4
2	11/09/2013	00:00	18.0	34.7	1.0	7.5	100.3	8.6	2.8
3	15/09/2013	00:00	17.6	34.7	1.0	7.5	100.0	3.9	1.3
4	19/09/2013	00:00	17.0	34.8	1.1	7.6	99.3	3.8	1.4
5	23/09/2013	00:00	17.0	34.8	1.2	7.5	98.0	12.3	0.3
6	27/09/2013	00:00	17.1	na	na	na	na	3.8	1.1
7	01/10/2013	00:00	16.8	na	na	na	na	5.4	1.7
8	05/10/2013	00:00	16.4	na	na	na	na	8.1	0.9
9	02/02/2014	23:59	9.5	35.2	0.4	9.0	100.9	9.9	1.2
10	06/02/2014	23:59	9.4	35.1	0.4	9.0	101.1	9.8	2.5
11	10/02/2014	23:59	9.2	35.1	0.3	9.0	100.5	14.2	1.0
12	14/02/2014	23:59	9.1	35.2	0.3	9.1	101.1	13.3	3.8
13	18/02/2014	23:59	8.9	35.0	0.3	9.2	101.5	14.0	0.7
14	22/02/2014	23:59	8.8	34.9	0.4	9.2	102.0	9.9	1.5
15	26/02/2014	23:59	8.8	34.9	0.4	9.3	102.5	10.8	1.1
16	02/03/2014	23:59	8.9	35.1	0.5	9.2	102.2	7.7	3.3
17	06/03/2014	23:59	9.1	35.1	0.4	9.2	102.6	6.7	0.7
18	10/03/2014	23:59	9.0	35.0	0.4	9.3	103.6	5.4	1.8
19	14/03/2014	23:59	8.6	34.7	0.4	9.4	103.8	7.0	0.8
20	18/03/2014	23:59	8.7	34.7	0.5	9.5	104.2	12.2	1.4
21	22/03/2014	23:59	9.3	35.0	0.7	9.4	104.8	5.6	1.2
22	26/03/2014	23:59	9.2	34.9	0.8	9.5	105.7	4.2	1.1
23	30/03/2014	23:59	9.3	34.5	0.7	9.5	105.6	6.3	0.4
24	03/04/2014	23:59	9.6	34.4	0.2	10.2	114.8	4.7	0.8
25	07/04/2014	23:59	na	na	na	na	na	na	0.9
26	11/04/2014	23:59	na	na	na	na	na	na	0.3
27	15/04/2014	23:59	na	na	na	na	na	na	1.3
28	19/04/2014	23:59	na	na	na	na	na	na	1.6
29	23/04/2014	23:59	na	na	na	na	na	na	0.4
30	27/04/2014	23:59	na	na	na	na	na	na	0.6
31	01/05/2014	23:59	na	na	na	na	na	na	1.1

na = data is not available

2) Dowsing SmartBuoy site

Analysed bag samples (unit in µM)

Sample	ID	Bag No.	Date of collection	Time of collection	TOxN	Ammonium	Phosphate	Silicate	DOC	DON	TDN	DIN
1	DS 33	1	30/07/2013	00:00	1.2	< 0.4	0.5	2.7	142.6	9.7	11.2	1.4
2	DS 33	2	03/08/2013	00:00	0.8	< 0.4	0.3	1.8	121.1	9.6	10.5	1.0
3	DS 33	4	07/08/2013	00:00	1.8	< 0.4	0.3	2.4	124.8	11.4	13.4	2.0
4	DS 33	5	11/08/2013	00:00	0.5	< 0.4	0.2	1.8	107.5	9.6	10.3	0.7
5	DS 33	7	15/08/2013	00:00	0.2	< 0.4	0.2	2.1	120.8	10.4	10.8	0.4
6	DS 33	8	19/08/2013	00:00	< 0.2	< 0.4	0.1	1.9	115.1	10.8	11.1	0.3
7	DS 33	10	23/08/2013	00:00	0.2	< 0.4	0.3	2.3	107.2	8.8	9.2	0.4
8	DS 33	11	27/08/2013	00:00	0.7	< 0.4	0.7	2.0	131.9	16.5	17.4	0.9
9	DS 33	13	31/08/2013	00:00	0.2	< 0.4	0.2	1.9	110.9	10.1	10.5	0.4
10	DS 33	14	04/09/2013	00:00	0.7	< 0.4	0.3	2.7	108.1	11.9	12.8	0.9
11	DS 33	16	08/09/2013	00:00	< 0.2	< 0.4	0.2	2.6	102.1	10.9	11.2	0.3
12	DS 33	17	12/09/2013	00:00	1.1	< 0.4	0.3	3.8	92.0	11.3	12.6	1.3
13	DS 33	19	16/09/2013	00:00	1.6	< 0.4	0.1	3.8	97.9	11.1	12.9	1.8
14	DS 33	20	20/09/2013	00:00	1.9	< 0.4	0.1	3.2	88.1	8.3	10.4	2.1
15	DS 33	22	24/09/2013	00:00	0.3	< 0.4	0.1	2.5	93.0	7.8	8.3	0.5
16	DS 33	23	28/09/2013	00:00	0.3	< 0.4	0.2	2.4	95.8	9.0	9.4	0.5
17	DS 33	25	02/10/2013	00:00	< 0.2	< 0.4	0.1	2.5	93.9	9.0	9.3	0.3
18	DS 33	26	06/10/2013	00:00	1.2	< 0.4	0.2	1.8	96.5	9.1	10.5	1.4
19	DS 34	1	09/10/2013	00:00	< 0.2	< 0.4	0.1	2.5	95.2	9.4	9.7	0.3
20	DS 34	2	13/10/2013	00:00	2.3	0.7	0.4	2.4	99.1	8.5	11.5	3.0
21	DS 34	4	17/10/2013	00:00	< 0.2	< 0.4	0.2	3.1	90.7	7.5	7.8	0.3
22	DS 34	5	21/10/2013	00:00	< 0.2	< 0.4	0.1	3.2	102.9	6.8	7.1	0.3
23	DS 34	7	25/10/2013	00:00	0.2	< 0.4	0.2	2.6	99.1	8.6	9.0	0.4
24	DS 34	8	29/10/2013	00:00	< 0.2	< 0.4	0.1	2.5	104.1	7.3	7.6	0.3
25	DS 34	10	02/11/2013	00:00	< 0.2	< 0.4	0.1	3.4	86.4	7.1	7.4	0.3
26	DS 34	11	06/11/2013	00:00	< 0.2	< 0.4	0.3	3.4	99.7	8.3	8.6	0.3
27	DS 34	13	10/11/2013	00:00	< 0.2	< 0.4	0.2	3.2	84.8	12.0	12.3	0.3
28	DS 34	14	14/11/2013	00:00	< 0.2	< 0.4	0.1	3.3	89.8	7.6	7.9	0.3
29	DS 34	16	18/11/2013	00:00	< 0.2	< 0.4	0.1	2.9	83.8	6.2	6.5	0.3
30	DS 34	17	22/11/2013	00:00	0.3	< 0.4	0.1	2.7	83.4	6.7	7.2	0.5
31	DS 34	19	26/11/2013	00:00	0.2	< 0.4	0.1	2.8	93.7	6.1	6.5	0.4
32	DS 34	20	30/11/2013	00:00	< 0.2	< 0.4	0.1	2.6	83.4	5.8	6.1	0.3
33	DS 34	22	04/12/2013	00:00	< 0.2	< 0.4	0.1	3.2	68.3	6.9	7.2	0.3
34	DS 34	23	08/12/2013	00:00	< 0.2	< 0.4	0.1	3.1	81.5	6.3	6.6	0.3
35	DS 34	25	12/12/2013	00:00	< 0.2	0.9	0.1	3.8	78.7	8.0	8.9	1.0
36	DS 34	26	16/12/2013	00:00	< 0.2	< 0.4	0.1	3.7	73.9	7.0	7.3	0.3
37	DS 34	28	20/12/2013	00:00	< 0.2	< 0.4	0.1	3.4	69.7	6.2	6.5	0.3
38	DS 34	29	24/12/2013	00:00	< 0.2	< 0.4	0.1	3.3	95.9	6.5	6.8	0.3
39	DS 34	31	28/12/2013	00:00	< 0.2	< 0.4	0.1	4.1	106.9	10.5	10.8	0.3
40	DS 34	32	01/01/2014	00:00	< 0.2	< 0.4	0.1	3.8	99.1	7.0	7.3	0.3
41	DS 34	34	05/01/2014	00:00	< 0.2	< 0.4	0.1	3.6	105.2	6.1	6.4	0.3
42	DS 34	35	09/01/2014	00:00	0.7	< 0.4	0.1	3.9	85.5	7.9	8.8	0.9

Sample	ID	Bag No.	Date of collection	Time of collection	TOxN	Ammonium	Phosphate	Silicate	DOC	DON	TDN	DIN
43	DS 34	37	13/01/2014	00:00	0.2	< 0.4	0.2	3.7	79.0	6.7	7.1	0.4
44	DS 34	38	17/01/2014	00:00	< 0.2	< 0.4	0.1	3.8	97.6	12.6	12.9	0.3
45	DS 34	40	21/01/2014	00:00	3.0	< 0.4	0.9	2.9	109.7	17.8	20.9	3.2
46	DS 34	41	25/01/2014	00:00	< 0.2	< 0.4	0.1	3.4	93.3	9.4	9.7	0.3
47	DS 34	50	29/01/2014	00:00	5.1	4.3	1.3	2.7	135.9	24.5	33.9	9.4
48	DS 35	1	30/01/2014	23:59	6.2	1.0	0.9	4.8	144.2	22.1	29.3	7.2
49	DS 35	2	03/02/2014	23:59	5.9	1.0	0.7	4.3	165.9	12.1	19.0	6.9
50	DS 35	4	07/02/2014	23:59	7.6	1.5	0.8	4.5	182.7	14.4	23.6	9.2
51	DS 35	5	11/02/2014	23:59	13.0	1.3	0.9	5.8	159.5	9.1	23.5	14.4
52	DS 35	6	15/02/2014	23:59	5.4	1.1	0.8	3.8	147.5	10.0	16.6	6.5
53	DS 35	7	19/02/2014	23:59	5.8	1.4	0.8	4.1	181.6	13.7	20.9	7.2
54	DS 35	9	23/02/2014	23:59	12.2	0.9	0.9	5.8	215.7	23.2	36.3	13.1
55	DS 35	10	27/02/2014	23:59	14.9	0.7	0.9	6.3	153.5	10.8	26.4	15.6
56	DS 35	11	03/03/2014	23:59	6.8	1.3	0.8	4.5	163.1	18.5	26.7	8.1
57	DS 35	12	07/03/2014	23:59	8.5	0.7	0.9	4.9	178.5	18.8	28.0	9.2
58	DS 35	14	11/03/2014	23:59	8.9	1.8	0.8	4.9	149.5	9.5	20.2	10.7
59	DS 35	15	15/03/2014	23:59	12.7	1.5	0.9	5.9	150.7	12.2	26.5	14.3
60	DS 35	17	19/03/2014	23:59	4.6	0.5	0.3	3.7	197.7	15.7	20.8	5.0
61	DS 35	18	23/03/2014	23:59	1.8	< 0.4	0.3	3.4	169.8	13.2	15.3	2.0
62	DS 35	20	27/03/2014	23:59	0.3	2.3	0.3	2.7	169.6	13.3	15.9	2.6
63	DS 35	21	31/03/2014	23:59	1.8	< 0.4	0.3	2.6	161.3	14.5	16.5	2.0
64	DS 35	22	04/04/2014	23:59	2.6	< 0.4	0.3	2.2	160.6	13.5	16.3	2.8
65	DS 35	25	12/04/2014	23:59	7.9	3.9	0.8	3.9	181.7	18.9	30.7	11.8
66	DS 35	26	16/04/2014	23:59	0.2	0.4	0.2	1.9	190.1	16.7	17.2	0.5
67	DS 35	27	20/04/2014	23:59	< 0.2	< 0.4	0.2	1.9	224.0	17.1	17.4	0.3
68	DS 35	28	24/04/2014	23:59	< 0.2	0.3	0.3	1.5	215.7	13.2	13.6	0.4
69	DS 35	30	28/04/2014	23:59	0.2	< 0.4	0.3	2.3	211.6	16.9	17.3	0.4

< 0.2 and < 0.4 = less than the detection limit of UEA instrument

In situ measurement at the time of bag sample collection

Sample	Date of collection	Time of collection	Temp (°C)	Salinity (unitless)	Chlorophyll Fluorescence (arbitrary unit)	Oxygen concentration (mg/l)	Oxygen saturation (%)	Turbidity (FTU)	Wave height (m)
1	30/07/2013	00:00	13.82	34.487	1.15	9.43	116.1	0.58	0.82
2	03/08/2013	00:00	14.92	34.367	1.28	9.04	113.6	0.37	0.52
3	07/08/2013	00:00	15.4	34.246	1.82	8.96	113.6	0.57	0.71
4	11/08/2013	00:00	13.84	34.549	1.06	8.99	110.6	0.47	0.62
5	15/08/2013	00:00	14.12	34.542	1.1	8.87	109.6	0.83	0.85
6	19/08/2013	00:00	14.98	34.429	1.32	8.85	111.3	0.75	0.46
7	23/08/2013	00:00	14.65	na	1.08	na	na	1.51	0.31
8	27/08/2013	00:00	14.82	na	na	na	na	0.88	0.8
9	31/08/2013	00:00	15.33	na	na	na	na	0.46	0.56
10	04/09/2013	00:00	15.43	na	na	na	na	0.53	0.37
11	08/09/2013	00:00	15.07	na	na	na	na	0.55	1.05
12	12/09/2013	00:00	14.51	na	na	na	na	3.75	1.19
13	16/09/2013	00:00	14.3	na	na	na	na	2.71	1.67
14	20/09/2013	00:00	13.47	na	na	na	na	2.21	1.04
15	24/09/2013	00:00	13.7	na	na	na	na	1.19	0.28
16	28/09/2013	00:00	13.74	na	na	na	na	0.67	0.68
17	02/10/2013	00:00	13.79	na	na	na	na	2.8	1.99
18	06/10/2013	00:00	13.85	na	na	na	na	1.99	0.34
19	09/10/2013	00:00	13.82	34.426	0.88	8.15	100	2.43	0.74
20	13/10/2013	00:00	13.14	34.445	0.59	8.31	100.5	8.3	2.32
21	17/10/2013	00:00	12.82	34.454	0.58	8.31	99.8	5.73	1.98
22	21/10/2013	00:00	13.07	34.413	0.37	8.09	97.6	8.6	1.56
23	25/10/2013	00:00	12.84	34.389	0.28	8.19	98.4	4.61	0.69
24	29/10/2013	00:00	12.55	34.376	0.35	8.17	97.6	3.08	1.68
25	02/11/2013	00:00	12.03	34.363	0.69	8.4	99.1	1.81	0.71
26	06/11/2013	00:00	11.3	34.381	0.43	8.32	96.7	3.75	1.69
27	10/11/2013	00:00	10.86	34.427	0.33	8.43	97.1	2.42	1.36
28	14/11/2013	00:00	10.5	34.349	0.32	8.69	99.2	2.04	1.82
29	18/11/2013	00:00	10.3	34.356	0.46	8.79	100	2.2	0.52
30	22/11/2013	00:00	9.66	34.35	0.45	8.82	98.9	2.04	2.11
31	26/11/2013	00:00	9.32	34.378	0.51	8.98	100	2.15	1.71
32	30/11/2013	00:00	9.19	34.354	0.64	9.07	100.6	2.68	4.34
33	04/12/2013	00:00	8.87	34.293	0.67	9.1	100.2	2.77	0.91
34	08/12/2013	00:00	8.43	34.352	0.65	9.18	100.2	6.11	1.75
35	12/12/2013	00:00	8.27	34.359	0.72	9.23	100.3	2.8	0.96
36	16/12/2013	00:00	8.11	34.183	0.75	9.26	100.2	5.76	1.76
37	20/12/2013	00:00	8.28	34.415	0.9	9.14	99.5	5.66	1.28
38	24/12/2013	00:00	8.16	34.388	0.95	9.14	99.1	4.06	2.49
39	28/12/2013	00:00	7.5	34.107	0.82	9.13	97.3	4.6	2.23
40	01/01/2014	00:00	7.61	34.289	0.69	9.2	98.4	3.41	1.22
41	05/01/2014	00:00	7.66	34.288	0.62	9.16	98.1	4.26	1.06
42	09/01/2014	00:00	7.65	34.308	0.62	9.21	98.7	2.97	0.93
43	13/01/2014	00:00	7	33.977	0.63	9.38	98.7	6.39	1.62

Sample	Date of collection	Time of collection	Temp (°C)	Salinity (unitless)	Chlorophyll Fluorescence (arbitrary unit)	Oxygen concentration (mg/l)	Oxygen saturation (%)	Turbidity (FTU)	Wave height (m)
44	17/01/2014	00:00	7.2	34.249	0.71	9.28	98.4	3.2	1.12
45	21/01/2014	00:00	7.31	34.291	0.65	9.21	97.9	1.61	1.11
46	25/01/2014	00:00	na	na	na	na	na	na	1.63
47	29/01/2014	00:00	na	na	na	na	na	na	2.28
48	30/01/2014	23:59	6.45	34.567	0.43	9.59	100.3	2.98	1.41
49	03/02/2014	23:59	6.6	34.63	0.5	9.68	101.6	2.97	1.39
50	07/02/2014	23:59	6.52	34.455	0.5	9.63	100.8	3.44	1.34
51	11/02/2014	23:59	6.21	34.032	0.41	9.66	100.1	4.8	1.89
52	15/02/2014	23:59	6.43	34.668	0.61	9.64	100.8	2.03	1.96
53	19/02/2014	23:59	6.51	34.626	0.75	9.77	102.3	1.58	0.86
54	23/02/2014	23:59	6.23	34.053	0.38	9.88	102.4	3.42	1.55
55	27/02/2014	23:59	6.27	33.826	0.44	9.89	102.5	4.59	0.57
56	03/03/2014	23:59	6.61	34.487	0.82	9.77	102.5	2.57	0.57
57	07/03/2014	23:59	6.67	34.313	0.8	9.84	103.2	3.85	0.88
58	11/03/2014	23:59	6.85	34.252	0.95	10.04	105.7	2.26	0.91
59	15/03/2014	23:59	6.95	33.925	0.83	9.97	105.1	4.39	1.65
60	19/03/2014	23:59	7.25	34.475	1.36	10.14	107.9	na	1.54
61	23/03/2014	23:59	7.22	34.455	1.71	10.12	107.7	na	1.19
62	27/03/2014	23:59	7.27	34.351	3.15	10.46	111.3	na	2.59
63	31/03/2014	23:59	7.41	34.431	3.8	10.73	114.7	na	0.46
64	04/04/2014	23:59	7.53	34.391	2.54	10.25	109.9	na	0.8
65	12/04/2014	23:59	8.3	na	2.11	na	na	na	0.79
66	16/04/2014	23:59	8.38	na	7.29	na	na	na	0.97
67	20/04/2014	23:59	8.44	na	6.45	na	na	na	1.64
68	24/04/2014	23:59	9.08	na	6.43	na	na	na	0.8
69	28/04/2014	23:59	9.14	na	6.52	na	na	na	0.42

na = data is not available

Appendix for chapter 4

Appendix 4.1: Results of TOxN, ammonium, DIN, TDN, DON and DOC concentrations (µM) during the incubation period.

An example of sample identification:

1) Incubation experiment onboard in summer 2012.

B1/D00_01-0

B1: batch 1 (B1 =West Gabbard station (WG)), whereas B2 and B3 indicate station 9 and station 24, respectively.

D00: day 0 of incubation (initial day), day of sub-sample collection

_01: treatment 1 (T1) (_01 to _06 are set 1 of treatment T1-T6 and _07 to _12 are set 2 of treatment T1-T6)

-0: single sub-sample collection (sub-samples collected in triplicate are indicated by -1, -2 and -3)

2) Laboratory based incubation experiment in autumn 2013, winter 2013 and spring 2014.

WG1/D00_01-0

WG1: West Gabbard station (WG) in autumn 2013, whereas DS1 indicate Dowsing station (DS) in autumn 2013.
WG2 and DS2 indicate each station collected in winter 2013,
WG3 and DS3 indicate each station collected in spring 2014.

D00: day 0 of incubation (initial day), day of sub-sample collection

_01: treatment 1 (T1) (_01 to _07 are set 1 of treatment T1-T7 and _08 to _14 are set 2 of treatment T1-T7)

-0: single sub-sample collection (sub-samples collected in triplicate are indicated by -1, -2 and -3)

1) Incubation experiment onboard in summer 2012.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1	B1/D00_01-0	< 0.2	< 0.4	0.3	6.8	6.5	76.6
2	B1/D02_01-1	< 0.2	< 0.4	0.3	5.7	5.4	71.7
3	B1/D02_01-2	< 0.2	< 0.4	0.3	6.0	5.7	70.4
4	B1/D02_01-3	< 0.2	< 0.4	0.3	5.8	5.5	68.8
5	B1/D04_01-0	< 0.2	< 0.4	0.3	6.6	6.3	76.0
6	B1/D05_01-1	< 0.2	0.4	0.5	7.1	6.6	74.5
7	B1/D05_01-2	0.2	< 0.4	0.4	6.5	6.1	66.6
8	B1/D05_01-3	< 0.2	< 0.4	0.3	6.3	6.0	69.0
9	B1/D07_01-0	< 0.2	0.5	0.6	6.1	5.5	66.2
10	B1/D10_01-1	< 0.2	0.7	0.8	7.3	6.4	67.0
11	B1/D10_01-2	< 0.2	0.7	0.8	6.8	6.0	69.7
12	B1/D10_01-3	< 0.2	0.6	0.7	6.2	5.5	61.3
13	B1/D15_01-1	< 0.2	0.9	1.0	6.0	5.1	62.8
14	B1/D15_01-2	< 0.2	0.8	0.9	6.6	5.7	60.1
15	B1/D15_01-3	0.2	0.9	1.1	7.0	5.8	57.1
16	B1/D20_01-1	< 0.2	1.0	1.1	4.6	3.5	55.8
17	B1/D20_01-2	< 0.2	1.1	1.2	6.4	5.2	46.6
18	B1/D20_01-3	< 0.2	0.7	0.8	2.7	1.9	47.2
19	B2/D00_01-0	< 0.2	< 0.4	0.3	4.4	4.1	90.5
20	B2/D02_01-1	< 0.2	< 0.4	0.3	6.1	5.8	59.3
21	B2/D02_01-2	< 0.2	< 0.4	0.3	6.0	5.7	56.5
22	B2/D02_01-3	1.1	< 0.4	1.3	7.2	5.9	55.3
23	B2/D04_01-0	< 0.2	< 0.4	0.3	5.4	5.1	66.5
24	B2/D05_01-1	0.3	< 0.4	0.5	6.7	6.2	64.3
25	B2/D05_01-2	0.2	< 0.4	0.4	6.5	6.1	60.9
26	B2/D05_01-3	0.2	< 0.4	0.4	6.1	5.8	62.6
27	B3/D00_01-0	0.3	0.7	1.0	7.3	6.3	82.6
28	B3/D02_01-1	< 0.2	0.4	0.5	5.5	5.0	74.5
29	B3/D02_01-2	< 0.2	1.1	1.2	5.7	4.4	79.8
30	B3/D02_01-3	0.2	< 0.4	0.4	5.8	5.4	76.8
31	B3/D04_01-0	0.2	0.6	0.8	4.5	3.7	60.5
32	B3/D05_01-1	0.2	< 0.4	0.4	6.5	6.1	63.1
33	B3/D05_01-2	0.2	1.1	1.3	5.8	4.5	62.6
34	B3/D05_01-3	0.2	0.4	0.6	5.1	4.5	62.9
35	B1/D00_02-0	< 0.2	6.1	6.2	na	na	na
36	B1/D02_02-1	< 0.2	4.3	4.4	na	na	na
37	B1/D02_02-2	< 0.2	4.8	4.9	na	na	na
38	B1/D02_02-3	< 0.2	3.0	3.1	na	na	na
39	B1/D04_02-0	< 0.2	4.3	4.4	na	na	na
40	B1/D05_02-1	1.2	4.7	5.8	na	na	na
41	B1/D05_02-2	0.3	4.7	5.0	na	na	na
42	B1/D05_02-3	< 0.2	4.2	4.3	na	na	na
43	B1/D07_02-0	< 0.2	4.5	4.6	na	na	na
44	B1/D10_02-1	< 0.2	4.3	4.4	na	na	na

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
45	B1/D10_02-2	< 0.2	4.8	4.9	na	na	na
46	B1/D10_02-3	< 0.2	4.7	4.8	na	na	na
47	B1/D15_02-1	< 0.2	3.5	3.6	na	na	na
48	B1/D15_02-2	< 0.2	4.0	4.1	na	na	na
49	B1/D15_02-3	< 0.2	3.5	3.6	na	na	na
50	B1/D20_02-1	< 0.2	3.6	3.7	na	na	na
51	B1/D20_02-2	< 0.2	3.2	3.3	na	na	na
52	B1/D20_02-3	< 0.2	3.2	3.3	na	na	na
53	B2/D00_02-0	< 0.2	3.1	3.2	na	na	na
54	B2/D02_02-1	1.4	4.4	5.8	na	na	na
55	B2/D02_02-2	0.4	5.0	5.3	na	na	na
56	B2/D02_02-3	0.3	4.5	4.7	na	na	na
57	B2/D04_02-0	< 0.2	4.1	4.2	na	na	na
58	B2/D05_02-1	< 0.2	4.7	4.8	na	na	na
59	B2/D05_02-2	< 0.2	4.7	4.8	na	na	na
60	B2/D05_02-3	< 0.2	5.5	5.6	na	na	na
61	B3/D00_02-0	< 0.2	4.6	4.7	na	na	na
62	B3/D02_02-1	< 0.2	5.2	5.3	na	na	na
63	B3/D02_02-2	< 0.2	4.4	4.5	na	na	na
64	B3/D02_02-3	< 0.2	5.3	5.4	na	na	na
65	B3/D04_02-0	< 0.2	5.8	5.9	na	na	na
66	B3/D05_02-1	< 0.2	4.9	5.0	na	na	na
67	B3/D05_02-2	< 0.2	5.8	5.9	na	na	na
68	B3/D05_02-3	< 0.2	4.5	4.6	na	na	na
69	B1/D00_03-0	0.2	5.5	5.7	11.0	5.3	82.7
70	B1/D02_03-1	< 0.2	4.6	4.7	11.0	6.3	78.7
71	B1/D02_03-2	2.5	6.8	9.3	15.3	6.0	79.4
72	B1/D02_03-3	1.2	4.8	6.0	12.5	6.4	78.7
73	B1/D04_03-0	0.3	5.5	5.8	11.7	5.9	71.6
74	B1/D05_03-1	2.3	5.0	7.3	12.2	4.9	68.7
75	B1/D05_03-2	3.0	6.2	9.2	14.7	5.5	67.9
76	B1/D05_03-3	2.4	6.6	9.1	15.3	6.3	67.2
77	B1/D07_03-0	0.4	2.6	2.9	11.2	8.3	65.5
78	B1/D10_03-1	0.2	2.8	3.1	12.0	9.0	58.8
79	B1/D10_03-2	0.2	3.6	3.8	12.0	8.2	60.1
80	B1/D10_03-3	0.3	2.6	2.9	10.4	7.5	58.2
81	B1/D15_03-1	< 0.2	3.1	3.2	9.1	5.9	58.6
82	B1/D15_03-2	0.2	5.9	6.1	11.7	5.6	53.2
83	B1/D15_03-3	0.4	5.4	5.8	11.0	5.3	51.5
84	B1/D20_03-1	< 0.2	5.3	5.4	11.1	5.7	55.5
85	B1/D20_03-2	0.3	5.7	5.9	10.5	4.6	55.4
86	B1/D20_03-3	< 0.2	4.4	4.5	10.1	5.5	51.7
87	B2/D00_03-0	0.4	1.7	2.1	8.0	5.9	88.2
88	B2/D02_03-1	0.2	1.9	2.1	10.4	8.2	73.1

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
89	B2/D02_03-2	0.3	3.9	4.2	12.4	8.2	71.8
90	B2/D02_03-3	< 0.2	3.9	4.0	11.4	7.4	69.0
91	B2/D04_03-0	0.2	4.2	4.4	11.4	7.0	62.0
92	B2/D05_03-1	0.2	4.4	4.6	11.4	6.8	66.1
93	B2/D05_03-2	0.4	6.3	6.7	12.0	5.3	64.4
94	B2/D05_03-3	0.5	4.6	5.0	10.9	5.8	62.6
95	B3/D00_03-0	< 0.2	3.8	3.9	8.8	4.9	78.9
96	B3/D02_03-1	< 0.2	3.3	3.4	7.9	4.5	69.1
97	B3/D02_03-2	0.2	3.5	3.8	8.7	4.9	59.0
98	B3/D02_03-3	< 0.2	4.9	5.0	9.8	4.7	60.8
99	B3/D04_03-0	0.2	4.4	4.6	9.2	4.6	76.9
100	B3/D05_03-1	< 0.2	4.5	4.6	8.4	3.8	74.8
101	B3/D05_03-2	< 0.2	4.6	4.7	8.8	4.2	70.5
102	B3/D05_03-3	0.2	3.5	3.7	7.9	4.2	76.6
103	B1/D00_04-0	0.3	0.8	1.1	6.9	5.8	84.4
104	B1/D02_04-1	4.6	0.8	5.4	14.3	9.0	75.2
105	B1/D02_04-2	1.8	< 0.4	2.0	13.3	11.3	74.9
106	B1/D02_04-3	0.7	< 0.4	0.9	7.9	7.0	74.4
107	B1/D04_04-0	0.5	0.7	1.2	6.6	5.5	73.9
108	B1/D05_04-1	2.2	0.8	3.0	8.4	5.4	76.1
109	B1/D05_04-2	1.2	0.7	1.9	8.0	6.1	75.1
110	B1/D05_04-3	0.9	0.7	1.6	6.5	4.9	71.7
111	B1/D07_04-0	0.8	1.1	1.9	5.9	4.0	69.9
112	B1/D10_04-1	< 0.2	1.3	1.4	7.3	5.9	70.1
113	B1/D10_04-2	< 0.2	1.8	1.9	9.3	7.4	70.2
114	B1/D10_04-3	< 0.2	1.5	1.6	7.0	5.4	66.2
115	B1/D15_04-1	< 0.2	1.4	1.5	7.8	6.3	71.7
116	B1/D15_04-2	< 0.2	1.6	1.7	7.7	5.9	71.1
117	B1/D15_04-3	0.3	1.6	2.0	7.6	5.6	67.5
118	B1/D20_04-1	< 0.2	2.0	2.1	7.4	5.3	56.6
119	B1/D20_04-2	< 0.2	1.9	2.0	7.2	5.1	67.6
120	B1/D20_04-3	< 0.2	2.4	2.5	7.7	5.3	68.7
121	B2/D00_04-0	0.6	< 0.4	0.8	7.0	6.2	88.0
122	B2/D02_04-1	0.1	< 0.4	0.3	8.2	7.9	74.1
123	B2/D02_04-2	0.3	< 0.4	0.5	9.4	8.9	73.2
124	B2/D02_04-3	< 0.2	< 0.4	0.3	4.9	4.6	75.2
125	B2/D04_04-0	< 0.2	< 0.4	0.3	5.6	5.3	75.2
126	B2/D05_04-1	< 0.2	< 0.4	0.3	8.1	7.8	63.8
127	B2/D05_04-2	< 0.2	0.4	0.5	5.0	4.5	64.7
128	B2/D05_04-3	0.5	< 0.4	0.7	8.5	7.8	66.0
129	B3/D00_04-0	< 0.2	< 0.4	0.3	5.4	5.1	80.6
130	B3/D02_04-1	0.4	< 0.4	0.6	5.8	5.2	77.7
131	B3/D02_04-2	< 0.2	< 0.4	0.3	6.3	6.0	77.8
132	B3/D02_04-3	< 0.2	< 0.4	0.3	5.4	5.1	75.2

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
133	B3/D04_04-0	< 0.2	0.5	0.6	5.4	4.8	58.3
134	B3/D05_04-1	< 0.2	0.8	0.9	5.0	4.1	68.8
135	B3/D05_04-2	< 0.2	< 0.4	0.3	5.4	5.1	68.1
136	B3/D05_04-3	< 0.2	0.9	1.0	5.8	4.8	72.6
137	B1/D00_05-0	< 0.2	0.4	0.5	6.5	6.0	73.1
138	B1/D02_05-1	< 0.2	< 0.4	0.3	5.4	5.1	73.0
139	B1/D02_05-2	< 0.2	< 0.4	0.3	5.9	5.6	69.8
140	B1/D02_05-3	0.2	< 0.4	0.4	7.3	6.9	73.5
141	B1/D04_05-0	< 0.2	< 0.4	0.3	5.5	5.2	67.0
142	B1/D05_05-1	< 0.2	< 0.4	0.3	5.6	5.3	56.0
143	B1/D05_05-2	< 0.2	< 0.4	0.3	4.5	4.2	53.6
144	B1/D05_05-3	< 0.2	< 0.4	0.3	4.8	4.5	53.8
145	B1/D07_05-0	< 0.2	< 0.4	0.3	4.6	4.3	65.0
146	B1/D10_05-1	< 0.2	< 0.4	0.3	3.8	3.5	61.7
147	B1/D10_05-2	< 0.2	< 0.4	0.3	5.5	5.2	62.2
148	B1/D10_05-3	< 0.2	< 0.4	0.3	4.7	4.4	63.8
149	B1/D15_05-1	< 0.2	< 0.4	0.3	5.2	4.9	74.9
150	B1/D15_05-2	< 0.2	< 0.4	0.3	3.9	3.6	74.7
151	B1/D15_05-3	< 0.2	< 0.4	0.3	6.6	6.3	79.6
152	B1/D20_05-1	0.4	< 0.4	0.6	5.7	5.1	74.7
153	B1/D20_05-2	< 0.2	< 0.4	0.3	5.1	4.8	71.4
154	B1/D20_05-3	< 0.2	< 0.4	0.3	4.9	4.6	67.5
155	B2/D00_05-0	0.2	< 0.4	0.4	6.9	6.5	92.2
156	B2/D02_05-1	0.3	< 0.4	0.5	3.7	3.3	61.7
157	B2/D02_05-2	0.4	< 0.4	0.6	5.6	5.0	61.2
158	B2/D02_05-3	0.2	< 0.4	0.4	4.9	4.5	61.5
159	B2/D04_05-0	< 0.2	< 0.4	0.3	4.4	4.1	43.1
160	B2/D05_05-1	< 0.2	< 0.4	0.3	3.7	3.4	74.3
161	B2/D05_05-2	0.2	< 0.4	0.4	3.7	3.3	74.0
162	B2/D05_05-3	0.2	0.6	0.9	3.9	3.0	77.3
163	B3/D00_05-0	0.3	0.6	0.9	7.0	6.1	86.7
164	B3/D02_05-1	< 0.2	< 0.4	0.3	4.1	3.8	79.3
165	B3/D02_05-2	0.2	0.6	0.8	5.2	4.4	80.2
166	B3/D02_05-3	< 0.2	< 0.4	0.3	4.2	3.9	75.4
167	B3/D04_05-0	0.2	1.1	1.3	5.0	3.7	65.3
168	B3/D05_05-1	0.2	< 0.4	0.4	5.0	4.6	71.4
169	B3/D05_05-2	0.2	< 0.4	0.4	5.9	5.5	72.2
170	B3/D05_05-3	0.2	< 0.4	0.4	6.1	5.8	73.4
171	B1/D00_06-0	< 0.2	3.5	3.6	na	na	na
172	B1/D02_06-1	0.5	7.0	7.5	na	na	na
173	B1/D02_06-2	1.3	9.2	10.5	na	na	na
174	B1/D02_06-3	< 0.2	6.5	6.6	na	na	na
175	B1/D04_06-0	< 0.2	11.7	11.8	na	na	na
176	B1/D05_06-1	0.4	13.1	13.5	na	na	na

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
177	B1/D05_06-2	< 0.2	9.4	9.5	na	na	na
178	B1/D05_06-3	< 0.2	12.8	12.9	na	na	na
179	B1/D07_06-0	< 0.2	13.5	13.6	na	na	na
180	B1/D10_06-1	< 0.2	26.7	26.8	na	na	na
181	B1/D10_06-2	< 0.2	29.0	29.1	na	na	na
182	B1/D10_06-3	< 0.2	24.5	24.6	na	na	na
183	B1/D15_06-1	< 0.2	33.4	33.5	na	na	na
184	B1/D15_06-2	< 0.2	34.2	34.3	na	na	na
185	B1/D15_06-3	< 0.2	32.4	32.5	na	na	na
186	B1/D20_06-1	< 0.2	49.5	49.6	na	na	na
187	B1/D20_06-2	< 0.2	44.7	44.8	na	na	na
188	B1/D20_06-3	< 0.2	44.0	44.1	na	na	na
189	B2/D00_06-0	< 0.2	3.8	3.9	na	na	na
190	B2/D02_06-1	< 0.2	7.6	7.7	na	na	na
191	B2/D02_06-2	0.2	8.0	8.2	na	na	na
192	B2/D02_06-3	< 0.2	7.4	7.5	na	na	na
193	B2/D04_06-0	0.3	11.7	12.0	na	na	na
194	B2/D05_06-1	< 0.2	14.0	14.1	na	na	na
195	B2/D05_06-2	< 0.2	12.0	12.1	na	na	na
196	B2/D05_06-3	< 0.2	11.6	11.7	na	na	na
197	B3/D00_06-0	< 0.2	3.5	3.6	na	na	na
198	B3/D02_06-1	< 0.2	5.6	5.7	na	na	na
199	B3/D02_06-2	< 0.2	5.0	5.1	na	na	na
200	B3/D02_06-3	< 0.2	4.9	5.0	na	na	na
201	B3/D04_06-0	< 0.2	11.1	11.2	na	na	na
202	B3/D05_06-1	0.5	10.3	10.8	na	na	na
203	B3/D05_06-2	< 0.2	11.3	11.4	na	na	na
204	B3/D05_06-3	< 0.2	10.3	10.4	na	na	na
205	B1/D00_07-0	< 0.2	0.4	0.5	5.9	5.4	74.3
206	B1/D02_07-1	< 0.2	< 0.4	0.3	5.5	5.2	66.5
207	B1/D02_07-2	< 0.2	< 0.4	0.3	4.2	3.9	67.3
208	B1/D02_07-3	< 0.2	< 0.4	0.3	3.3	3.0	67.3
209	B1/D04_07-0	< 0.2	< 0.4	0.3	6.7	6.4	61.9
210	B1/D05_07-1	< 0.2	< 0.4	0.3	8.6	8.3	60.2
211	B1/D05_07-2	< 0.2	< 0.4	0.3	5.2	4.9	62.2
212	B1/D05_07-3	0.2	< 0.4	0.4	6.9	6.5	65.4
213	B2/D00_07-0	0.2	< 0.4	0.4	7.0	6.6	86.4
214	B2/D02_07-1	< 0.2	< 0.4	0.3	6.4	6.1	78.5
215	B2/D02_07-2	< 0.2	< 0.4	0.3	6.1	5.8	79.9
216	B2/D02_07-3	0.7	< 0.4	0.9	6.4	5.5	78.2
217	B2/D04_07-0	< 0.2	< 0.4	0.3	5.2	4.9	71.0
218	B2/D05_07-1	0.4	< 0.4	0.6	5.2	4.7	62.5
219	B2/D05_07-2	0.2	0.4	0.6	5.4	4.8	62.8
220	B2/D05_07-3	0.2	0.4	0.6	5.7	5.1	68.4

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
221	B3/D00_07-0	< 0.2	< 0.4	0.3	7.2	6.9	82.0
222	B3/D02_07-1	< 0.2	< 0.4	0.3	4.8	4.5	80.7
223	B3/D02_07-2	< 0.2	0.7	0.8	5.0	4.3	81.3
224	B3/D02_07-3	< 0.2	< 0.4	0.3	4.7	4.4	82.0
225	B3/D04_07-0	< 0.2	< 0.4	0.3	6.1	5.8	70.9
226	B3/D05_07-1	< 0.2	1.1	1.2	5.9	4.7	65.0
227	B3/D05_07-2	< 0.2	0.7	0.8	6.7	6.0	66.2
228	B3/D05_07-3	< 0.2	< 0.4	0.3	4.0	3.7	68.8
229	B1/D00_08-0	< 0.2	5.3	5.4	na	na	na
230	B1/D02_08-1	< 0.2	3.6	3.7	na	na	na
231	B1/D02_08-2	< 0.2	4.0	4.1	na	na	na
232	B1/D02_08-3	< 0.2	4.8	4.9	na	na	na
233	B1/D04_08-0	< 0.2	5.2	5.3	na	na	na
234	B1/D05_08-1	0.9	4.6	5.5	na	na	na
235	B1/D05_08-2	0.2	4.3	4.5	na	na	na
236	B1/D05_08-3	0.2	5.2	5.4	na	na	na
237	B2/D00_08-0	0.9	7.7	8.7	na	na	na
238	B2/D02_08-1	0.7	4.8	5.5	na	na	na
239	B2/D02_08-2	0.3	6.0	6.3	na	na	na
240	B2/D02_08-3	< 0.2	3.9	4.0	na	na	na
241	B2/D04_08-0	< 0.2	5.2	5.3	na	na	na
242	B2/D05_08-1	< 0.2	6.6	6.7	na	na	na
243	B2/D05_08-2	< 0.2	4.8	4.9	na	na	na
244	B2/D05_08-3	0.3	5.3	5.6	na	na	na
245	B3/D00_08-0	< 0.2	4.3	4.4	na	na	na
246	B3/D02_08-1	< 0.2	4.2	4.3	na	na	na
247	B3/D02_08-2	< 0.2	5.1	5.2	na	na	na
248	B3/D02_08-3	< 0.2	5.0	5.1	na	na	na
249	B3/D04_08-0	< 0.2	5.4	5.5	na	na	na
250	B3/D05_08-1	< 0.2	4.4	4.5	na	na	na
251	B3/D05_08-2	0.5	6.2	6.7	na	na	na
252	B3/D05_08-3	< 0.2	4.5	4.6	na	na	na
253	B1/D00_09-0	0.2	6.5	6.6	10.8	4.1	84.4
254	B1/D02_09-1	1.1	4.0	5.1	8.6	3.5	74.7
255	B1/D02_09-2	0.9	5.7	6.6	10.6	4.0	70.8
256	B1/D02_09-3	0.7	5.7	6.4	11.0	4.6	69.1
257	B1/D04_09-0	0.4	6.2	6.6	9.6	2.9	71.3
258	B1/D05_09-1	5.2	5.4	10.6	17.1	6.5	62.5
259	B1/D05_09-2	3.0	4.7	7.8	12.0	4.2	63.4
260	B1/D05_09-3	2.4	2.6	5.1	12.4	7.3	62.3
261	B2/D00_09-0	1.2	1.5	2.7	8.8	6.1	87.6
262	B2/D02_09-1	0.5	1.3	1.7	7.5	5.8	71.7
263	B2/D02_09-2	< 0.2	4.7	4.8	9.0	4.2	71.0
264	B2/D02_09-3	0.2	3.1	3.3	7.5	4.2	71.7

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
265	B2/D04_09-0	< 0.2	4.8	4.9	8.6	3.7	71.1
266	B2/D05_09-1	0.2	3.8	4.0	9.2	5.2	70.8
267	B2/D05_09-2	0.3	4.3	4.6	8.8	4.2	70.7
268	B2/D05_09-3	0.4	5.3	5.7	10.4	4.7	71.0
269	B3/D00_09-0	< 0.2	3.1	3.2	9.5	6.3	84.1
270	B3/D02_09-1	< 0.2	2.8	2.9	8.6	5.7	68.9
271	B3/D02_09-2	< 0.2	3.2	3.3	9.6	6.4	69.4
272	B3/D02_09-3	0.2	3.3	3.4	9.6	6.1	68.6
273	B3/D04_09-0	< 0.2	3.7	3.8	9.6	5.8	85.4
274	B3/D05_09-1	0.2	3.2	3.4	8.1	4.7	77.7
275	B3/D05_09-2	0.3	4.7	5.0	9.9	4.8	77.5
276	B3/D05_09-3	0.2	3.3	3.5	9.0	5.5	70.8
277	B1/D00_10-0	< 0.2	0.4	0.5	5.8	5.3	80.9
278	B1/D02_10-1	1.1	< 0.4	1.3	10.5	9.2	74.3
279	B1/D02_10-2	0.7	< 0.4	0.9	10.0	9.1	77.2
280	B1/D02_10-3	0.6	< 0.4	0.8	6.1	5.3	74.4
281	B1/D04_10-0	< 0.2	0.4	0.5	6.6	6.1	71.4
282	B1/D05_10-1	1.0	< 0.4	1.2	7.4	6.3	74.8
283	B1/D05_10-2	0.7	< 0.4	0.9	8.3	7.5	70.1
284	B1/D05_10-3	0.6	< 0.4	0.8	6.1	5.3	72.9
285	B2/D00_10-0	0.4	< 0.4	0.6	7.7	7.1	88.2
286	B2/D02_10-1	< 0.2	< 0.4	0.3	5.7	5.4	70.3
287	B2/D02_10-2	< 0.2	< 0.4	0.3	5.3	5.0	74.2
288	B2/D02_10-3	< 0.2	< 0.4	0.3	5.8	5.5	73.9
289	B2/D04_10-0	< 0.2	0.5	0.6	5.3	4.7	76.4
290	B2/D05_10-1	< 0.2	0.4	0.5	4.9	4.5	72.7
291	B2/D05_10-2	< 0.2	1.7	1.8	6.5	4.7	76.4
292	B2/D05_10-3	< 0.2	0.4	0.5	4.8	4.4	73.9
293	B3/D00_10-0	< 0.2	< 0.4	0.3	7.7	7.4	79.8
294	B3/D02_10-1	0.3	0.6	0.9	5.9	5.0	75.4
295	B3/D02_10-2	< 0.2	0.9	1.0	6.3	5.3	75.1
296	B3/D02_10-3	< 0.2	< 0.4	0.3	6.3	6.0	76.7
297	B3/D04_10-0	< 0.2	< 0.4	0.3	6.7	6.4	74.6
298	B3/D05_10-1	< 0.2	0.6	0.7	6.0	5.3	73.4
299	B3/D05_10-2	< 0.2	0.7	0.8	6.5	5.7	73.3
300	B3/D05_10-3	< 0.2	0.5	0.6	4.9	4.3	71.1
301	B1/D00_11-0	< 0.2	< 0.4	0.3	5.0	4.7	81.5
302	B1/D02_11-1	2.8	< 0.4	3.0	9.7	6.7	73.1
303	B1/D02_11-2	0.6	< 0.4	0.8	7.2	6.4	72.6
304	B1/D02_11-3	1.1	< 0.4	1.3	8.3	6.9	74.6
305	B1/D04_11-0	< 0.2	< 0.4	0.3	6.5	6.2	75.2
306	B1/D05_11-1	< 0.2	< 0.4	0.3	5.9	5.6	74.0
307	B1/D05_11-2	< 0.2	< 0.4	0.3	6.6	6.3	72.8
308	B1/D05_11-3	0.4	< 0.4	0.6	6.8	6.3	74.1

1) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
309	B2/D00_11-0	< 0.2	< 0.4	0.3	6.1	5.8	89.9
310	B2/D02_11-1	< 0.2	< 0.4	0.3	6.1	5.8	68.3
311	B2/D02_11-2	0.2	< 0.4	0.4	4.3	4.0	65.1
312	B2/D02_11-3	0.6	< 0.4	0.8	6.4	5.5	68.1
313	B2/D04_11-0	< 0.2	< 0.4	0.3	4.8	4.5	50.7
314	B2/D05_11-1	0.2	< 0.4	0.4	5.8	5.4	71.9
315	B2/D05_11-2	0.2	< 0.4	0.4	5.3	4.9	68.2
316	B2/D05_11-3	0.2	< 0.4	0.4	5.4	5.0	67.6
317	B3/D00_11-0	0.3	0.7	1.0	7.2	6.2	84.9
318	B3/D02_11-1	< 0.2	< 0.4	0.3	6.7	6.4	80.3
319	B3/D02_11-2	0.2	0.9	1.1	6.4	5.4	84.9
320	B3/D02_11-3	0.2	< 0.4	0.4	7.3	6.9	80.2
321	B3/D04_11-0	< 0.2	< 0.4	0.3	6.3	6.0	66.6
322	B3/D05_11-1	0.2	0.7	0.9	5.9	5.0	70.3
323	B3/D05_11-2	0.2	< 0.4	0.4	5.4	5.0	73.5
324	B3/D05_11-3	< 0.2	< 0.4	0.3	5.3	5.0	67.4
325	B1/D00_12-0	< 0.2	6.1	6.2	na	na	na
326	B1/D02_12-1	0.2	8.4	8.6	na	na	na
327	B1/D02_12-2	< 0.2	9.2	9.3	na	na	na
328	B1/D02_12-3	< 0.2	10.5	10.6	na	na	na
329	B1/D04_12-0	< 0.2	16.8	16.9	na	na	na
330	B1/D05_12-1	0.3	22.3	22.6	na	na	na
331	B1/D05_12-2	< 0.2	15.2	15.3	na	na	na
332	B1/D05_12-3	0.2	21.6	21.8	na	na	na
333	B2/D00_12-0	0.7	5.2	5.8	na	na	na
334	B2/D02_12-1	< 0.2	8.8	8.9	na	na	na
335	B2/D02_12-2	0.6	9.5	10.1	na	na	na
336	B2/D02_12-3	< 0.2	7.5	7.6	na	na	na
337	B2/D04_12-0	< 0.2	11.7	11.8	na	na	na
338	B2/D05_12-1	< 0.2	12.4	12.5	na	na	na
339	B2/D05_12-2	< 0.2	14.8	14.9	na	na	na
340	B2/D05_12-3	0.2	13.1	13.3	na	na	na
341	B3/D00_12-0	0.2	4.2	4.4	na	na	na
342	B3/D02_12-1	< 0.2	5.2	5.3	na	na	na
343	B3/D02_12-2	< 0.2	5.5	5.6	na	na	na
344	B3/D02_12-3	< 0.2	4.9	5.0	na	na	na
345	B3/D04_12-0	< 0.2	8.6	8.7	na	na	na
346	B3/D05_12-1	< 0.2	10.7	10.8	na	na	na
347	B3/D05_12-2	< 0.2	10.7	10.8	na	na	na
348	B3/D05_12-3	< 0.2	9.5	9.6	na	na	na

na = Data is not available for antibiotics treated samples (treatment 2 (T2) and treatment 6 (T6))

< 0.2 and < 0.4 = less than the detection limit of UEA instrument

2) Laboratory based incubation experiment in autumn 2013, winter 2013 and spring 2014.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1	WG1/D00_01-0	8.8	< 0.4	9.0	25.1	16.0	148.1
2	WG1/D02_01-1	6.4	< 0.4	6.6	17.5	10.9	87.3
3	WG1/D02_01-2	9.6	0.6	10.2	24.0	13.8	86.5
4	WG1/D02_01-3	7.5	< 0.4	7.7	20.1	12.4	86.2
5	WG1/D04_01-0	7.5	< 0.4	7.8	20.1	12.4	61.8
6	WG1/D05_01-1	7.2	< 0.4	7.4	18.2	10.8	80.7
7	WG1/D05_01-2	8.2	< 0.4	8.4	19.5	11.0	83.0
8	WG1/D05_01-3	9.4	0.7	10.1	19.5	9.4	*94.4*
9	WG1/D07_01-0	8.6	< 0.4	8.9	22.4	13.5	115.8
10	WG1/D10_01-1	9.4	0.5	9.9	23.9	14.1	81.0
11	WG1/D10_01-2	9.4	< 0.4	9.7	23.9	14.3	*103.3*
12	WG1/D10_01-3	9.3	< 0.4	9.5	23.5	14.0	82.3
13	WG1/D15_01-1	5.5	< 0.4	5.8	11.7	6.0	*82.5*
14	WG1/D15_01-2	6.6	< 0.4	6.8	14.5	7.6	75.1
15	WG1/D15_01-3	6.2	< 0.4	6.5	13.6	7.2	72.2
16	WG1/D20_01-1	8.6	< 0.4	8.8	13.8	5.1	58.5
17	WG1/D20_01-2	9.1	< 0.4	9.3	14.2	4.9	57.2
18	WG1/D20_01-3	10.7	1.0	11.8	17.1	5.3	*70.1*
19	WG1/D00_02-0	7.6	0.9	8.5	18.6	10.1	116.1
20	WG1/D02_02-1	9.1	0.9	10.0	22.3	12.4	101.2
21	WG1/D02_02-2	8.9	0.5	9.4	24.9	15.5	101.5
22	WG1/D02_02-3	8.6	0.9	9.5	27.9	18.4	*113.3*
23	WG1/D04_02-0	6.6	< 0.4	6.8	16.0	9.2	75.0
24	WG1/D05_02-1	6.5	< 0.4	6.8	14.4	7.7	72.8
25	WG1/D05_02-2	7.5	< 0.4	7.7	20.7	13.0	78.5
26	WG1/D05_02-3	8.3	< 0.4	8.5	19.8	11.3	*92.5*
27	WG1/D07_02-0	8.2	< 0.4	8.5	22.7	14.2	82.0
28	WG1/D10_02-1	8.3	< 0.4	8.5	22.6	14.1	105.8
29	WG1/D10_02-2	9.4	< 0.4	9.6	22.2	12.5	109.0
30	WG1/D10_02-3	9.4	0.7	10.1	22.2	12.0	*91.9*
31	WG1/D15_02-1	6.2	< 0.4	6.5	15.8	9.3	102.3
32	WG1/D15_02-2	8.0	< 0.4	8.2	18.4	10.2	102.8
33	WG1/D15_02-3	9.4	< 0.4	9.6	20.0	10.4	105.9
34	WG1/D20_02-1	5.9	< 0.4	6.1	14.5	8.3	80.2
35	WG1/D20_02-2	9.0	< 0.4	9.2	19.8	10.6	81.4
36	WG1/D20_02-3	7.9	< 0.4	8.1	17.0	8.9	82.3
37	WG1/D00_03-0	8.1	4.3	12.4	28.1	15.7	138.5
38	WG1/D02_03-1	8.6	4.3	12.9	26.5	13.6	94.6
39	WG1/D02_03-2	9.5	5.4	14.8	27.6	12.8	97.8
40	WG1/D02_03-3	9.5	5.2	14.7	27.7	13.0	100.7
41	WG1/D04_03-0	8.5	3.7	12.2	21.6	9.4	95.4
42	WG1/D05_03-1	8.0	3.4	11.3	22.0	10.7	81.3
43	WG1/D05_03-2	7.3	3.1	10.4	19.0	*8.5*	80.0
44	WG1/D05_03-3	10.3	5.1	15.4	26.3	10.8	82.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
45	WG1/D07_03-0	10.5	5.3	15.9	26.7	10.8	101.2
46	WG1/D10_03-1	12.1	2.8	14.9	29.0	14.0	69.5
47	WG1/D10_03-2	12.2	2.7	14.9	24.6	*9.7*	71.8
48	WG1/D10_03-3	11.8	2.9	14.7	29.2	14.4	*83.3*
49	WG1/D15_03-1	10.6	0.5	11.1	19.8	8.6	*79.6*
50	WG1/D15_03-2	14.3	< 0.4	14.5	25.2	10.7	103.9
51	WG1/D15_03-3	14.3	< 0.4	14.5	25.8	11.3	108.6
52	WG1/D20_03-1	14.3	0.4	14.6	23.9	9.3	96.3
53	WG1/D20_03-2	14.6	0.7	15.3	25.6	10.3	93.1
54	WG1/D20_03-3	13.9	< 0.4	14.1	24.8	10.8	90.1
55	WG1/D00_04-0	5.9	< 0.4	6.0	17.5	11.5	98.9
56	WG1/D02_04-1	9.6	0.6	10.1	24.2	14.1	92.5
57	WG1/D02_04-2	8.3	< 0.4	8.5	21.5	13.0	91.8
58	WG1/D02_04-3	6.0	< 0.4	6.2	18.0	11.8	92.1
59	WG1/D04_04-0	7.1	< 0.4	7.4	17.0	9.7	85.1
60	WG1/D05_04-1	6.8	< 0.4	7.1	17.7	10.6	80.0
61	WG1/D05_04-2	6.7	< 0.4	6.9	15.9	9.0	79.3
62	WG1/D05_04-3	9.5	0.7	10.2	23.2	13.0	78.6
63	WG1/D07_04-0	7.2	< 0.4	7.5	19.2	11.7	71.1
64	WG1/D10_04-1	9.3	< 0.4	9.5	23.5	14.0	71.4
65	WG1/D10_04-2	9.3	< 0.4	9.6	25.5	15.9	71.3
66	WG1/D10_04-3	9.3	< 0.4	9.5	24.0	14.5	71.5
67	WG1/D15_04-1	8.4	0.5	8.9	18.9	10.0	103.9
68	WG1/D15_04-2	9.7	< 0.4	10.0	19.1	9.1	*94.3*
69	WG1/D15_04-3	9.5	1.0	10.5	20.6	10.1	107.8
70	WG1/D20_04-1	7.8	< 0.4	8.0	19.6	11.6	95.2
71	WG1/D20_04-2	8.2	< 0.4	8.4	20.1	11.7	93.4
72	WG1/D20_04-3	9.5	< 0.4	9.6	20.3	10.7	92.4
73	WG1/D00_05-0	9.4	1.6	11.0	22.6	11.6	130.7
74	WG1/D02_05-1	7.7	< 0.4	7.8	21.7	13.9	96.2
75	WG1/D02_05-2	9.6	0.6	10.2	24.8	14.7	96.3
76	WG1/D02_05-3	9.1	0.4	9.5	23.4	13.9	96.1
77	WG1/D04_05-0	7.7	< 0.4	7.9	18.4	10.5	95.8
78	WG1/D05_05-1	7.2	< 0.4	7.4	18.2	10.8	73.2
79	WG1/D05_05-2	9.6	0.8	10.4	19.8	9.3	73.4
80	WG1/D05_05-3	6.9	< 0.4	7.2	14.9	7.7	73.0
81	WG1/D07_05-0	10.2	4.1	14.3	22.9	8.6	121.4
82	WG1/D10_05-1	9.4	0.8	10.2	25.1	14.9	70.1
83	WG1/D10_05-2	8.3	< 0.4	8.6	23.3	14.7	70.6
84	WG1/D10_05-3	9.4	< 0.4	9.6	25.7	16.0	70.6
85	WG1/D15_05-1	6.3	< 0.4	6.5	14.5	7.9	*75.8*
86	WG1/D15_05-2	9.1	< 0.4	9.3	21.4	12.1	104.9
87	WG1/D15_05-3	9.2	< 0.4	9.5	21.1	11.6	108.4
88	WG1/D20_05-1	2.6	< 0.4	2.8	10.4	7.6	65.8

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
89	WG1/D20_05-2	2.2	< 0.4	2.4	9.5	7.2	60.0
90	WG1/D20_05-3	2.8	< 0.4	3.0	10.7	7.8	67.6
91	WG1/D00_06-0	9.4	1.1	10.5	23.4	12.9	129.5
92	WG1/D02_06-1	9.4	1.6	11.1	23.3	12.2	104.7
93	WG1/D02_06-2	8.4	0.9	9.3	20.3	11.0	104.1
94	WG1/D02_06-3	9.4	1.1	10.5	23.7	13.2	104.0
95	WG1/D04_06-0	6.5	< 0.4	6.7	18.1	11.4	85.9
96	WG1/D05_06-1	8.1	1.3	9.4	20.1	10.8	91.2
97	WG1/D05_06-2	6.2	0.8	7.0	16.4	9.4	*63.5*
98	WG1/D05_06-3	9.1	0.9	10.1	22.4	12.4	94.2
99	WG1/D07_06-0	8.6	0.3	8.9	21.6	12.7	125.1
100	WG1/D10_06-1	9.3	1.0	10.4	23.9	13.6	56.6
101	WG1/D10_06-2	8.3	0.5	8.8	21.3	12.5	60.9
102	WG1/D10_06-3	9.4	1.7	11.1	26.1	15.1	*87.6*
103	WG1/D15_06-1	7.8	0.6	8.4	18.6	10.2	92.4
104	WG1/D15_06-2	9.4	0.6	10.0	19.7	9.7	95.4
105	WG1/D15_06-3	7.4	1.5	8.8	16.5	7.7	*84.0*
106	WG1/D20_06-1	8.7	0.8	9.5	19.4	9.9	92.3
107	WG1/D20_06-2	8.0	0.8	8.8	18.3	9.5	101.1
108	WG1/D20_06-3	8.7	0.9	9.6	19.9	10.3	107.4
109	WG1/D00_07-0	7.8	< 0.4	8.0	15.2	7.2	100.8
110	WG1/D02_07-1	8.8	< 0.4	9.0	18.9	9.9	73.6
111	WG1/D02_07-2	9.0	0.6	9.5	19.1	9.5	74.1
112	WG1/D02_07-3	9.4	0.6	10.0	19.9	9.9	76.2
113	WG1/D04_07-0	8.2	< 0.4	8.5	15.4	6.9	80.5
114	WG1/D05_07-1	5.2	< 0.4	5.5	10.4	*5.0*	60.1
115	WG1/D05_07-2	7.7	< 0.4	7.9	15.0	7.1	60.6
116	WG1/D05_07-3	8.0	< 0.4	8.2	15.6	7.4	65.7
117	WG1/D07_07-0	5.9	< 0.4	6.2	13.9	7.7	66.3
118	WG1/D10_07-1	2.7	1.0	3.7	10.9	7.2	71.8
119	WG1/D10_07-2	2.7	0.7	3.4	10.0	6.6	72.3
120	WG1/D10_07-3	2.5	< 0.4	2.8	10.9	8.2	72.5
121	WG1/D15_07-1	0.1	0.7	0.9	7.7	6.8	78.1
122	WG1/D15_07-2	0.0	0.5	0.6	7.4	6.8	77.0
123	WG1/D15_07-3	0.0	< 0.4	0.2	6.5	6.3	77.8
124	WG1/D20_07-1	0.0	< 0.4	0.2	4.5	*4.3*	*58.5*
125	WG1/D20_07-2	0.1	< 0.4	0.3	7.9	7.6	89.7
126	WG1/D20_07-3	0.1	< 0.4	0.3	8.0	7.6	89.4
127	WG1/D00_08-0	8.9	< 0.4	9.0	22.6	13.5	123.8
128	WG1/D02_08-1	9.5	1.0	10.6	23.7	13.2	*102.8*
129	WG1/D02_08-2	8.3	< 0.4	8.5	23.3	14.8	93.1
130	WG1/D02_08-3	7.9	< 0.4	8.1	21.2	13.1	91.3
131	WG1/D04_08-0	7.7	< 0.4	8.0	20.6	12.7	83.7
132	WG1/D05_08-1	6.0	< 0.4	6.2	15.3	9.0	61.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
133	WG1/D05_08-2	9.3	0.8	10.1	20.6	10.5	*85.5*
134	WG1/D05_08-3	6.3	< 0.4	6.5	14.6	8.1	61.2
135	WG1/D07_08-0	9.0	< 0.4	9.2	23.5	14.3	86.0
136	WG1/D10_08-1	9.4	1.3	10.7	25.6	14.9	49.1
137	WG1/D10_08-2	4.8	< 0.4	5.1	13.8	*8.8*	*54.2*
138	WG1/D10_08-3	9.4	< 0.4	9.6	25.0	15.4	49.1
139	WG1/D15_08-1	7.4	< 0.4	7.6	16.9	9.3	87.0
140	WG1/D15_08-2	8.4	< 0.4	8.7	21.3	12.6	*102.9*
141	WG1/D15_08-3	6.8	< 0.4	7.0	17.9	10.9	89.9
142	WG1/D20_08-1	8.3	< 0.4	8.4	19.0	10.6	102.5
143	WG1/D20_08-2	5.3	< 0.4	5.5	16.8	*14.2*	102.4
144	WG1/D20_08-3	9.3	0.6	9.9	21.2	11.3	103.3
145	WG1/D00_09-0	9.1	1.1	10.2	23.3	13.1	127.2
146	WG1/D02_09-1	8.8	1.0	9.8	27.1	17.3	105.3
147	WG1/D02_09-2	7.3	< 0.4	7.5	24.3	16.8	105.8
148	WG1/D02_09-3	7.1	0.4	7.6	23.0	15.4	105.2
149	WG1/D04_09-0	9.0	0.6	9.6	20.1	10.5	105.2
150	WG1/D05_09-1	9.1	0.9	10.0	27.2	*17.2*	115.3
151	WG1/D05_09-2	7.8	< 0.4	8.1	22.6	14.5	*97.2*
152	WG1/D05_09-3	9.3	1.1	10.4	24.9	14.5	118.1
153	WG1/D07_09-0	8.9	0.5	9.5	23.2	13.7	96.3
154	WG1/D10_09-1	7.5	< 0.4	7.8	24.2	16.4	114.9
155	WG1/D10_09-2	9.4	0.7	10.1	29.2	19.0	113.3
156	WG1/D10_09-3	6.9	< 0.4	7.1	24.8	17.6	117.9
157	WG1/D15_09-1	9.1	< 0.4	9.3	26.8	17.5	129.3
158	WG1/D15_09-2	9.5	0.4	9.9	26.5	16.7	128.4
159	WG1/D15_09-3	8.0	< 0.4	8.3	23.6	15.4	*103.8*
160	WG1/D20_09-1	5.7	< 0.4	5.9	20.8	14.9	114.0
161	WG1/D20_09-2	5.7	< 0.4	5.9	17.4	11.4	113.3
162	WG1/D20_09-3	9.1	< 0.4	9.3	28.3	19.0	114.7
163	WG1/D00_10-0	7.8	4.2	12.1	24.2	12.1	114.7
164	WG1/D02_10-1	7.7	4.0	11.6	24.2	12.6	90.0
165	WG1/D02_10-2	9.2	4.8	14.1	28.7	14.6	90.0
166	WG1/D02_10-3	7.2	3.5	10.7	22.0	11.3	89.5
167	WG1/D04_10-0	9.1	4.3	13.4	22.8	9.4	95.9
168	WG1/D05_10-1	10.0	5.2	15.1	26.0	10.8	88.1
169	WG1/D05_10-2	6.6	3.1	9.6	18.8	9.1	*58.9*
170	WG1/D05_10-3	9.8	4.7	14.6	25.6	11.0	91.8
171	WG1/D07_10-0	10.2	4.1	14.3	26.7	12.3	92.5
172	WG1/D10_10-1	12.1	2.5	14.6	31.3	16.7	74.3
173	WG1/D10_10-2	12.1	2.8	14.9	29.9	15.0	75.7
174	WG1/D10_10-3	9.1	1.3	10.5	24.8	14.3	75.6
175	WG1/D15_10-1	9.8	< 0.4	10.1	20.1	10.0	79.4
176	WG1/D15_10-2	9.9	< 0.4	10.1	19.9	9.8	75.7

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
177	WG1/D15_10-3	10.7	< 0.4	10.9	20.8	9.8	77.7
178	WG1/D20_10-1	15.8	0.5	16.3	24.2	7.9	*105.4*
179	WG1/D20_10-2	15.2	< 0.4	15.4	22.2	6.9	81.3
180	WG1/D20_10-3	15.4	< 0.4	15.5	22.7	7.2	87.6
181	WG1/D00_11-0	7.7	< 0.4	7.9	20.7	12.8	107.0
182	WG1/D02_11-1	7.6	< 0.4	7.8	21.2	13.4	91.0
183	WG1/D02_11-2	8.1	< 0.4	8.3	21.9	13.6	92.9
184	WG1/D02_11-3	7.8	< 0.4	8.0	21.7	13.8	89.5
185	WG1/D04_11-0	6.3	< 0.4	6.6	15.9	9.3	79.5
186	WG1/D05_11-1	7.0	< 0.4	7.2	16.8	9.6	*68.3*
187	WG1/D05_11-2	9.3	0.5	9.8	22.2	12.4	90.3
188	WG1/D05_11-3	9.3	1.2	10.5	22.2	11.7	86.4
189	WG1/D07_11-0	8.6	< 0.4	8.9	20.8	11.9	84.0
190	WG1/D10_11-1	8.8	< 0.4	9.1	23.7	14.6	86.2
191	WG1/D10_11-2	8.0	< 0.4	8.3	22.6	14.3	87.4
192	WG1/D10_11-3	9.5	0.6	10.1	25.5	15.5	86.9
193	WG1/D15_11-1	10.0	1.2	11.2	18.6	7.4	*88.2*
194	WG1/D15_11-2	7.0	< 0.4	7.3	13.3	6.0	56.7
195	WG1/D15_11-3	5.7	< 0.4	5.9	13.2	7.3	53.4
196	WG1/D20_11-1	6.2	< 0.4	6.4	11.7	5.3	59.2
197	WG1/D20_11-2	6.7	< 0.4	6.9	12.7	5.8	54.6
198	WG1/D20_11-3	8.7	< 0.4	8.9	15.2	6.2	*72.0*
199	WG1/D00_12-0	9.1	< 0.4	9.3	25.3	15.9	129.3
200	WG1/D02_12-1	8.3	< 0.4	8.5	21.6	13.1	100.1
201	WG1/D02_12-2	8.8	< 0.4	9.0	24.4	*15.4*	115.4
202	WG1/D02_12-3	7.6	< 0.4	7.7	20.8	13.1	94.5
203	WG1/D04_12-0	5.6	< 0.4	5.8	14.7	8.9	72.8
204	WG1/D05_12-1	8.2	< 0.4	8.4	19.5	11.1	92.4
205	WG1/D05_12-2	6.6	< 0.4	6.9	16.2	9.4	63.3
206	WG1/D05_12-3	8.6	< 0.4	8.8	20.7	11.9	82.6
207	WG1/D07_12-0	7.6	< 0.4	7.9	19.1	11.2	76.0
208	WG1/D10_12-1	9.4	0.6	10.0	24.9	14.8	47.3
209	WG1/D10_12-2	9.3	0.6	9.8	24.6	14.8	80.7
210	WG1/D10_12-3	8.2	< 0.4	8.4	23.9	15.5	56.9
211	WG1/D15_12-1	9.2	0.6	9.9	23.7	13.9	105.6
212	WG1/D15_12-2	9.2	0.2	9.4	22.3	12.9	101.1
213	WG1/D15_12-3	7.7	< 0.4	8.0	18.8	10.8	87.6
214	WG1/D20_12-1	3.8	< 0.4	4.0	13.1	9.1	*100.6*
215	WG1/D20_12-2	3.9	< 0.4	4.1	13.8	9.7	85.7
216	WG1/D20_12-3	4.4	0.7	5.2	13.3	8.2	89.3
217	WG1/D00_13-0	8.3	< 0.4	8.5	21.6	13.1	107.1
218	WG1/D02_13-1	8.7	0.7	9.4	25.3	15.9	*111.3*
219	WG1/D02_13-2	6.3	< 0.4	6.5	22.7	16.2	97.7
220	WG1/D02_13-3	8.0	< 0.4	8.2	24.2	16.1	97.5

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
221	WG1/D04_13-0	7.3	< 0.4	7.6	18.0	10.4	79.1
222	WG1/D05_13-1	6.9	< 0.4	7.1	18.1	11.0	85.1
223	WG1/D05_13-2	6.1	< 0.4	6.3	16.1	9.8	*57.8*
224	WG1/D05_13-3	8.6	< 0.4	8.8	19.6	10.8	90.9
225	WG1/D07_13-0	8.3	< 0.4	8.6	21.6	13.1	85.1
226	WG1/D10_13-1	8.7	< 0.4	8.9	22.5	13.5	79.2
227	WG1/D10_13-2	6.0	0.5	6.5	17.0	10.5	75.3
228	WG1/D10_13-3	9.3	1.1	10.4	25.1	14.7	81.3
229	WG1/D15_13-1	7.9	0.8	8.7	18.9	10.2	85.2
230	WG1/D15_13-2	8.1	< 0.4	8.4	18.3	9.9	78.9
231	WG1/D15_13-3	8.8	0.8	9.6	20.3	10.7	90.0
232	WG1/D20_13-1	8.9	0.9	9.8	20.5	10.7	97.6
233	WG1/D20_13-2	8.0	0.4	8.4	19.0	10.6	*105.8*
234	WG1/D20_13-3	9.2	1.3	10.5	20.7	10.2	97.5
235	WG1/D00_14-0	8.8	< 0.4	8.9	17.1	8.2	96.7
236	WG1/D02_14-1	9.3	0.4	9.7	20.7	11.0	81.7
237	WG1/D02_14-2	9.3	0.8	10.1	18.8	8.7	82.4
238	WG1/D02_14-3	9.3	0.9	10.2	20.6	10.4	84.2
239	WG1/D04_14-0	5.6	< 0.4	5.9	10.8	4.9	51.8
240	WG1/D05_14-1	5.7	< 0.4	5.9	12.0	6.0	50.5
241	WG1/D05_14-2	5.8	< 0.4	6.0	11.8	5.8	46.0
242	WG1/D05_14-3	5.6	0.6	6.3	12.2	5.9	45.7
243	WG1/D07_14-0	6.3	0.7	7.1	14.5	7.4	66.2
244	WG1/D10_14-1	2.7	< 0.4	2.9	11.1	8.2	*51.8*
245	WG1/D10_14-2	2.6	< 0.4	2.8	11.0	8.2	71.4
246	WG1/D10_14-3	3.1	1.1	4.3	11.6	7.3	73.9
247	WG1/D15_14-1	< 0.2	1.1	1.1	7.7	6.6	67.4
248	WG1/D15_14-2	< 0.2	< 0.4	0.3	7.9	7.6	68.1
249	WG1/D15_14-3	< 0.2	< 0.4	0.3	7.5	7.2	62.5
250	WG1/D20_14-1	< 0.2	< 0.4	0.3	5.5	5.2	70.7
251	WG1/D20_14-2	< 0.2	< 0.4	0.3	6.9	6.6	*89.7*
252	WG1/D20_14-3	< 0.2	< 0.4	0.3	6.1	5.8	70.0
253	DS1/D00_01-0	1.5	< 0.4	1.8	11.4	9.6	85.8
254	DS1/D02_01-1	1.0	< 0.4	1.2	10.4	9.1	82.2
255	DS1/D02_01-2	1.0	< 0.4	1.2	10.5	9.3	80.4
256	DS1/D02_01-3	1.4	0.6	2.0	12.3	10.3	81.6
257	DS1/D04_01-0	1.4	0.6	2.0	10.0	8.0	76.1
258	DS1/D05_01-1	1.0	0.7	1.7	8.1	6.4	61.6
259	DS1/D05_01-2	1.1	< 0.4	1.4	8.4	7.1	65.5
260	DS1/D05_01-3	1.4	0.5	1.9	9.2	7.3	81.0
261	DS1/D07_01-0	1.3	0.5	1.8	9.4	7.6	74.8
262	DS1/D10_01-1	0.9	< 0.4	1.2	7.9	6.7	74.5
263	DS1/D10_01-2	1.3	0.5	1.8	8.0	6.2	74.5
264	DS1/D10_01-3	1.0	< 0.4	1.2	7.6	6.4	74.9

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
265	DS1/D15_01-1	1.3	0.9	2.2	9.5	7.3	73.1
266	DS1/D15_01-2	1.3	0.6	1.9	9.7	7.8	65.6
267	DS1/D15_01-3	1.3	1.0	2.3	10.1	7.9	71.2
268	DS1/D20_01-1	1.3	0.5	1.8	7.7	6.0	68.5
269	DS1/D20_01-2	1.0	0.4	1.4	6.9	5.5	49.3
270	DS1/D20_01-3	1.3	0.6	1.9	8.7	6.8	71.5
271	DS1/D00_02-0	1.2	< 0.4	1.5	9.4	7.9	76.3
272	DS1/D02_02-1	1.0	< 0.4	1.3	10.3	9.1	71.1
273	DS1/D02_02-2	1.0	< 0.4	1.3	9.6	8.3	75.2
274	DS1/D02_02-3	1.3	< 0.4	1.6	11.0	9.5	76.9
275	DS1/D04_02-0	1.0	< 0.4	1.3	7.4	6.1	53.7
276	DS1/D05_02-1	1.0	< 0.4	1.3	8.1	6.8	61.4
277	DS1/D05_02-2	1.1	< 0.4	1.4	7.8	6.4	73.0
278	DS1/D05_02-3	1.0	< 0.4	1.3	8.0	6.7	70.9
279	DS1/D07_02-0	1.1	< 0.4	1.4	7.9	6.5	76.6
280	DS1/D10_02-1	1.3	< 0.4	1.6	9.2	7.6	92.0
281	DS1/D10_02-2	1.3	< 0.4	1.5	7.7	6.2	86.7
282	DS1/D10_02-3	1.3	< 0.4	1.6	8.9	7.3	95.0
283	DS1/D15_02-1	1.3	< 0.4	1.5	7.5	6.0	72.3
284	DS1/D15_02-2	0.9	< 0.4	1.1	7.2	6.1	52.2
285	DS1/D15_02-3	1.3	0.6	1.9	9.2	7.3	69.5
286	DS1/D20_02-1	1.1	< 0.4	1.3	6.4	5.1	64.4
287	DS1/D20_02-2	0.8	< 0.4	1.0	5.2	4.2	62.1
288	DS1/D20_02-3	1.0	< 0.4	1.2	7.4	6.2	64.4
289	DS1/D00_03-0	1.6	4.3	5.9	15.0	9.2	86.1
290	DS1/D02_03-1	1.0	3.5	4.6	12.7	8.1	63.5
291	DS1/D02_03-2	1.1	3.8	4.9	12.5	7.6	60.1
292	DS1/D02_03-3	1.1	3.7	4.8	12.9	8.1	70.5
293	DS1/D04_03-0	1.2	4.3	5.5	12.6	7.1	68.4
294	DS1/D05_03-1	1.0	3.3	4.3	10.3	6.0	58.5
295	DS1/D05_03-2	1.2	4.1	5.3	11.5	6.2	63.8
296	DS1/D05_03-3	1.3	4.7	6.0	13.1	7.1	62.6
297	DS1/D07_03-0	1.2	< 0.4	6.2	10.2	4.0	63.3
298	DS1/D10_03-1	1.3	4.9	6.2	12.9	6.7	89.5
299	DS1/D10_03-2	0.9	3.2	4.1	10.6	6.5	72.7
300	DS1/D10_03-3	1.3	4.9	6.2	12.1	5.8	78.5
301	DS1/D15_03-1	0.9	3.5	4.4	9.5	5.1	57.4
302	DS1/D15_03-2	0.8	3.3	4.0	9.1	5.0	51.9
303	DS1/D15_03-3	0.9	3.6	4.5	8.8	4.3	50.0
304	DS1/D20_03-1	1.3	5.0	6.3	9.8	3.5	68.9
305	DS1/D20_03-2	0.7	2.7	3.4	6.4	3.0	41.4
306	DS1/D20_03-3	1.3	5.1	6.4	10.0	3.6	64.8
307	DS1/D00_04-0	1.3	< 0.4	1.6	9.3	7.7	72.3
308	DS1/D02_04-1	1.0	< 0.4	1.3	9.7	8.4	86.5

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
309	DS1/D02_04-2	1.4	< 0.4	1.6	10.6	9.0	85.9
310	DS1/D02_04-3	1.3	< 0.4	1.6	10.7	9.0	86.0
311	DS1/D04_04-0	1.3	< 0.4	1.5	9.5	8.0	73.9
312	DS1/D05_04-1	1.4	< 0.4	1.7	9.0	7.3	71.3
313	DS1/D05_04-2	1.4	< 0.4	1.7	8.7	7.0	71.8
314	DS1/D05_04-3	0.9	< 0.4	1.2	6.7	5.5	72.0
315	DS1/D07_04-0	1.2	< 0.4	1.4	7.9	6.4	67.6
316	DS1/D10_04-1	1.3	< 0.4	1.6	7.4	5.8	67.2
317	DS1/D10_04-2	1.0	< 0.4	1.2	7.7	6.5	68.5
318	DS1/D10_04-3	0.9	< 0.4	1.2	7.2	6.0	65.8
319	DS1/D15_04-1	1.0	< 0.4	1.2	6.8	5.6	51.4
320	DS1/D15_04-2	1.0	< 0.4	1.2	6.5	5.4	56.5
321	DS1/D15_04-3	1.3	0.6	1.9	7.5	5.6	51.9
322	DS1/D20_04-1	1.3	< 0.4	1.5	7.3	5.8	62.3
323	DS1/D20_04-2	0.8	0.4	1.3	6.7	5.4	41.5
324	DS1/D20_04-3	1.3	< 0.4	1.5	6.7	5.2	65.1
325	DS1/D00_05-0	1.6	< 0.4	1.8	9.7	7.8	69.9
326	DS1/D02_05-1	1.0	< 0.4	1.3	8.6	7.3	64.7
327	DS1/D02_05-2	1.0	< 0.4	1.3	6.6	5.3	62.6
328	DS1/D02_05-3	1.1	< 0.4	1.3	7.9	6.6	62.7
329	DS1/D04_05-0	1.1	1.6	2.7	8.2	5.5	60.4
330	DS1/D05_05-1	1.3	< 0.4	1.5	8.7	7.1	67.6
331	DS1/D05_05-2	1.1	< 0.4	1.4	7.7	6.4	67.8
332	DS1/D05_05-3	1.4	< 0.4	1.7	8.8	7.1	67.6
333	DS1/D07_05-0	1.1	< 0.4	1.3	8.0	6.7	68.0
334	DS1/D10_05-1	0.2	< 0.4	0.4	5.7	5.2	80.6
335	DS1/D10_05-2	0.2	< 0.4	0.4	5.8	5.4	67.9
336	DS1/D10_05-3	0.2	< 0.4	0.5	6.5	6.1	71.2
337	DS1/D15_05-1	< 0.2	< 0.4	0.3	5.0	4.7	50.2
338	DS1/D15_05-2	< 0.2	< 0.4	0.3	7.0	6.7	65.0
339	DS1/D15_05-3	< 0.2	< 0.4	0.3	6.4	6.1	65.6
340	DS1/D20_05-1	< 0.2	< 0.4	0.3	6.5	6.1	85.8
341	DS1/D20_05-2	< 0.2	< 0.4	0.3	4.9	4.6	53.0
342	DS1/D20_05-3	< 0.2	< 0.4	0.3	6.7	6.4	59.7
343	DS1/D00_06-0	1.5	< 0.4	1.8	9.5	7.6	74.4
344	DS1/D02_06-1	0.8	< 0.4	1.1	5.7	4.6	71.7
345	DS1/D02_06-2	0.9	< 0.4	1.2	8.0	6.9	71.4
346	DS1/D02_06-3	1.4	0.8	2.2	9.2	7.0	73.2
347	DS1/D04_06-0	1.2	< 0.4	1.5	9.1	7.5	70.8
348	DS1/D05_06-1	1.4	0.5	1.9	8.8	6.9	69.4
349	DS1/D05_06-2	1.3	< 0.4	1.6	8.2	6.6	67.8
350	DS1/D05_06-3	1.3	< 0.4	1.6	9.2	7.6	65.9
351	DS1/D07_06-0	1.2	< 0.4	1.4	8.1	6.7	69.6
352	DS1/D10_06-1	1.3	< 0.4	1.6	7.5	5.9	76.8

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
353	DS1/D10_06-2	1.3	< 0.4	1.5	8.0	6.5	71.3
354	DS1/D10_06-3	1.3	< 0.4	1.5	8.5	6.9	73.1
355	DS1/D15_06-1	0.9	< 0.4	1.1	7.3	6.2	48.7
356	DS1/D15_06-2	1.3	< 0.4	1.5	7.8	6.2	62.2
357	DS1/D15_06-3	0.9	< 0.4	1.2	5.9	4.8	46.1
358	DS1/D20_06-1	1.2	< 0.4	1.4	6.8	5.4	57.1
359	DS1/D20_06-2	1.3	< 0.4	1.5	7.5	5.9	71.5
360	DS1/D20_06-3	1.1	< 0.4	1.3	7.8	6.4	61.2
361	DS1/D00_07-0	1.0	< 0.4	1.3	8.3	7.0	63.4
362	DS1/D02_07-1	0.9	< 0.4	1.2	8.8	7.6	93.5
363	DS1/D02_07-2	0.9	< 0.4	1.1	8.3	7.1	79.7
364	DS1/D02_07-3	0.9	< 0.4	1.2	8.5	7.3	82.2
365	DS1/D04_07-0	0.3	< 0.4	0.5	7.3	6.8	75.1
366	DS1/D05_07-1	0.2	< 0.4	0.5	7.0	6.6	69.8
367	DS1/D05_07-2	0.2	< 0.4	0.5	7.7	7.2	71.9
368	DS1/D05_07-3	0.2	< 0.4	0.5	7.2	6.8	69.1
369	DS1/D07_07-0	< 0.2	< 0.4	0.3	6.5	6.1	73.5
370	DS1/D10_07-1	0.2	< 0.4	0.4	8.1	7.6	75.9
371	DS1/D10_07-2	0.2	< 0.4	0.5	7.9	7.4	76.8
372	DS1/D10_07-3	0.2	< 0.4	0.4	7.1	6.7	76.8
373	DS1/D15_07-1	< 0.2	1.5	1.6	6.3	4.7	66.2
374	DS1/D15_07-2	< 0.2	< 0.4	0.3	5.7	5.3	59.5
375	DS1/D15_07-3	< 0.2	< 0.4	0.3	5.7	5.3	62.5
376	DS1/D20_07-1	0.3	< 0.4	0.5	6.6	6.1	71.4
377	DS1/D20_07-2	< 0.2	< 0.4	0.3	6.0	5.6	60.3
378	DS1/D20_07-3	0.3	< 0.4	0.5	6.0	5.5	68.0
379	DS1/D00_08-0	1.4	< 0.4	1.7	10.0	8.4	69.6
380	DS1/D02_08-1	1.0	< 0.4	1.3	8.7	7.4	81.4
381	DS1/D02_08-2	1.2	< 0.4	1.4	8.9	7.4	78.1
382	DS1/D02_08-3	1.3	< 0.4	1.5	9.6	8.0	82.0
383	DS1/D04_08-0	1.1	< 0.4	1.4	7.8	6.4	58.4
384	DS1/D05_08-1	1.3	< 0.4	1.6	7.8	6.2	79.1
385	DS1/D05_08-2	1.3	< 0.4	1.6	8.0	6.5	79.7
386	DS1/D05_08-3	1.3	0.7	2.0	8.0	6.0	75.5
387	DS1/D07_08-0	0.7	< 0.4	0.9	5.6	4.7	47.0
388	DS1/D10_08-1	0.9	< 0.4	1.2	7.4	6.2	55.6
389	DS1/D10_08-2	1.2	< 0.4	1.4	8.3	6.9	64.5
390	DS1/D10_08-3	0.9	< 0.4	1.2	6.9	5.8	61.9
391	DS1/D15_08-1	0.9	0.9	1.9	6.2	4.4	53.1
392	DS1/D15_08-2	1.2	< 0.4	1.4	7.7	6.3	60.1
393	DS1/D15_08-3	1.3	1.5	2.7	8.7	6.0	63.8
394	DS1/D20_08-1	1.2	0.6	1.8	8.8	6.9	66.2
395	DS1/D20_08-2	1.1	1.3	2.4	7.1	4.7	57.7
396	DS1/D20_08-3	1.2	< 0.4	1.4	8.9	7.5	68.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
397	DS1/D00_09-0	1.4	< 0.4	1.7	8.9	7.2	70.7
398	DS1/D02_09-1	1.1	< 0.4	1.4	7.8	6.4	69.6
399	DS1/D02_09-2	1.0	< 0.4	1.3	7.9	6.7	59.0
400	DS1/D02_09-3	0.9	< 0.4	1.2	7.2	6.0	63.0
401	DS1/D04_09-0	1.0	< 0.4	1.3	7.5	6.2	59.6
402	DS1/D05_09-1	1.3	< 0.4	1.5	7.9	6.4	67.2
403	DS1/D05_09-2	1.1	< 0.4	1.3	7.7	6.3	67.2
404	DS1/D05_09-3	1.2	< 0.4	1.5	7.5	6.0	70.7
405	DS1/D07_09-0	1.0	< 0.4	1.2	6.8	5.7	58.7
406	DS1/D10_09-1	1.2	< 0.4	1.4	8.2	6.8	78.6
407	DS1/D10_09-2	1.2	0.5	1.7	8.4	6.6	68.6
408	DS1/D10_09-3	1.0	< 0.4	1.2	7.2	6.0	63.2
409	DS1/D15_09-1	1.3	< 0.4	1.6	7.5	6.0	61.2
410	DS1/D15_09-2	1.2	< 0.4	1.4	7.1	5.7	54.6
411	DS1/D15_09-3	1.1	< 0.4	1.4	7.0	5.7	56.4
412	DS1/D20_09-1	1.1	< 0.4	1.3	6.7	5.4	64.5
413	DS1/D20_09-2	1.2	< 0.4	1.4	7.7	6.3	70.7
414	DS1/D20_09-3	1.0	< 0.4	1.2	6.4	5.2	58.7
415	DS1/D00_10-0	1.5	3.9	5.4	13.0	7.6	74.9
416	DS1/D02_10-1	1.3	4.9	6.2	12.0	5.8	83.0
417	DS1/D02_10-2	1.3	5.3	6.6	12.2	5.6	83.5
418	DS1/D02_10-3	1.3	5.2	6.5	12.5	5.9	87.4
419	DS1/D04_10-0	1.3	4.4	5.7	12.8	7.1	67.4
420	DS1/D05_10-1	1.0	3.3	4.4	11.2	6.9	58.7
421	DS1/D05_10-2	1.0	3.3	4.3	9.3	5.0	53.7
422	DS1/D05_10-3	1.4	5.1	6.5	11.7	5.2	73.5
423	DS1/D07_10-0	1.2	4.6	5.8	10.1	4.3	65.7
424	DS1/D10_10-1	1.3	5.6	6.8	11.7	4.9	70.0
425	DS1/D10_10-2	0.7	3.0	3.7	8.7	5.0	51.7
426	DS1/D10_10-3	1.2	5.4	6.6	11.0	4.4	68.3
427	DS1/D15_10-1	1.1	4.0	5.1	9.0	3.9	53.5
428	DS1/D15_10-2	0.8	4.6	5.4	7.3	1.8	41.6
429	DS1/D15_10-3	1.3	5.5	6.8	10.2	3.5	58.7
430	DS1/D20_10-1	1.1	4.0	5.1	9.3	4.2	62.7
431	DS1/D20_10-2	1.2	5.4	6.7	10.2	3.6	65.6
432	DS1/D20_10-3	1.2	4.7	5.9	10.3	4.4	64.4
433	DS1/D00_11-0	1.5	< 0.4	1.8	9.7	7.9	70.3
434	DS1/D02_11-1	1.3	< 0.4	1.9	9.9	8.1	77.9
435	DS1/D02_11-2	1.0	< 0.4	1.3	8.2	6.9	64.2
436	DS1/D02_11-3	1.3	< 0.4	1.5	8.9	7.3	84.6
437	DS1/D04_11-0	1.0	< 0.4	1.3	7.2	6.0	59.7
438	DS1/D05_11-1	1.4	< 0.4	1.7	8.6	6.9	70.8
439	DS1/D05_11-2	1.2	< 0.4	1.5	7.9	6.4	67.7
440	DS1/D05_11-3	0.9	< 0.4	1.2	6.2	5.0	49.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
441	DS1/D07_11-0	0.9	< 0.4	1.1	6.7	5.5	55.6
442	DS1/D10_11-1	0.9	< 0.4	1.1	6.7	5.7	58.1
443	DS1/D10_11-2	0.9	< 0.4	1.1	6.9	5.9	59.0
444	DS1/D10_11-3	1.2	< 0.4	1.4	9.7	8.3	72.2
445	DS1/D15_11-1	1.3	0.6	1.9	8.6	6.7	52.0
446	DS1/D15_11-2	1.1	< 0.4	1.3	7.2	5.9	54.1
447	DS1/D15_11-3	1.2	< 0.4	1.4	7.4	6.0	57.3
448	DS1/D20_11-1	0.8	< 0.4	1.0	7.1	6.1	56.1
449	DS1/D20_11-2	1.1	< 0.4	1.3	7.4	6.1	62.6
450	DS1/D20_11-3	1.0	< 0.4	1.2	6.9	5.7	54.9
451	DS1/D00_12-0	1.6	0.6	2.2	10.7	8.5	73.3
452	DS1/D02_12-1	1.0	< 0.4	1.3	8.2	6.9	60.9
453	DS1/D02_12-2	1.0	< 0.4	1.3	7.7	6.4	67.4
454	DS1/D02_12-3	1.3	< 0.4	1.6	8.6	7.0	71.2
455	DS1/D04_12-0	1.2	< 0.4	1.5	9.7	8.3	71.0
456	DS1/D05_12-1	1.0	< 0.4	1.2	7.1	5.8	61.1
457	DS1/D05_12-2	1.1	< 0.4	1.3	7.1	5.8	60.3
458	DS1/D05_12-3	1.3	< 0.4	1.6	8.7	7.2	77.3
459	DS1/D07_12-0	0.8	< 0.4	1.0	5.7	4.6	51.5
460	DS1/D10_12-1	< 0.2	< 0.4	0.3	7.1	6.8	78.2
461	DS1/D10_12-2	< 0.2	< 0.4	0.3	6.9	6.6	74.8
462	DS1/D10_12-3	< 0.2	< 0.4	0.3	7.2	6.9	66.3
463	DS1/D15_12-1	< 0.2	< 0.4	0.3	6.2	5.9	59.7
464	DS1/D15_12-2	< 0.2	< 0.4	0.3	6.7	6.4	63.9
465	DS1/D15_12-3	< 0.2	< 0.4	0.3	5.6	5.2	60.7
466	DS1/D20_12-1	< 0.2	< 0.4	0.3	7.4	7.0	80.8
467	DS1/D20_12-2	< 0.2	< 0.4	0.3	7.3	7.0	80.7
468	DS1/D20_12-3	< 0.2	< 0.4	0.3	8.7	8.4	73.5
469	DS1/D00_13-0	1.5	< 0.4	1.8	10.1	8.3	74.6
470	DS1/D02_13-1	1.3	< 0.4	1.6	9.2	7.6	80.2
471	DS1/D02_13-2	0.9	< 0.4	1.2	8.4	7.2	55.5
472	DS1/D02_13-3	1.4	< 0.4	1.7	9.2	7.6	79.4
473	DS1/D04_13-0	1.4	< 0.4	1.6	9.3	7.6	72.2
474	DS1/D05_13-1	1.3	0.6	1.9	8.8	6.9	74.6
475	DS1/D05_13-2	1.3	0.5	1.9	8.5	6.6	73.3
476	DS1/D05_13-3	1.3	< 0.4	1.6	8.4	6.8	72.8
477	DS1/D07_13-0	1.2	< 0.4	1.4	8.1	6.7	67.4
478	DS1/D10_13-1	0.8	< 0.4	1.0	6.8	5.8	63.8
479	DS1/D10_13-2	1.1	< 0.4	1.3	6.7	5.4	72.6
480	DS1/D10_13-3	1.2	0.7	1.9	7.8	5.8	72.9
481	DS1/D15_13-1	1.2	< 0.4	1.4	7.1	5.7	60.7
482	DS1/D15_13-2	1.2	< 0.4	1.4	6.7	5.3	62.6
483	DS1/D15_13-3	1.2	< 0.4	1.4	7.5	6.1	57.9
484	DS1/D20_13-1	0.9	< 0.4	1.1	7.5	6.4	61.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
485	DS1/D20_13-2	0.9	< 0.4	1.1	7.2	6.0	56.6
486	DS1/D20_13-3	1.2	< 0.4	1.4	7.8	6.3	69.0
487	DS1/D00_14-0	1.5	0.6	2.1	9.7	7.5	90.4
488	DS1/D02_14-1	0.7	< 0.4	0.9	7.1	6.2	71.2
489	DS1/D02_14-2	0.7	< 0.4	0.9	6.9	6.0	71.4
490	DS1/D02_14-3	0.9	< 0.4	1.2	8.8	7.6	72.2
491	DS1/D04_14-0	0.2	< 0.4	0.4	7.7	7.2	68.5
492	DS1/D05_14-1	0.2	< 0.4	0.4	6.1	5.7	68.9
493	DS1/D05_14-2	0.2	< 0.4	0.5	7.5	7.1	89.1
494	DS1/D05_14-3	< 0.2	< 0.4	0.4	6.9	6.5	70.5
495	DS1/D07_14-0	< 0.2	< 0.4	0.3	6.7	6.3	72.3
496	DS1/D10_14-1	< 0.2	< 0.4	0.3	6.1	5.8	73.0
497	DS1/D10_14-2	< 0.2	< 0.4	0.3	5.0	4.7	60.6
498	DS1/D10_14-3	< 0.2	< 0.4	0.3	4.7	4.4	65.3
499	DS1/D15_14-1	< 0.2	< 0.4	0.3	6.2	5.8	62.1
500	DS1/D15_14-2	< 0.2	< 0.4	0.3	6.5	6.2	62.3
501	DS1/D15_14-3	< 0.2	< 0.4	0.3	6.0	5.7	64.7
502	DS1/D20_14-1	< 0.2	< 0.4	0.3	6.7	6.4	76.4
503	DS1/D20_14-2	< 0.2	< 0.4	0.3	7.0	6.7	67.1
504	DS1/D20_14-3	0.9	< 0.4	1.2	7.8	6.6	68.3
505	WG2/D00_01-0	6.5	< 0.4	6.7	12.1	5.4	64.0
506	WG2/D02_01-1	4.9	< 0.4	5.1	9.2	4.2	51.8
507	WG2/D02_01-2	5.8	0.7	6.4	10.5	4.1	57.1
508	WG2/D02_01-3	5.4	< 0.4	5.6	10.6	4.9	56.5
509	WG2/D04_01-0	6.1	< 0.4	6.2	11.3	5.1	86.3
510	WG2/D05_01-1	7.1	1.3	8.4	13.8	5.4	69.2
511	WG2/D05_01-2	7.1	1.1	8.3	13.1	4.9	65.1
512	WG2/D05_01-3	7.2	1.0	8.2	12.7	4.4	63.6
513	WG2/D07_01-0	5.2	< 0.4	5.3	11.2	5.8	56.0
514	WG2/D10_01-1	7.2	1.0	8.1	14.1	6.0	67.8
515	WG2/D10_01-2	7.1	0.8	7.9	13.5	5.6	60.8
516	WG2/D10_01-3	7.1	1.0	8.1	12.3	4.2	64.1
517	WG2/D15_01-1	7.1	1.1	8.2	12.6	4.4	75.4
518	WG2/D15_01-2	5.7	< 0.4	5.9	10.7	4.8	57.1
519	WG2/D15_01-3	7.2	1.7	8.8	12.4	3.6	60.7
520	WG2/D20_01-1	7.0	0.8	7.8	13.6	5.8	62.1
521	WG2/D20_01-2	7.1	0.8	7.9	14.1	6.2	57.8
522	WG2/D20_01-3	7.1	0.7	7.8	14.3	6.5	61.1
523	WG2/D00_02-0	7.0	0.7	7.7	13.5	5.8	63.5
524	WG2/D02_02-1	6.8	1.0	7.7	12.7	4.9	65.3
525	WG2/D02_02-2	6.8	0.7	7.6	12.9	5.4	64.3
526	WG2/D02_02-3	5.1	< 0.4	5.3	10.2	4.9	50.2
527	WG2/D04_02-0	6.4	< 0.4	6.5	10.9	4.4	62.5
528	WG2/D05_02-1	7.2	0.9	8.1	13.7	5.6	69.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
529	WG2/D05_02-2	7.3	1.2	8.5	13.5	5.0	58.0
530	WG2/D05_02-3	7.4	1.3	8.7	13.6	4.9	62.4
531	WG2/D07_02-0	7.3	1.1	8.4	11.8	3.4	57.8
532	WG2/D10_02-1	7.3	1.0	8.3	13.2	4.9	62.9
533	WG2/D10_02-2	7.2	1.0	8.2	13.5	5.3	62.0
534	WG2/D10_02-3	7.2	1.0	8.2	13.1	4.9	62.5
535	WG2/D15_02-1	6.2	< 0.4	6.3	11.3	5.0	56.6
536	WG2/D15_02-2	5.7	< 0.4	5.8	10.6	4.7	52.1
537	WG2/D15_02-3	7.3	1.1	8.4	13.0	4.6	58.7
538	WG2/D20_02-1	7.2	0.8	8.1	13.8	5.7	61.7
539	WG2/D20_02-2	7.1	1.1	8.2	14.0	5.8	61.2
540	WG2/D20_02-3	7.4	1.4	8.8	14.6	5.8	60.0
541	WG2/D00_03-0	5.2	3.2	8.4	15.0	6.6	60.6
542	WG2/D02_03-1	5.6	3.3	8.9	14.9	6.1	69.3
543	WG2/D02_03-2	6.6	4.9	11.6	16.5	4.9	61.6
544	WG2/D02_03-3	5.8	3.8	9.6	14.7	5.1	83.7
545	WG2/D04_03-0	7.2	5.6	12.8	15.1	2.3	52.2
546	WG2/D05_03-1	7.3	6.4	13.7	17.2	3.5	60.4
547	WG2/D05_03-2	7.3	6.1	13.4	16.2	2.8	58.1
548	WG2/D05_03-3	7.3	6.1	13.4	16.3	2.9	55.7
549	WG2/D07_03-0	7.2	5.6	12.9	14.6	1.8	82.9
550	WG2/D10_03-1	7.3	6.0	13.3	16.6	3.3	58.1
551	WG2/D10_03-2	7.3	6.0	13.3	16.1	2.8	57.3
552	WG2/D10_03-3	7.3	5.8	13.2	15.8	2.7	60.9
553	WG2/D15_03-1	7.5	5.9	13.4	16.0	2.6	56.5
554	WG2/D15_03-2	6.3	3.7	10.1	14.4	4.3	56.9
555	WG2/D15_03-3	7.4	5.8	13.2	15.9	2.6	58.1
556	WG2/D20_03-1	7.3	5.2	12.6	16.1	3.5	58.6
557	WG2/D20_03-2	7.4	5.4	12.8	16.2	3.3	58.2
558	WG2/D20_03-3	7.5	5.4	12.9	16.6	3.7	61.8
559	WG2/D00_04-0	6.4	< 0.4	6.6	12.1	5.5	63.2
560	WG2/D02_04-1	5.5	< 0.4	5.7	10.9	5.2	59.0
561	WG2/D02_04-2	6.6	0.7	7.3	12.0	4.7	60.2
562	WG2/D02_04-3	5.3	< 0.4	5.5	9.7	4.2	60.2
563	WG2/D04_04-0	6.9	0.5	7.4	10.8	3.4	60.4
564	WG2/D05_04-1	7.2	0.8	8.0	13.1	5.1	60.4
565	WG2/D05_04-2	7.2	1.2	8.4	13.8	5.5	58.3
566	WG2/D05_04-3	7.3	0.9	8.2	14.1	5.9	58.3
567	WG2/D07_04-0	6.5	< 0.4	6.7	10.7	4.0	51.5
568	WG2/D10_04-1	7.1	1.1	8.3	13.7	5.5	53.4
569	WG2/D10_04-2	7.1	0.9	8.1	12.9	4.8	56.7
570	WG2/D10_04-3	7.2	0.8	8.0	12.6	4.6	51.5
571	WG2/D15_04-1	7.1	1.1	8.2	12.1	3.8	59.6
572	WG2/D15_04-2	5.8	< 0.4	5.9	11.0	5.1	56.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
573	WG2/D15_04-3	7.0	0.9	7.8	12.1	4.2	60.1
574	WG2/D20_04-1	7.0	0.7	7.7	13.1	5.4	57.1
575	WG2/D20_04-2	7.0	0.6	7.7	13.6	5.9	57.0
576	WG2/D20_04-3	7.1	0.9	8.0	13.5	5.5	56.7
577	WG2/D00_05-0	6.9	0.8	7.6	12.9	5.3	64.1
578	WG2/D02_05-1	5.2	< 0.4	5.4	9.8	4.4	64.2
579	WG2/D02_05-2	6.2	0.6	6.8	11.4	4.6	57.0
580	WG2/D02_05-3	6.8	1.5	8.3	11.3	3.0	55.7
581	WG2/D04_05-0	5.3	< 0.4	5.5	11.2	5.8	54.2
582	WG2/D05_05-1	7.3	0.7	7.9	14.0	6.1	53.2
583	WG2/D05_05-2	7.3	0.9	8.2	13.7	5.5	51.7
584	WG2/D05_05-3	7.2	0.8	8.1	13.4	5.4	54.7
585	WG2/D07_05-0	7.0	0.5	7.5	11.4	3.9	52.7
586	WG2/D10_05-1	7.1	0.7	7.9	13.1	5.2	54.9
587	WG2/D10_05-2	7.1	0.8	7.9	12.0	4.0	52.7
588	WG2/D10_05-3	7.2	0.7	7.9	12.6	4.8	56.4
589	WG2/D15_05-1	7.2	1.1	8.2	12.4	4.2	44.0
590	WG2/D15_05-2	5.1	< 0.4	5.3	8.5	3.2	43.1
591	WG2/D15_05-3	5.1	< 0.4	5.2	9.2	4.0	45.0
592	WG2/D20_05-1	7.3	1.6	8.9	13.9	5.0	58.2
593	WG2/D20_05-2	7.2	0.9	8.1	13.5	5.4	59.6
594	WG2/D20_05-3	7.1	0.8	8.0	13.3	5.3	58.2
595	WG2/D00_06-0	6.6	< 0.4	6.8	12.3	5.4	63.6
596	WG2/D02_06-1	6.9	0.9	7.7	12.9	5.2	60.5
597	WG2/D02_06-2	6.9	1.1	8.0	12.0	3.9	59.7
598	WG2/D02_06-3	6.9	1.2	8.1	12.1	4.1	58.2
599	WG2/D04_06-0	7.0	0.6	7.6	11.0	3.4	92.5
600	WG2/D05_06-1	7.4	0.9	8.3	13.8	5.5	63.4
601	WG2/D05_06-2	7.4	0.7	8.1	13.9	5.8	61.9
602	WG2/D05_06-3	7.4	0.9	8.3	14.0	5.7	61.0
603	WG2/D07_06-0	5.6	< 0.4	5.8	11.2	5.4	61.5
604	WG2/D10_06-1	7.4	1.0	8.4	12.7	4.3	51.7
605	WG2/D10_06-2	7.3	1.1	8.4	12.5	4.0	52.4
606	WG2/D10_06-3	7.2	0.7	8.0	12.6	4.6	50.9
607	WG2/D15_06-1	6.9	0.6	7.5	12.1	4.5	55.6
608	WG2/D15_06-2	5.7	< 0.4	5.8	10.2	4.4	50.0
609	WG2/D15_06-3	7.0	1.0	8.0	12.4	4.5	59.8
610	WG2/D20_06-1	7.2	1.0	8.2	13.7	5.5	53.4
611	WG2/D20_06-2	7.4	1.0	8.4	14.3	6.0	57.7
612	WG2/D20_06-3	7.3	1.1	8.3	13.1	4.8	56.0
613	WG2/D00_07-0	5.2	< 0.4	5.4	10.2	4.9	57.7
614	WG2/D02_07-1	5.2	< 0.4	5.4	10.1	4.7	43.0
615	WG2/D02_07-2	6.7	0.4	7.1	12.0	4.9	52.0
616	WG2/D02_07-3	5.8	< 0.4	6.0	10.8	4.7	51.1

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
617	WG2/D04_07-0	6.4	< 0.4	6.6	10.9	4.3	57.1
618	WG2/D05_07-1	7.4	0.7	8.0	13.6	5.6	64.3
619	WG2/D05_07-2	7.4	0.8	8.2	13.7	5.5	57.4
620	WG2/D05_07-3	7.4	0.8	8.1	13.9	5.7	60.1
621	WG2/D07_07-0	5.6	< 0.4	5.7	11.4	5.6	89.4
622	WG2/D10_07-1	6.8	0.9	7.8	11.8	4.0	48.2
623	WG2/D10_07-2	6.8	0.7	7.5	12.0	4.5	49.3
624	WG2/D10_07-3	6.8	0.8	7.6	12.0	4.4	51.3
625	WG2/D15_07-1	4.7	1.2	5.9	9.6	3.7	54.9
626	WG2/D15_07-2	4.6	1.2	5.8	9.5	3.7	59.3
627	WG2/D15_07-3	4.5	0.8	5.3	9.9	4.6	57.0
628	WG2/D20_07-1	0.2	0.8	1.0	5.9	4.9	60.7
629	WG2/D20_07-2	0.1	0.8	0.9	5.5	4.6	55.1
630	WG2/D20_07-3	1.6	2.3	3.9	6.1	2.2	59.6
631	WG2/D00_08-0	4.9	< 0.4	5.1	10.7	5.6	58.5
632	WG2/D02_08-1	6.4	0.6	7.0	11.5	4.5	49.0
633	WG2/D02_08-2	5.4	< 0.4	5.6	10.1	4.6	48.4
634	WG2/D02_08-3	6.8	0.9	7.7	12.8	5.1	56.4
635	WG2/D04_08-0	7.1	0.9	8.0	10.1	2.1	78.3
636	WG2/D05_08-1	7.2	0.9	8.1	13.3	5.2	55.9
637	WG2/D05_08-2	7.1	0.4	7.5	13.3	5.8	57.2
638	WG2/D05_08-3	7.3	0.7	7.9	13.3	5.4	58.8
639	WG2/D07_08-0	6.8	< 0.4	7.0	10.9	3.9	82.6
640	WG2/D10_08-1	7.1	1.3	8.4	12.7	4.3	54.7
641	WG2/D10_08-2	7.3	1.4	8.7	12.2	3.5	50.9
642	WG2/D10_08-3	7.1	1.1	8.2	12.7	4.5	51.7
643	WG2/D15_08-1	7.2	1.2	8.4	12.7	4.4	61.6
644	WG2/D15_08-2	7.1	1.1	8.2	12.5	4.3	62.9
645	WG2/D15_08-3	5.8	< 0.4	5.9	10.8	4.9	55.5
646	WG2/D20_08-1	7.1	0.9	8.0	13.5	5.5	55.1
647	WG2/D20_08-2	7.1	0.7	7.9	13.7	5.8	59.3
648	WG2/D20_08-3	7.1	0.7	7.8	12.7	4.8	58.5
649	WG2/D00_09-0	5.7	< 0.4	5.9	13.5	7.6	63.6
650	WG2/D02_09-1	6.6	0.8	7.3	13.1	5.8	43.1
651	WG2/D02_09-2	4.9	< 0.4	5.1	9.2	4.1	40.6
652	WG2/D02_09-3	5.1	< 0.4	5.3	9.5	4.2	45.6
653	WG2/D04_09-0	7.0	0.6	7.7	10.8	3.1	67.0
654	WG2/D05_09-1	7.2	0.2	7.4	13.4	6.0	60.9
655	WG2/D05_09-2	7.2	0.5	7.6	14.0	6.4	61.2
656	WG2/D05_09-3	7.2	0.3	7.5	13.5	6.0	60.0
657	WG2/D07_09-0	6.2	< 0.4	6.3	11.4	5.0	59.4
658	WG2/D10_09-1	7.1	0.9	8.1	12.7	4.7	56.3
659	WG2/D10_09-2	7.2	1.2	8.4	12.7	4.3	57.4
660	WG2/D10_09-3	7.1	0.8	8.0	13.3	5.4	53.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
661	WG2/D15_09-1	5.5	< 0.4	5.7	10.0	4.3	53.4
662	WG2/D15_09-2	7.2	1.0	8.2	12.9	4.7	65.3
663	WG2/D15_09-3	7.2	1.0	8.2	12.7	4.5	63.2
664	WG2/D20_09-1	7.3	0.7	8.1	13.6	5.5	57.4
665	WG2/D20_09-2	7.1	0.6	7.7	13.3	5.6	60.2
666	WG2/D20_09-3	7.3	0.9	8.2	12.9	4.7	60.0
667	WG2/D00_10-0	7.1	5.8	12.9	19.6	6.7	59.5
668	WG2/D02_10-1	6.9	6.1	13.0	15.9	3.0	53.2
669	WG2/D02_10-2	5.5	4.3	9.8	13.3	3.5	44.2
670	WG2/D02_10-3	5.9	3.9	9.8	15.1	5.3	49.1
671	WG2/D04_10-0	7.1	5.0	12.0	14.5	2.5	66.2
672	WG2/D05_10-1	7.2	5.3	12.6	16.5	3.9	63.0
673	WG2/D05_10-2	7.3	5.3	12.6	17.4	4.8	56.9
674	WG2/D05_10-3	7.4	5.5	12.8	16.2	3.4	53.2
675	WG2/D07_10-0	6.4	3.7	10.1	15.1	5.0	58.1
676	WG2/D10_10-1	7.4	5.8	13.2	15.0	1.8	57.8
677	WG2/D10_10-2	7.4	5.7	13.0	14.8	1.8	53.7
678	WG2/D10_10-3	7.4	5.8	13.1	14.1	1.0	51.3
679	WG2/D15_10-1	7.5	5.5	13.0	16.7	3.7	58.7
680	WG2/D15_10-2	7.5	5.8	13.2	16.5	3.3	57.0
681	WG2/D15_10-3	5.3	2.8	8.1	12.4	4.3	59.1
682	WG2/D20_10-1	7.5	5.0	12.6	15.4	2.9	57.2
683	WG2/D20_10-2	7.6	5.2	12.8	16.2	3.4	54.2
684	WG2/D20_10-3	7.5	5.2	12.7	16.1	3.4	60.3
685	WG2/D00_11-0	6.6	< 0.4	6.8	13.3	6.5	64.4
686	WG2/D02_11-1	6.9	0.9	7.7	11.9	4.2	64.5
687	WG2/D02_11-2	5.6	< 0.4	5.8	9.7	3.9	63.9
688	WG2/D02_11-3	5.5	< 0.4	5.7	9.7	4.1	57.4
689	WG2/D04_11-0	5.3	< 0.4	5.4	9.7	4.3	61.1
690	WG2/D05_11-1	7.1	< 0.4	7.4	14.2	6.8	60.1
691	WG2/D05_11-2	7.0	< 0.4	7.3	14.1	6.8	61.9
692	WG2/D05_11-3	7.2	< 0.4	7.3	13.3	6.0	59.4
693	WG2/D07_11-0	6.4	< 0.4	6.5	14.3	7.8	66.3
694	WG2/D10_11-1	7.1	1.0	8.1	12.3	4.2	50.3
695	WG2/D10_11-2	7.0	0.9	7.9	12.1	4.2	48.8
696	WG2/D10_11-3	7.2	0.9	8.0	12.7	4.7	49.1
697	WG2/D15_11-1	7.1	1.2	8.2	12.9	4.7	59.3
698	WG2/D15_11-2	5.8	< 0.4	6.0	10.4	4.4	50.4
699	WG2/D15_11-3	7.3	1.2	8.5	12.1	3.5	59.3
700	WG2/D20_11-1	7.1	0.8	7.9	14.2	6.3	59.0
701	WG2/D20_11-2	7.0	0.8	7.8	14.6	6.8	57.3
702	WG2/D20_11-3	7.1	1.2	8.3	14.3	6.0	55.7
703	WG2/D00_12-0	6.2	< 0.4	6.4	12.5	6.1	62.1
704	WG2/D02_12-1	6.9	1.2	8.1	12.7	4.6	54.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
705	WG2/D02_12-2	5.6	< 0.4	5.8	10.2	4.3	54.6
706	WG2/D02_12-3	5.4	< 0.4	5.6	9.4	3.8	53.9
707	WG2/D04_12-0	6.6	< 0.4	6.7	10.9	4.2	66.2
708	WG2/D05_12-1	7.0	< 0.4	7.1	13.4	6.3	60.0
709	WG2/D05_12-2	7.1	0.4	7.5	13.1	5.6	59.1
710	WG2/D05_12-3	7.0	< 0.4	7.1	13.4	6.3	60.2
711	WG2/D07_12-0	6.8	< 0.4	6.9	14.6	7.7	66.6
712	WG2/D10_12-1	7.2	0.9	8.1	12.2	4.1	49.4
713	WG2/D10_12-2	7.1	1.0	8.1	12.9	4.8	52.0
714	WG2/D10_12-3	7.1	1.2	8.3	12.8	4.6	52.7
715	WG2/D15_12-1	7.2	1.2	8.4	12.1	3.7	57.5
716	WG2/D15_12-2	5.3	< 0.4	5.5	9.9	4.4	42.5
717	WG2/D15_12-3	7.1	0.8	7.9	12.3	4.4	54.7
718	WG2/D20_12-1	7.1	1.1	8.2	14.4	6.2	59.3
719	WG2/D20_12-2	7.1	0.9	8.0	13.5	5.5	60.5
720	WG2/D20_12-3	7.2	1.0	8.1	13.7	5.6	57.8
721	WG2/D00_13-0	6.3	< 0.4	6.5	11.6	5.1	55.5
722	WG2/D02_13-1	6.9	0.9	7.8	12.3	4.5	59.3
723	WG2/D02_13-2	5.2	< 0.4	5.4	9.7	4.3	47.6
724	WG2/D02_13-3	7.0	0.9	7.9	12.8	4.9	62.5
725	WG2/D04_13-0	6.3	< 0.4	6.5	10.9	4.4	68.4
726	WG2/D05_13-1	7.1	0.4	7.5	14.0	6.5	56.4
727	WG2/D05_13-2	6.9	< 0.4	7.0	13.3	6.3	56.0
728	WG2/D05_13-3	7.1	< 0.4	7.4	14.4	7.0	61.3
729	WG2/D07_13-0	5.6	< 0.4	5.8	12.7	7.0	56.9
730	WG2/D10_13-1	7.2	0.9	8.1	12.8	4.7	49.6
731	WG2/D10_13-2	7.3	1.0	8.3	12.0	3.7	48.1
732	WG2/D10_13-3	7.3	1.1	8.4	12.4	4.0	56.3
733	WG2/D15_13-1	5.5	< 0.4	5.7	10.3	4.6	45.8
734	WG2/D15_13-2	7.2	0.8	8.0	12.4	4.4	59.9
735	WG2/D15_13-3	6.9	0.4	7.4	11.9	4.6	57.1
736	WG2/D20_13-1	7.3	1.3	8.6	13.1	4.5	58.7
737	WG2/D20_13-2	7.2	0.9	8.1	13.8	5.7	57.5
738	WG2/D20_13-3	7.2	0.8	8.0	13.6	5.5	62.1
739	WG2/D00_14-0	6.9	1.0	7.9	12.6	4.7	63.5
740	WG2/D02_14-1	7.0	0.8	7.8	12.1	4.3	57.4
741	WG2/D02_14-2	7.0	0.9	7.9	12.4	4.5	55.8
742	WG2/D02_14-3	6.7	0.4	7.1	11.7	4.5	56.4
743	WG2/D04_14-0	5.0	< 0.4	5.1	11.2	6.1	74.8
744	WG2/D05_14-1	7.1	0.3	7.4	13.5	6.1	59.7
745	WG2/D05_14-2	7.1	0.3	7.4	13.4	6.0	56.6
746	WG2/D05_14-3	7.2	0.2	7.4	13.2	5.8	58.1
747	WG2/D07_14-0	6.7	< 0.4	6.9	13.8	6.9	63.7
748	WG2/D10_14-1	6.9	1.3	8.2	12.2	4.0	52.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
749	WG2/D10_14-2	6.8	1.1	7.9	12.2	4.3	51.3
750	WG2/D10_14-3	6.9	1.1	7.9	11.9	4.0	56.3
751	WG2/D15_14-1	3.0	< 0.4	3.1	7.2	4.0	58.9
752	WG2/D15_14-2	4.4	1.0	5.3	9.4	4.1	59.9
753	WG2/D15_14-3	4.2	< 0.4	4.4	9.5	5.1	59.7
754	WG2/D20_14-1	< 0.2	1.0	1.0	5.9	4.8	62.9
755	WG2/D20_14-2	0.2	1.0	1.2	6.1	4.9	63.1
756	WG2/D20_14-3	< 0.2	0.8	0.9	6.3	5.3	61.8
757	DS2/D00_01-0	4.0	< 0.4	4.2	9.3	5.1	62.9
758	DS2/D02_01-1	4.5	< 0.4	4.7	10.7	6.0	67.1
759	DS2/D02_01-2	5.2	< 0.4	5.5	10.7	5.3	69.2
760	DS2/D02_01-3	5.3	0.6	5.9	10.8	4.9	61.4
761	DS2/D04_01-0	5.4	0.8	6.2	11.8	5.6	63.9
762	DS2/D05_01-1	5.6	0.8	6.3	12.2	5.9	63.8
763	DS2/D05_01-2	5.9	1.6	7.5	12.3	4.8	66.6
764	DS2/D05_01-3	6.0	2.4	8.4	12.3	3.9	65.2
765	DS2/D07_01-0	5.1	0.5	5.7	12.9	7.2	72.6
766	DS2/D10_01-1	5.8	2.8	8.6	11.8	3.2	71.1
767	DS2/D10_01-2	5.8	2.6	8.4	12.2	3.8	68.9
768	DS2/D10_01-3	5.9	2.4	8.3	12.1	3.8	69.2
769	DS2/D15_01-1	5.6	1.6	7.2	13.3	6.1	62.0
770	DS2/D15_01-2	5.7	1.8	7.5	11.8	4.3	59.6
771	DS2/D15_01-3	5.6	1.4	7.1	13.2	6.1	60.8
772	DS2/D20_01-1	5.6	1.5	7.1	12.2	5.1	75.5
773	DS2/D20_01-2	5.5	0.8	6.3	12.2	5.9	71.9
774	DS2/D20_01-3	5.7	1.3	7.0	12.2	5.1	72.6
775	DS2/D00_02-0	5.6	0.6	6.2	11.8	5.6	72.5
776	DS2/D02_02-1	5.1	< 0.4	5.3	11.0	5.7	73.4
777	DS2/D02_02-2	5.1	< 0.4	5.3	10.1	4.7	76.8
778	DS2/D02_02-3	4.3	< 0.4	4.5	10.5	6.0	67.4
779	DS2/D04_02-0	5.9	1.5	7.4	12.4	5.0	75.5
780	DS2/D05_02-1	5.8	1.3	7.1	13.7	6.6	80.7
781	DS2/D05_02-2	5.9	1.6	7.4	13.5	6.0	77.6
782	DS2/D05_02-3	4.3	0.5	4.7	10.3	5.6	58.6
783	DS2/D07_02-0	5.1	< 0.4	5.3	12.0	6.8	69.8
784	DS2/D10_02-1	5.7	1.9	7.6	11.7	4.1	70.0
785	DS2/D10_02-2	5.7	1.9	7.6	11.3	3.7	67.8
786	DS2/D10_02-3	5.8	1.9	7.7	11.3	3.7	71.7
787	DS2/D15_02-1	5.6	1.2	6.8	11.7	4.9	63.2
788	DS2/D15_02-2	5.6	1.5	7.1	11.1	4.0	61.1
789	DS2/D15_02-3	5.6	1.6	7.2	12.8	5.6	65.3
790	DS2/D20_02-1	5.6	1.1	6.7	12.1	5.4	66.8
791	DS2/D20_02-2	5.6	0.7	6.3	11.8	5.5	69.7
792	DS2/D20_02-3	5.6	1.0	6.6	12.2	5.5	58.9

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
793	DS2/D00_03-0	5.1	3.4	8.5	14.6	6.1	74.6
794	DS2/D02_03-1	4.9	3.1	8.0	14.9	6.9	60.7
795	DS2/D02_03-2	4.0	2.8	6.8	13.4	6.5	64.6
796	DS2/D02_03-3	3.8	2.5	6.3	10.5	4.2	56.9
797	DS2/D04_03-0	5.5	4.2	9.7	14.2	4.5	60.1
798	DS2/D05_03-1	4.8	3.2	8.0	13.7	5.7	65.7
799	DS2/D05_03-2	5.1	3.2	8.3	15.2	6.9	65.3
800	DS2/D05_03-3	4.5	2.9	7.4	13.4	6.0	66.2
801	DS2/D07_03-0	5.5	4.5	10.0	14.5	4.6	70.4
802	DS2/D10_03-1	5.8	5.7	11.4	14.0	2.6	70.9
803	DS2/D10_03-2	5.9	5.5	11.4	15.6	4.3	70.0
804	DS2/D10_03-3	5.9	5.4	11.3	15.0	3.7	71.7
805	DS2/D15_03-1	5.6	5.4	11.0	14.5	3.4	62.8
806	DS2/D15_03-2	5.7	5.4	11.0	14.7	3.6	62.8
807	DS2/D15_03-3	5.7	5.5	11.2	14.6	3.4	62.0
808	DS2/D20_03-1	4.7	2.8	7.5	12.7	5.2	57.9
809	DS2/D20_03-2	5.7	5.1	10.8	14.3	3.5	63.7
810	DS2/D20_03-3	5.7	5.0	10.7	15.2	4.5	60.7
811	DS2/D00_04-0	5.7	1.0	6.7	11.0	4.3	64.4
812	DS2/D02_04-1	4.4	< 0.4	4.6	10.1	5.5	60.2
813	DS2/D02_04-2	2.7	< 0.4	2.9	8.1	5.2	57.3
814	DS2/D02_04-3	5.2	< 0.4	5.4	11.1	5.6	63.2
815	DS2/D04_04-0	5.4	< 0.4	5.6	11.7	6.1	63.7
816	DS2/D05_04-1	5.9	1.3	7.2	12.9	5.7	80.0
817	DS2/D05_04-2	6.0	1.8	7.8	13.2	5.4	77.4
818	DS2/D05_04-3	4.3	< 0.4	4.6	9.7	5.1	78.8
819	DS2/D07_04-0	5.4	0.4	5.8	12.2	6.3	68.7
820	DS2/D10_04-1	5.8	1.2	6.9	11.3	4.4	65.9
821	DS2/D10_04-2	5.7	1.2	6.9	11.1	4.3	66.3
822	DS2/D10_04-3	5.8	1.1	6.9	12.1	5.2	66.2
823	DS2/D15_04-1	5.2	< 0.4	5.4	12.9	7.5	64.9
824	DS2/D15_04-2	5.5	0.8	6.3	12.8	6.5	63.1
825	DS2/D15_04-3	5.5	0.7	6.2	12.1	5.9	61.8
826	DS2/D20_04-1	4.5	< 0.4	4.7	10.1	5.4	63.1
827	DS2/D20_04-2	5.5	0.9	6.4	11.6	5.2	70.0
828	DS2/D20_04-3	4.8	< 0.4	5.0	10.2	5.2	64.2
829	DS2/D00_05-0	5.9	2.2	8.0	10.9	2.8	67.4
830	DS2/D02_05-1	5.3	1.0	6.3	12.8	6.5	86.1
831	DS2/D02_05-2	4.9	< 0.4	5.1	11.2	6.1	83.6
832	DS2/D02_05-3	5.0	< 0.4	5.2	13.6	8.4	81.0
833	DS2/D04_05-0	5.7	1.2	7.0	12.4	5.4	64.9
834	DS2/D05_05-1	5.9	1.8	7.8	13.2	5.4	70.2
835	DS2/D05_05-2	5.6	1.2	6.9	12.6	5.8	67.4
836	DS2/D05_05-3	4.3	0.4	4.7	10.4	5.7	68.5

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
837	DS2/D07_05-0	4.6	< 0.4	4.8	11.6	6.8	62.9
838	DS2/D10_05-1	5.8	1.9	7.7	11.6	4.0	62.7
839	DS2/D10_05-2	5.8	2.1	7.9	13.1	5.3	62.7
840	DS2/D10_05-3	5.8	1.9	7.7	11.8	4.2	63.2
841	DS2/D15_05-1	5.6	1.3	6.9	12.4	5.5	64.3
842	DS2/D15_05-2	5.6	1.4	7.0	12.7	5.7	60.8
843	DS2/D15_05-3	5.5	1.4	7.0	12.8	5.8	64.3
844	DS2/D20_05-1	5.6	1.5	7.1	12.2	5.1	65.4
845	DS2/D20_05-2	5.5	1.5	7.0	12.5	5.4	67.1
846	DS2/D20_05-3	5.5	1.4	7.0	12.2	5.2	70.0
847	DS2/D00_06-0	4.9	< 0.4	5.1	11.1	6.0	63.7
848	DS2/D02_06-1	5.8	2.4	8.2	10.9	2.7	53.4
849	DS2/D02_06-2	4.7	< 0.4	4.9	9.8	4.9	51.9
850	DS2/D02_06-3	4.8	< 0.4	5.0	10.5	5.5	54.9
851	DS2/D04_06-0	5.4	< 0.4	5.6	11.3	5.7	65.4
852	DS2/D05_06-1	5.3	< 0.4	5.5	13.3	7.8	67.8
853	DS2/D05_06-2	4.3	< 0.4	4.5	10.3	5.7	55.1
854	DS2/D05_06-3	5.2	< 0.4	5.5	12.1	6.6	66.8
855	DS2/D07_06-0	5.4	< 0.4	5.6	12.4	6.8	65.4
856	DS2/D10_06-1	5.8	1.4	7.2	11.9	4.7	61.8
857	DS2/D10_06-2	5.8	1.2	7.0	11.2	4.2	61.6
858	DS2/D10_06-3	5.9	1.4	7.2	11.7	4.4	61.1
859	DS2/D15_06-1	5.6	1.2	6.9	12.8	5.9	61.6
860	DS2/D15_06-2	5.6	1.5	7.2	12.2	5.0	64.3
861	DS2/D15_06-3	5.7	1.7	7.4	12.6	5.2	63.1
862	DS2/D20_06-1	5.5	1.9	7.4	11.4	4.0	59.1
863	DS2/D20_06-2	5.5	1.1	6.6	12.0	5.4	63.6
864	DS2/D20_06-3	5.5	0.5	6.0	11.7	5.7	61.0
865	DS2/D00_07-0	3.6	< 0.4	3.8	9.9	6.1	52.7
866	DS2/D02_07-1	3.5	< 0.4	3.7	8.5	4.8	42.2
867	DS2/D02_07-2	4.2	< 0.4	4.4	10.9	6.5	42.9
868	DS2/D02_07-3	3.0	< 0.4	3.2	7.9	4.7	47.2
869	DS2/D04_07-0	4.8	< 0.4	5.0	10.6	5.6	56.2
870	DS2/D05_07-1	5.4	0.6	6.1	11.5	5.4	62.9
871	DS2/D05_07-2	5.7	1.3	7.0	12.3	5.3	67.6
872	DS2/D05_07-3	4.3	< 0.4	4.5	10.4	5.9	55.8
873	DS2/D07_07-0	5.0	< 0.4	5.2	12.1	6.9	65.7
874	DS2/D10_07-1	5.6	1.3	6.9	11.9	5.0	59.2
875	DS2/D10_07-2	5.6	1.3	6.9	11.5	4.6	58.0
876	DS2/D10_07-3	5.6	1.3	7.0	10.9	4.0	56.9
877	DS2/D15_07-1	4.6	1.4	6.0	11.9	5.9	62.7
878	DS2/D15_07-2	4.6	2.2	6.8	11.0	4.2	60.2
879	DS2/D15_07-3	4.6	1.2	5.8	11.5	5.8	65.3
880	DS2/D20_07-1	0.9	0.5	1.5	7.6	6.1	82.5

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
881	DS2/D20_07-2	0.6	< 0.4	0.8	5.7	4.9	82.6
882	DS2/D20_07-3	1.0	1.1	2.1	9.3	7.2	85.1
883	DS2/D00_08-0	5.2	0.6	5.8	11.9	6.2	68.1
884	DS2/D02_08-1	4.3	< 0.4	4.5	10.7	6.2	59.6
885	DS2/D02_08-2	5.9	1.8	7.7	12.9	5.2	60.6
886	DS2/D02_08-3	3.9	< 0.4	4.2	10.7	6.6	60.1
887	DS2/D04_08-0	5.3	< 0.4	5.5	11.8	6.3	61.8
888	DS2/D05_08-1	5.8	1.6	7.3	11.5	4.2	77.5
889	DS2/D05_08-2	4.9	< 0.4	5.1	11.6	6.5	76.6
890	DS2/D05_08-3	4.4	< 0.4	4.7	11.5	6.8	68.1
891	DS2/D07_08-0	3.7	< 0.4	3.9	10.0	6.1	50.1
892	DS2/D10_08-1	5.8	2.0	7.8	11.9	4.1	55.0
893	DS2/D10_08-2	5.8	2.4	8.2	12.4	4.1	61.3
894	DS2/D10_08-3	5.8	1.9	7.7	12.1	4.4	59.2
895	DS2/D15_08-1	5.6	1.4	7.0	13.4	6.4	67.6
896	DS2/D15_08-2	5.6	1.7	7.3	13.0	5.7	67.4
897	DS2/D15_08-3	5.6	1.5	7.0	13.6	6.5	67.2
898	DS2/D20_08-1	5.5	1.4	6.8	14.9	8.1	69.7
899	DS2/D20_08-2	5.5	1.3	6.8	14.5	7.7	69.7
900	DS2/D20_08-3	5.6	1.4	7.0	14.5	7.5	69.8
901	DS2/D00_09-0	5.8	0.9	6.7	13.4	6.7	71.9
902	DS2/D02_09-1	5.7	< 0.4	5.9	11.4	5.5	54.3
903	DS2/D02_09-2	4.5	< 0.4	4.7	9.5	4.8	53.0
904	DS2/D02_09-3	4.8	< 0.4	5.0	9.4	4.4	53.6
905	DS2/D04_09-0	5.3	< 0.4	5.5	11.8	6.2	61.3
906	DS2/D05_09-1	5.1	0.5	5.6	9.8	4.2	67.3
907	DS2/D05_09-2	5.8	0.9	6.7	11.6	4.9	71.0
908	DS2/D05_09-3	4.1	1.0	5.1	9.0	3.9	69.1
909	DS2/D07_09-0	5.4	0.7	6.0	12.5	6.5	66.5
910	DS2/D10_09-1	5.8	1.6	7.3	12.2	4.8	63.2
911	DS2/D10_09-2	5.7	1.4	7.1	12.3	5.2	69.0
912	DS2/D10_09-3	5.7	1.4	7.1	11.4	4.2	66.1
913	DS2/D15_09-1	5.7	0.9	6.6	12.7	6.2	69.8
914	DS2/D15_09-2	5.7	1.4	7.1	14.0	6.9	69.5
915	DS2/D15_09-3	5.6	0.9	6.5	15.1	8.6	70.7
916	DS2/D20_09-1	5.6	1.6	7.2	14.0	6.8	65.0
917	DS2/D20_09-2	5.6	1.2	6.8	13.5	6.7	63.6
918	DS2/D20_09-3	5.0	< 0.4	5.2	12.6	7.4	61.9
919	DS2/D00_10-0	5.7	5.5	11.2	15.0	3.9	70.0
920	DS2/D02_10-1	3.2	2.5	5.7	12.4	6.7	67.4
921	DS2/D02_10-2	4.3	3.3	7.6	11.3	3.8	65.5
922	DS2/D02_10-3	4.3	3.2	7.4	11.7	4.3	69.2
923	DS2/D04_10-0	5.2	4.1	9.3	14.4	5.0	61.8
924	DS2/D05_10-1	4.3	3.2	7.5	14.8	7.3	64.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
925	DS2/D05_10-2	5.5	4.6	10.1	12.9	2.8	61.3
926	DS2/D05_10-3	4.4	3.2	7.6	14.3	6.7	67.9
927	DS2/D07_10-0	5.4	5.1	10.5	14.3	3.8	64.8
928	DS2/D10_10-1	5.9	6.0	11.9	14.1	2.2	53.6
929	DS2/D10_10-2	5.8	6.1	11.9	13.5	1.7	53.0
930	DS2/D10_10-3	5.9	5.7	11.6	13.3	1.8	56.7
931	DS2/D15_10-1	5.7	5.5	11.2	18.1	6.8	75.9
932	DS2/D15_10-2	5.7	5.8	11.5	17.6	6.1	70.7
933	DS2/D15_10-3	5.8	6.0	11.8	15.7	3.9	73.3
934	DS2/D20_10-1	5.6	5.4	11.0	17.1	6.1	61.1
935	DS2/D20_10-2	5.4	4.8	10.2	16.1	5.9	59.5
936	DS2/D20_10-3	5.4	4.6	10.0	15.9	5.9	64.3
937	DS2/D00_11-0	5.4	< 0.4	5.6	12.0	6.4	64.3
938	DS2/D02_11-1	4.2	< 0.4	4.4	9.2	4.7	40.2
939	DS2/D02_11-2	4.0	< 0.4	4.2	8.9	4.6	43.0
940	DS2/D02_11-3	4.9	< 0.4	5.1	9.3	4.2	43.6
941	DS2/D04_11-0	4.9	< 0.4	5.1	11.2	6.1	57.6
942	DS2/D05_11-1	5.5	0.5	6.1	12.3	6.2	66.3
943	DS2/D05_11-2	4.0	< 0.4	4.3	12.1	7.8	67.4
944	DS2/D05_11-3	5.7	0.6	6.3	12.3	5.9	69.6
945	DS2/D07_11-0	5.5	0.4	5.8	11.6	5.8	63.7
946	DS2/D10_11-1	5.7	1.2	6.9	11.2	4.3	52.1
947	DS2/D10_11-2	5.7	1.2	6.9	11.5	4.6	53.2
948	DS2/D10_11-3	5.8	1.2	7.0	11.0	4.1	55.4
949	DS2/D15_11-1	5.7	2.0	7.7	13.3	5.6	59.9
950	DS2/D15_11-2	5.6	1.5	7.1	12.6	5.5	63.6
951	DS2/D15_11-3	5.6	1.7	7.3	14.6	7.4	61.7
952	DS2/D20_11-1	4.6	< 0.4	4.8	11.4	6.6	60.9
953	DS2/D20_11-2	4.4	< 0.4	4.6	10.3	5.8	59.2
954	DS2/D20_11-3	5.5	0.5	6.0	12.9	6.9	59.0
955	DS2/D00_12-0	5.7	1.6	7.4	12.5	5.1	67.2
956	DS2/D02_12-1	4.0	< 0.4	4.2	9.8	5.6	43.6
957	DS2/D02_12-2	5.8	2.0	7.7	13.5	5.7	56.3
958	DS2/D02_12-3	3.1	0.5	3.6	9.5	6.0	48.3
959	DS2/D04_12-0	5.6	0.9	6.5	12.4	5.9	62.8
960	DS2/D05_12-1	4.6	< 0.4	4.8	11.3	6.4	54.7
961	DS2/D05_12-2	5.1	< 0.4	5.3	11.4	6.1	60.4
962	DS2/D05_12-3	4.7	< 0.4	5.0	11.8	6.8	61.2
963	DS2/D07_12-0	5.2	0.5	5.7	12.8	7.2	67.9
964	DS2/D10_12-1	5.8	1.9	7.6	11.1	3.4	49.7
965	DS2/D10_12-2	5.9	1.7	7.6	10.9	3.3	51.1
966	DS2/D10_12-3	5.7	1.6	7.3	10.9	3.6	50.2
967	DS2/D15_12-1	5.5	1.6	7.1	16.3	9.2	73.0
968	DS2/D15_12-2	5.7	2.1	7.7	14.7	7.0	64.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
969	DS2/D15_12-3	5.5	1.8	7.4	16.2	8.8	68.6
970	DS2/D20_12-1	5.6	1.4	7.0	11.0	4.0	43.6
971	DS2/D20_12-2	5.5	0.9	6.5	12.1	5.6	50.3
972	DS2/D20_12-3	5.4	1.2	6.7	12.5	5.8	46.9
973	DS2/D00_13-0	5.2	< 0.4	5.4	12.4	7.0	64.7
974	DS2/D02_13-1	5.3	< 0.4	5.6	11.0	5.5	70.5
975	DS2/D02_13-2	5.5	< 0.4	5.7	10.7	5.0	61.2
976	DS2/D02_13-3	4.4	< 0.4	4.6	9.5	4.9	65.8
977	DS2/D04_13-0	5.6	0.5	6.1	11.8	5.7	66.0
978	DS2/D05_13-1	4.3	< 0.4	4.5	11.0	6.5	67.3
979	DS2/D05_13-2	5.3	< 0.4	5.5	11.6	6.1	68.2
980	DS2/D05_13-3	5.0	< 0.4	5.3	11.7	6.4	65.7
981	DS2/D07_13-0	3.9	< 0.4	4.1	9.4	5.3	51.1
982	DS2/D10_13-1	5.8	1.3	7.2	11.3	4.1	53.7
983	DS2/D10_13-2	5.9	1.5	7.4	10.5	3.1	52.7
984	DS2/D10_13-3	5.8	1.3	7.1	11.7	4.6	52.6
985	DS2/D15_13-1	5.7	1.4	7.1	14.0	7.0	64.7
986	DS2/D15_13-2	5.6	1.1	6.7	13.6	7.0	68.1
987	DS2/D15_13-3	5.6	1.1	6.7	13.7	7.0	71.5
988	DS2/D20_13-1	5.6	1.1	6.7	12.1	5.3	53.9
989	DS2/D20_13-2	6.1	1.7	7.8	12.7	4.9	52.8
990	DS2/D20_13-3	5.3	0.7	6.0	11.1	5.0	51.6
991	DS2/D00_14-0	5.2	< 0.4	5.4	11.8	6.4	65.4
992	DS2/D02_14-1	5.5	< 0.4	5.8	11.6	5.9	54.1
993	DS2/D02_14-2	3.9	< 0.4	4.1	9.3	5.2	53.8
994	DS2/D02_14-3	4.1	< 0.4	4.3	9.8	5.5	54.4
995	DS2/D04_14-0	5.0	< 0.4	5.3	10.6	5.3	59.7
996	DS2/D05_14-1	5.4	0.7	6.2	10.2	4.0	76.8
997	DS2/D05_14-2	5.6	1.4	7.0	11.5	4.5	73.1
998	DS2/D05_14-3	4.7	< 0.4	4.9	12.6	7.7	69.5
999	DS2/D07_14-0	5.3	< 0.4	5.5	11.9	6.5	69.0
1000	DS2/D10_14-1	5.6	1.1	6.7	10.8	4.1	55.9
1001	DS2/D10_14-2	5.6	1.2	6.7	10.9	4.2	55.1
1002	DS2/D10_14-3	5.6	1.8	7.4	11.2	3.7	58.9
1003	DS2/D15_14-1	4.7	1.2	5.8	13.4	7.6	69.2
1004	DS2/D15_14-2	4.6	1.4	6.1	13.1	7.0	67.2
1005	DS2/D15_14-3	4.6	1.4	6.0	14.0	8.0	68.2
1006	DS2/D20_14-1	0.9	< 0.4	1.1	6.5	5.3	73.4
1007	DS2/D20_14-2	1.0	< 0.4	1.2	6.1	4.9	68.9
1008	DS1/D20_14-3	1.0	< 0.4	1.2	6.2	5.0	77.8
1009	WG3/D00_01-0	< 0.2	< 0.4	0.3	7.1	6.7	88.0
1010	WG3/D02_01-1	< 0.2	< 0.4	0.3	6.2	5.9	83.9
1011	WG3/D02_01-2	< 0.2	< 0.4	0.3	6.4	6.1	80.3
1012	WG3/D02_01-3	0.3	< 0.4	0.4	6.3	5.8	80.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1013	WG3/D04_01-1	< 0.2	< 0.4	0.3	7.0	6.7	80.2
1014	WG3/D04_01-2	< 0.2	< 0.4	0.3	6.1	5.7	76.8
1015	WG3/D04_01-3	< 0.2	< 0.4	0.3	5.9	5.5	76.4
1016	WG3/D05_01-0	< 0.2	< 0.4	0.3	6.3	6.0	80.3
1017	WG3/D07_01-0	< 0.2	< 0.4	0.3	5.5	5.2	80.5
1018	WG3/D10_01-1	< 0.2	< 0.4	0.3	5.5	5.2	81.2
1019	WG3/D10_01-2	< 0.2	< 0.4	0.3	6.1	5.8	75.8
1020	WG3/D10_01-3	< 0.2	< 0.4	0.3	5.9	5.5	74.6
1021	WG3/D15_01-1	< 0.2	< 0.4	0.4	6.2	5.8	77.6
1022	WG3/D15_01-2	< 0.2	< 0.4	0.4	6.5	6.1	74.1
1023	WG3/D15_01-3	< 0.2	< 0.4	0.4	6.8	6.4	73.2
1024	WG3/D20_01-1	< 0.2	< 0.4	0.4	6.5	6.1	73.2
1025	WG3/D20_01-2	< 0.2	< 0.4	0.4	6.6	6.2	75.6
1026	WG3/D20_01-3	< 0.2	< 0.4	0.4	6.0	5.6	68.7
1027	WG3/D45_01-0	< 0.2	1.0	1.1	6.2	5.1	70.5
1028	WG3/D70_01-0	< 0.2	0.7	0.8	6.9	6.1	68.9
1029	WG3/D00_02-0	< 0.2	< 0.4	0.3	6.6	6.2	88.7
1030	WG3/D02_02-1	0.3	< 0.4	0.5	6.2	5.8	84.2
1031	WG3/D02_02-2	< 0.2	< 0.4	0.3	6.2	5.9	83.6
1032	WG3/D02_02-3	0.3	< 0.4	0.4	6.1	5.7	78.7
1033	WG3/D04_02-1	< 0.2	< 0.4	0.3	5.9	5.6	78.8
1034	WG3/D04_02-2	< 0.2	< 0.4	0.3	6.4	6.1	79.6
1035	WG3/D04_02-3	< 0.2	< 0.4	0.3	5.2	4.9	76.0
1036	WG3/D05_02-0	< 0.2	< 0.4	0.3	6.3	6.0	88.9
1037	WG3/D07_02-0	< 0.2	< 0.4	0.3	5.9	5.5	84.0
1038	WG3/D10_02-1	< 0.2	< 0.4	0.3	5.6	5.3	78.8
1039	WG3/D10_02-2	< 0.2	< 0.4	0.3	6.2	5.9	78.2
1040	WG3/D10_02-3	< 0.2	< 0.4	0.3	5.6	5.3	77.6
1041	WG3/D15_02-1	< 0.2	< 0.4	0.4	7.0	6.6	88.8
1042	WG3/D15_02-2	< 0.2	< 0.4	0.4	6.4	6.0	83.7
1043	WG3/D15_02-3	< 0.2	< 0.4	0.4	6.1	5.7	82.0
1044	WG3/D20_02-1	< 0.2	< 0.4	0.4	6.7	6.3	77.1
1045	WG3/D20_02-2	< 0.2	< 0.4	0.4	7.0	6.6	74.0
1046	WG3/D20_02-3	< 0.2	< 0.4	0.4	7.1	6.7	71.8
1047	WG3/D45_02-0	< 0.2	1.2	1.3	6.6	5.3	71.9
1048	WG3/D70_02-0	< 0.2	1.1	1.2	6.6	5.4	78.4
1049	WG3/D00_03-0	< 0.2	4.9	5.0	11.0	6.0	85.7
1050	WG3/D02_03-1	< 0.2	4.8	4.9	9.9	5.0	80.8
1051	WG3/D02_03-2	< 0.2	5.0	5.2	9.3	4.2	81.1
1052	WG3/D02_03-3	< 0.2	4.8	5.0	9.5	4.5	81.2
1053	WG3/D04_03-1	< 0.2	5.6	5.7	10.2	4.4	78.4
1054	WG3/D04_03-2	< 0.2	5.6	5.7	9.9	4.2	80.8
1055	WG3/D04_03-3	< 0.2	5.6	5.7	10.7	5.0	78.7
1056	WG3/D05_03-0	< 0.2	4.2	4.3	9.9	5.6	81.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1057	WG3/D07_03-0	< 0.2	3.4	3.6	7.3	3.7	73.4
1058	WG3/D10_03-1	< 0.2	5.3	5.5	11.4	5.9	75.5
1059	WG3/D10_03-2	< 0.2	5.5	5.6	11.3	5.7	70.6
1060	WG3/D10_03-3	< 0.2	5.3	5.4	10.6	5.2	72.3
1061	WG3/D15_03-1	< 0.2	5.4	5.5	11.0	5.4	82.6
1062	WG3/D15_03-2	< 0.2	5.7	5.8	10.3	4.5	71.8
1063	WG3/D15_03-3	< 0.2	5.3	5.5	10.5	5.0	74.5
1064	WG3/D20_03-1	< 0.2	5.5	5.6	10.4	4.8	66.5
1065	WG3/D20_03-2	< 0.2	5.5	5.6	9.9	4.3	66.3
1066	WG3/D20_03-3	< 0.2	5.4	5.6	10.4	4.8	66.9
1067	WG3/D45_03-0	< 0.2	5.0	5.2	11.3	6.1	66.3
1068	WG3/D70_03-0	< 0.2	5.0	5.2	10.3	5.1	68.1
1069	WG3/D00_04-0	< 0.2	< 0.4	0.3	6.8	6.5	86.8
1070	WG3/D02_04-1	< 0.2	< 0.4	0.3	6.2	5.9	80.5
1071	WG3/D02_04-2	< 0.2	< 0.4	0.3	6.1	5.8	76.5
1072	WG3/D02_04-3	< 0.2	< 0.4	0.3	5.3	5.0	81.4
1073	WG3/D04_04-1	< 0.2	< 0.4	0.3	6.3	6.0	79.9
1074	WG3/D04_04-2	< 0.2	< 0.4	0.3	6.4	6.1	78.7
1075	WG3/D04_04-3	< 0.2	< 0.4	0.3	5.8	5.5	78.4
1076	WG3/D05_04-0	< 0.2	< 0.4	0.3	5.5	5.1	72.1
1077	WG3/D07_04-0	< 0.2	< 0.4	0.3	4.8	4.5	69.2
1078	WG3/D10_04-1	< 0.2	< 0.4	0.3	6.6	6.3	73.9
1079	WG3/D10_04-2	< 0.2	< 0.4	0.3	6.9	6.6	67.3
1080	WG3/D10_04-3	< 0.2	< 0.4	0.3	5.8	5.5	71.8
1081	WG3/D15_04-1	< 0.2	< 0.4	0.4	6.5	6.1	74.2
1082	WG3/D15_04-2	< 0.2	< 0.4	0.4	5.8	5.4	71.2
1083	WG3/D15_04-3	< 0.2	< 0.4	0.4	7.0	6.6	72.1
1084	WG3/D20_04-1	< 0.2	< 0.4	0.4	6.8	6.4	68.0
1085	WG3/D20_04-2	< 0.2	< 0.4	0.4	6.6	6.2	67.6
1086	WG3/D20_04-3	< 0.2	< 0.4	0.4	6.6	6.2	67.5
1087	WG3/D45_04-0	< 0.2	0.9	1.0	6.7	5.6	67.3
1088	WG3/D70_04-0	< 0.2	1.2	1.3	6.5	5.3	68.4
1089	WG3/D00_05-0	< 0.2	< 0.4	0.3	6.4	6.0	87.5
1090	WG3/D02_05-1	0.3	< 0.4	0.5	5.5	5.1	77.5
1091	WG3/D02_05-2	0.3	< 0.4	0.4	5.7	5.2	78.6
1092	WG3/D02_05-3	0.4	< 0.4	0.5	6.3	5.7	79.1
1093	WG3/D04_05-1	< 0.2	< 0.4	0.3	5.7	5.3	77.4
1094	WG3/D04_05-2	< 0.2	< 0.4	0.3	6.0	5.7	76.6
1095	WG3/D04_05-3	< 0.2	< 0.4	0.3	6.2	5.9	77.4
1096	WG3/D05_05-0	< 0.2	< 0.4	0.3	5.5	5.2	81.5
1097	WG3/D07_05-0	< 0.2	< 0.4	0.3	5.0	4.7	68.3
1098	WG3/D10_05-1	< 0.2	< 0.4	0.3	7.6	7.3	79.6
1099	WG3/D10_05-2	< 0.2	< 0.4	0.3	6.5	6.2	72.8
1100	WG3/D10_05-3	< 0.2	< 0.4	0.3	6.0	5.7	72.1

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1101	WG3/D15_05-1	< 0.2	< 0.4	0.4	6.7	6.3	74.6
1102	WG3/D15_05-2	< 0.2	< 0.4	0.4	5.9	5.5	74.6
1103	WG3/D15_05-3	< 0.2	< 0.4	0.4	5.7	5.3	71.9
1104	WG3/D20_05-1	< 0.2	< 0.4	0.4	6.4	6.0	71.3
1105	WG3/D20_05-2	< 0.2	< 0.4	0.4	6.9	6.5	70.5
1106	WG3/D20_05-3	< 0.2	< 0.4	0.4	6.6	6.2	70.0
1107	WG3/D45_05-0	< 0.2	< 0.4	0.3	6.1	5.8	69.3
1108	WG3/D70_05-0	< 0.2	< 0.4	0.3	6.0	5.7	69.0
1109	WG3/D00_06-0	0.2	< 0.4	0.5	6.8	6.3	88.3
1110	WG3/D02_06-1	0.3	< 0.4	0.5	6.0	5.5	79.8
1111	WG3/D02_06-2	0.3	< 0.4	0.5	6.5	6.0	93.7
1112	WG3/D02_06-3	0.3	< 0.4	0.4	6.1	5.6	85.1
1113	WG3/D04_06-1	< 0.2	< 0.4	0.3	6.6	6.2	86.7
1114	WG3/D04_06-2	< 0.2	< 0.4	0.3	6.6	6.3	83.9
1115	WG3/D04_06-3	< 0.2	< 0.4	0.3	6.4	6.1	84.9
1116	WG3/D05_06-0	< 0.2	< 0.4	0.3	6.7	6.4	89.6
1117	WG3/D07_06-0	< 0.2	< 0.4	0.3	6.6	6.3	75.7
1118	WG3/D10_06-1	< 0.2	< 0.4	0.3	7.9	7.6	83.4
1119	WG3/D10_06-2	< 0.2	< 0.4	0.3	6.1	5.8	77.6
1120	WG3/D10_06-3	< 0.2	< 0.4	0.3	7.1	6.8	77.1
1121	WG3/D15_06-1	< 0.2	< 0.4	0.4	6.4	6.0	83.3
1122	WG3/D15_06-2	< 0.2	< 0.4	0.4	6.6	6.3	79.2
1123	WG3/D15_06-3	< 0.2	< 0.4	0.4	6.6	6.2	85.1
1124	WG3/D20_06-1	< 0.2	< 0.4	0.4	6.9	6.5	80.1
1125	WG3/D20_06-2	< 0.2	< 0.4	0.4	6.6	6.2	69.7
1126	WG3/D20_06-3	< 0.2	< 0.4	0.4	6.5	6.1	78.1
1127	WG3/D45_06-0	< 0.2	< 0.4	0.3	5.5	5.2	71.9
1128	WG3/D70_06-0	< 0.2	< 0.4	0.3	5.9	5.6	73.5
1129	WG3/D00_07-0	< 0.2	< 0.4	0.3	7.0	6.7	85.5
1130	WG3/D02_07-1	< 0.2	< 0.4	0.3	5.3	5.0	81.1
1131	WG3/D02_07-2	< 0.2	< 0.4	0.3	5.7	5.4	81.2
1132	WG3/D02_07-3	0.2	< 0.4	0.4	5.8	5.4	82.9
1133	WG3/D04_07-1	< 0.2	< 0.4	0.3	6.6	6.3	86.1
1134	WG3/D04_07-2	< 0.2	1.1	1.2	6.2	5.0	77.5
1135	WG3/D04_07-3	< 0.2	< 0.4	0.3	5.9	5.5	78.6
1136	WG3/D05_07-0	< 0.2	< 0.4	0.3	4.3	4.0	77.2
1137	WG3/D07_07-0	< 0.2	< 0.4	0.3	6.2	5.8	78.8
1138	WG3/D10_07-1	< 0.2	< 0.4	0.3	7.0	6.7	81.3
1139	WG3/D10_07-2	< 0.2	< 0.4	0.3	7.1	6.8	80.0
1140	WG3/D10_07-3	< 0.2	< 0.4	0.3	7.6	7.2	78.2
1141	WG3/D15_07-1	< 0.2	< 0.4	0.4	6.4	6.0	81.7
1142	WG3/D15_07-2	< 0.2	< 0.4	0.4	6.5	6.1	78.8
1143	WG3/D15_07-3	< 0.2	< 0.4	0.4	6.1	5.7	82.2
1144	WG3/D20_07-1	< 0.2	< 0.4	0.4	6.8	6.4	79.8

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1145	WG3/D20_07-2	< 0.2	< 0.4	0.4	7.0	6.6	78.9
1146	WG3/D20_07-3	< 0.2	< 0.4	0.4	6.7	6.4	82.0
1147	WG3/D45_07-0	< 0.2	< 0.4	0.3	6.0	5.7	79.8
1148	WG3/D70_07-0	< 0.2	< 0.4	0.3	5.9	5.6	77.1
1149	WG3/D00_08-0	< 0.2	< 0.4	0.3	6.5	6.1	86.3
1150	WG3/D02_08-1	0.3	< 0.4	0.4	7.5	7.0	82.7
1151	WG3/D02_08-2	< 0.2	< 0.4	0.3	6.8	6.5	83.7
1152	WG3/D02_08-3	0.3	< 0.4	0.4	6.3	5.9	83.8
1153	WG3/D04_08-1	< 0.2	< 0.4	0.3	6.0	5.7	81.7
1154	WG3/D04_08-2	< 0.2	< 0.4	0.3	6.2	5.9	76.0
1155	WG3/D04_08-3	< 0.2	< 0.4	0.3	6.7	6.4	76.6
1156	WG3/D05_08-0	< 0.2	< 0.4	0.3	6.3	5.9	83.1
1157	WG3/D07_08-0	< 0.2	< 0.4	0.3	5.7	5.4	78.9
1158	WG3/D10_08-1	< 0.2	< 0.4	0.3	6.6	6.3	76.9
1159	WG3/D10_08-2	< 0.2	< 0.4	0.3	6.8	6.5	76.7
1160	WG3/D10_08-3	< 0.2	< 0.4	0.3	6.7	6.4	77.2
1161	WG3/D15_08-1	< 0.2	< 0.4	0.4	7.3	6.9	76.8
1162	WG3/D15_08-2	< 0.2	< 0.4	0.4	6.8	6.4	76.8
1163	WG3/D15_08-3	< 0.2	< 0.4	0.4	6.7	6.3	75.8
1164	WG3/D20_08-1	< 0.2	< 0.4	0.4	6.4	6.0	83.9
1165	WG3/D20_08-2	< 0.2	< 0.4	0.4	6.6	6.2	78.0
1166	WG3/D20_08-3	< 0.2	< 0.4	0.4	6.5	6.1	78.4
1167	WG3/D45_08-0	< 0.2	0.4	0.5	6.2	5.7	71.9
1168	WG3/D70_08-0	0.3	0.4	0.8	6.1	5.3	71.5
1169	WG3/D00_09-0	< 0.2	< 0.4	0.3	6.7	6.4	86.1
1170	WG3/D02_09-1	0.3	< 0.4	0.5	7.3	6.8	88.6
1171	WG3/D02_09-2	0.3	< 0.4	0.5	6.8	6.3	82.4
1172	WG3/D02_09-3	0.3	< 0.4	0.4	7.0	6.5	86.1
1173	WG3/D04_09-1	< 0.2	< 0.4	0.3	6.5	6.2	79.2
1174	WG3/D04_09-2	< 0.2	< 0.4	0.3	6.3	5.9	77.1
1175	WG3/D04_09-3	< 0.2	< 0.4	0.3	5.9	5.6	79.5
1176	WG3/D05_09-0	< 0.2	< 0.4	0.3	6.5	6.2	86.3
1177	WG3/D07_09-0	< 0.2	< 0.4	0.3	5.6	5.2	82.3
1178	WG3/D10_09-1	< 0.2	< 0.4	0.3	8.0	7.6	83.6
1179	WG3/D10_09-2	< 0.2	< 0.4	0.3	6.5	6.2	76.1
1180	WG3/D10_09-3	< 0.2	< 0.4	0.3	7.2	6.9	78.2
1181	WG3/D15_09-1	< 0.2	< 0.4	0.4	7.6	7.2	85.8
1182	WG3/D15_09-2	< 0.2	< 0.4	0.4	6.4	6.0	85.3
1183	WG3/D15_09-3	< 0.2	< 0.4	0.4	6.6	6.2	87.3
1184	WG3/D20_09-1	< 0.2	< 0.4	0.4	7.0	6.6	84.5
1185	WG3/D20_09-2	< 0.2	< 0.4	0.4	7.0	6.7	82.3
1186	WG3/D20_09-3	< 0.2	< 0.4	0.4	6.5	6.1	80.8
1187	WG3/D45_09-0	< 0.2	1.6	1.7	6.6	4.9	77.1
1188	WG3/D70_09-0	< 0.2	0.9	1.1	5.9	4.9	79.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1189	WG3/D00_10-0	< 0.2	5.1	5.2	12.0	6.8	87.4
1190	WG3/D02_10-1	< 0.2	4.8	4.9	10.6	5.7	84.7
1191	WG3/D02_10-2	< 0.2	4.9	5.1	11.2	6.1	81.1
1192	WG3/D02_10-3	< 0.2	5.1	5.2	10.2	5.0	78.0
1193	WG3/D04_10-1	< 0.2	5.2	5.4	10.2	4.8	77.4
1194	WG3/D04_10-2	< 0.2	5.3	5.4	10.0	4.6	75.4
1195	WG3/D04_10-3	< 0.2	5.3	5.4	10.1	4.7	80.1
1196	WG3/D05_10-0	< 0.2	3.6	3.8	9.0	5.2	75.8
1197	WG3/D07_10-0	< 0.2	5.2	5.4	9.6	4.2	73.8
1198	WG3/D10_10-1	< 0.2	5.2	5.3	11.1	5.8	78.6
1199	WG3/D10_10-2	< 0.2	5.4	5.5	11.0	5.5	75.4
1200	WG3/D10_10-3	< 0.2	5.2	5.3	10.8	5.4	78.1
1201	WG3/D15_10-1	< 0.2	5.5	5.6	10.6	4.9	78.0
1202	WG3/D15_10-2	< 0.2	5.3	5.4	10.3	4.9	77.8
1203	WG3/D15_10-3	< 0.2	5.3	5.4	11.1	5.7	77.3
1204	WG3/D20_10-1	< 0.2	5.4	5.6	11.3	5.7	79.6
1205	WG3/D20_10-2	< 0.2	5.6	5.7	11.7	6.0	79.6
1206	WG3/D20_10-3	< 0.2	5.4	5.5	11.4	5.9	80.6
1207	WG3/D45_10-0	< 0.2	4.8	4.9	11.4	6.5	74.1
1208	WG3/D70_10-0	< 0.2	4.9	5.1	10.3	5.2	73.1
1209	WG3/D00_11-0	< 0.2	< 0.4	0.3	7.2	6.8	84.8
1210	WG3/D02_11-1	< 0.2	< 0.4	0.3	6.7	6.4	79.8
1211	WG3/D02_11-2	< 0.2	< 0.4	0.3	6.3	6.0	78.5
1212	WG3/D02_11-3	< 0.2	< 0.4	0.3	6.1	5.8	79.0
1213	WG3/D04_11-1	< 0.2	< 0.4	0.3	6.6	6.2	73.7
1214	WG3/D04_11-2	< 0.2	< 0.4	0.3	5.9	5.6	75.8
1215	WG3/D04_11-3	< 0.2	< 0.4	0.3	6.0	5.7	75.7
1216	WG3/D05_11-0	< 0.2	< 0.4	0.3	5.3	5.0	66.3
1217	WG3/D07_11-0	< 0.2	< 0.4	0.3	5.0	4.7	62.1
1218	WG3/D10_11-1	< 0.2	0.6	0.7	7.1	6.4	79.5
1219	WG3/D10_11-2	< 0.2	< 0.4	0.3	6.6	6.3	77.7
1220	WG3/D10_11-3	< 0.2	< 0.4	0.3	7.2	6.9	77.7
1221	WG3/D15_11-1	< 0.2	< 0.4	0.4	6.7	6.3	86.2
1222	WG3/D15_11-2	< 0.2	< 0.4	0.4	7.3	6.9	81.9
1223	WG3/D15_11-3	< 0.2	< 0.4	0.4	7.2	6.8	83.2
1224	WG3/D20_11-1	< 0.2	< 0.4	0.4	7.2	6.8	76.1
1225	WG3/D20_11-2	< 0.2	< 0.4	0.4	7.4	7.0	74.3
1226	WG3/D20_11-3	< 0.2	< 0.4	0.4	7.3	6.9	77.3
1227	WG3/D45_11-0	< 0.2	0.4	0.6	6.3	5.8	69.9
1228	WG3/D70_11-0	< 0.2	0.4	0.6	6.6	6.0	70.3
1229	WG3/D00_12-0	< 0.2	< 0.4	0.3	6.3	6.0	87.9
1230	WG3/D02_12-1	0.3	< 0.4	0.5	6.5	6.1	80.3
1231	WG3/D02_12-2	0.3	< 0.4	0.4	6.5	6.1	80.4
1232	WG3/D02_12-3	0.4	< 0.4	0.5	6.2	5.7	81.0

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1233	WG3/D04_12-1	< 0.2	< 0.4	0.3	6.5	6.1	81.0
1234	WG3/D04_12-2	< 0.2	< 0.4	0.3	6.5	6.2	78.7
1235	WG3/D04_12-3	< 0.2	< 0.4	0.3	6.1	5.7	79.7
1236	WG3/D05_12-0	< 0.2	< 0.4	0.3	5.5	5.1	73.0
1237	WG3/D07_12-0	< 0.2	< 0.4	0.3	5.9	5.5	73.6
1238	WG3/D10_12-1	< 0.2	< 0.4	0.3	6.6	6.3	79.4
1239	WG3/D10_12-2	< 0.2	< 0.4	0.3	6.4	6.1	77.1
1240	WG3/D10_12-3	< 0.2	< 0.4	0.3	6.3	5.9	81.4
1241	WG3/D15_12-1	< 0.2	< 0.4	0.4	7.1	6.7	84.9
1242	WG3/D15_12-2	< 0.2	< 0.4	0.4	7.5	7.1	83.0
1243	WG3/D15_12-3	< 0.2	< 0.4	0.4	6.2	5.9	81.5
1244	WG3/D20_12-1	< 0.2	< 0.4	0.4	6.7	6.3	78.9
1245	WG3/D20_12-2	< 0.2	< 0.4	0.4	7.3	6.9	77.4
1246	WG3/D20_12-3	< 0.2	< 0.4	0.4	6.6	6.2	70.0
1247	WG3/D45_12-0	< 0.2	0.5	0.6	5.5	4.9	75.4
1248	WG3/D70_12-0	0.7	< 0.4	0.8	5.8	5.0	74.9
1249	WG3/D00_13-0	< 0.2	< 0.4	0.3	6.6	6.3	82.1
1250	WG3/D02_13-1	0.4	< 0.4	0.6	7.2	6.6	83.4
1251	WG3/D02_13-2	0.4	< 0.4	0.6	6.3	5.7	79.0
1252	WG3/D02_13-3	0.4	< 0.4	0.6	7.5	6.9	83.5
1253	WG3/D04_13-1	< 0.2	< 0.4	0.3	6.7	6.4	75.5
1254	WG3/D04_13-2	< 0.2	< 0.4	0.3	6.9	6.6	75.6
1255	WG3/D04_13-3	< 0.2	< 0.4	0.3	6.0	5.7	76.7
1256	WG3/D05_13-0	< 0.2	< 0.4	0.3	6.6	6.3	82.2
1257	WG3/D07_13-0	< 0.2	< 0.4	0.3	6.6	6.3	78.8
1258	WG3/D10_13-1	< 0.2	< 0.4	0.3	7.1	6.7	86.7
1259	WG3/D10_13-2	< 0.2	< 0.4	0.3	6.5	6.2	81.2
1260	WG3/D10_13-3	< 0.2	< 0.4	0.3	6.6	6.3	83.6
1261	WG3/D15_13-1	< 0.2	< 0.4	0.4	7.3	6.9	87.2
1262	WG3/D15_13-2	< 0.2	< 0.4	0.4	6.3	5.9	81.5
1263	WG3/D15_13-3	< 0.2	< 0.4	0.4	6.2	5.8	81.7
1264	WG3/D20_13-1	< 0.2	< 0.4	0.4	6.9	6.5	80.1
1265	WG3/D20_13-2	< 0.2	< 0.4	0.4	6.6	6.2	69.7
1266	WG3/D20_13-3	< 0.2	< 0.4	0.4	6.5	6.1	78.1
1267	WG3/D45_13-0	< 0.2	< 0.4	0.4	6.2	5.8	73.9
1268	WG3/D70_13-0	0.5	< 0.4	0.7	5.6	4.9	70.7
1269	WG3/D00_14-0	< 0.2	< 0.4	0.3	6.7	6.3	85.2
1270	WG3/D02_14-1	0.4	< 0.4	0.6	7.2	6.6	80.2
1271	WG3/D02_14-2	0.3	< 0.4	0.4	6.9	6.4	82.3
1272	WG3/D02_14-3	0.5	< 0.4	0.7	6.3	5.7	81.4
1273	WG3/D04_14-1	< 0.2	< 0.4	0.3	5.9	5.6	81.5
1274	WG3/D04_14-2	< 0.2	< 0.4	0.3	6.1	5.8	72.2
1275	WG3/D04_14-3	< 0.2	< 0.4	0.3	6.3	6.0	78.6
1276	WG3/D05_14-0	< 0.2	< 0.4	0.3	5.8	5.4	88.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1277	WG3/D07_14-0	< 0.2	< 0.4	0.3	6.6	6.3	80.8
1278	WG3/D10_14-1	< 0.2	< 0.4	0.3	7.3	7.0	89.2
1279	WG3/D10_14-2	< 0.2	< 0.4	0.3	7.1	6.8	86.0
1280	WG3/D10_14-3	< 0.2	< 0.4	0.3	7.4	7.1	86.2
1281	WG3/D15_14-1	< 0.2	< 0.4	0.4	7.1	6.7	86.1
1282	WG3/D15_14-2	< 0.2	< 0.4	0.4	6.7	6.3	84.8
1283	WG3/D15_14-3	< 0.2	< 0.4	0.4	6.9	6.5	86.8
1284	WG3/D20_14-1	< 0.2	< 0.4	0.4	6.8	6.4	79.8
1285	WG3/D20_14-2	< 0.2	< 0.4	0.4	7.0	6.6	78.9
1286	WG3/D20_14-3	< 0.2	< 0.4	0.4	6.7	6.4	82.0
1287	WG3/D45_14-0	0.3	0.5	0.8	6.6	5.8	79.1
1288	WG3/D70_14-0	0.3	0.6	0.8	6.2	5.4	76.7
1289	DS3/D00_01-0	2.7	< 0.4	3.0	9.0	6.0	92.3
1290	DS3/D02_01-1	2.7	< 0.4	2.8	9.7	6.8	83.5
1291	DS3/D02_01-2	2.7	< 0.4	2.8	8.7	5.9	74.7
1292	DS3/D02_01-3	2.6	< 0.4	2.8	8.3	5.5	74.9
1293	DS3/D04_01-1	2.9	< 0.4	3.1	6.4	3.2	63.1
1294	DS3/D04_01-2	2.7	< 0.4	2.9	6.9	3.9	62.1
1295	DS3/D04_01-3	2.7	< 0.4	3.0	7.0	4.0	61.5
1296	DS3/D05_01-0	3.0	< 0.4	3.1	8.1	5.0	74.8
1297	DS3/D07_01-0	2.5	< 0.4	2.7	7.1	4.5	65.5
1298	DS3/D10_01-1	3.0	0.5	3.5	9.4	5.9	83.2
1299	DS3/D10_01-2	2.5	< 0.4	2.7	8.9	6.2	83.5
1300	DS3/D10_01-3	2.5	< 0.4	2.7	8.9	6.1	83.4
1301	DS3/D15_01-1	2.9	0.7	3.6	9.8	6.2	73.6
1302	DS3/D15_01-2	2.7	0.8	3.5	9.0	5.4	72.8
1303	DS3/D15_01-3	2.8	0.7	3.4	8.9	5.4	72.4
1304	DS3/D20_01-1	2.9	< 0.4	3.0	8.0	4.9	85.4
1305	DS3/D20_01-2	2.9	0.5	3.4	7.9	4.5	83.7
1306	DS3/D20_01-3	2.7	< 0.4	2.8	8.6	5.7	78.0
1307	DS3/D45_01-0	4.6	1.1	5.7	10.4	4.7	64.8
1308	DS3/D70_01-0	3.8	1.5	5.3	11.2	5.9	79.5
1309	DS3/D00_02-0	2.6	1.6	4.2	8.1	3.9	93.4
1310	DS3/D02_02-1	2.5	0.7	3.3	8.4	5.2	94.7
1311	DS3/D02_02-2	2.5	0.9	3.4	8.6	5.2	91.2
1312	DS3/D02_02-3	2.4	0.9	3.3	8.2	4.9	87.7
1313	DS3/D04_02-1	2.6	1.1	3.6	6.8	3.1	83.6
1314	DS3/D04_02-2	2.4	< 0.4	2.6	6.9	4.3	74.5
1315	DS3/D04_02-3	2.3	0.8	3.0	6.3	3.3	79.2
1316	DS3/D05_02-0	2.6	0.7	3.3	7.3	4.0	95.4
1317	DS3/D07_02-0	2.8	0.6	3.3	6.8	3.5	83.4
1318	DS3/D10_02-1	2.4	0.8	3.2	9.2	5.9	102.1
1319	DS3/D10_02-2	2.5	0.9	3.3	9.1	5.7	102.6
1320	DS3/D10_02-3	2.5	0.8	3.2	8.7	5.4	104.6

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1321	DS3/D15_02-1	2.6	0.6	3.2	8.8	5.6	92.0
1322	DS3/D15_02-2	2.6	0.5	3.1	8.6	5.5	87.9
1323	DS3/D15_02-3	2.6	0.9	3.6	8.5	4.9	90.8
1324	DS3/D20_02-1	2.6	< 0.4	2.8	8.3	5.4	90.3
1325	DS3/D20_02-2	3.0	0.9	3.9	8.6	4.7	84.8
1326	DS3/D20_02-3	2.6	< 0.4	2.8	8.3	5.5	87.3
1327	DS3/D45_02-0	5.8	1.5	7.3	9.2	1.9	89.9
1328	DS3/D70_02-0	3.2	1.5	4.7	8.2	3.5	84.0
1329	DS3/D00_03-0	2.6	5.0	7.6	13.6	6.0	83.8
1330	DS3/D02_03-1	2.7	4.9	7.6	12.9	5.3	73.5
1331	DS3/D02_03-2	2.7	4.9	7.7	12.5	4.9	71.6
1332	DS3/D02_03-3	2.7	4.8	7.4	11.4	4.0	70.5
1333	DS3/D04_03-1	2.7	4.9	7.6	11.1	3.5	59.7
1334	DS3/D04_03-2	2.6	5.0	7.6	9.3	1.7	57.9
1335	DS3/D04_03-3	2.6	4.8	7.4	9.4	2.0	56.1
1336	DS3/D05_03-0	2.5	4.1	6.6	11.4	4.7	72.2
1337	DS3/D07_03-0	2.6	4.1	6.7	11.3	4.7	63.3
1338	DS3/D10_03-1	2.5	4.7	7.2	14.4	7.2	83.2
1339	DS3/D10_03-2	2.6	4.7	7.3	13.5	6.1	88.6
1340	DS3/D10_03-3	2.8	5.1	7.9	13.8	5.9	85.9
1341	DS3/D15_03-1	2.9	6.0	8.9	13.7	4.8	68.6
1342	DS3/D15_03-2	2.9	5.7	8.6	13.6	5.1	68.9
1343	DS3/D15_03-3	2.5	4.5	7.0	14.3	7.3	72.0
1344	DS3/D20_03-1	2.2	3.8	6.0	13.7	7.7	81.3
1345	DS3/D20_03-2	3.0	5.7	8.7	13.4	4.7	75.2
1346	DS3/D20_03-3	3.0	5.4	8.4	13.1	4.7	66.7
1347	DS3/D45_03-0	3.3	5.6	8.9	15.3	6.4	63.0
1348	DS3/D70_03-0	3.6	5.9	9.5	15.8	6.2	69.2
1349	DS3/D00_04-0	2.7	< 0.4	2.9	9.5	6.6	79.2
1350	DS3/D02_04-1	2.8	< 0.4	2.9	8.1	5.2	71.4
1351	DS3/D02_04-2	2.7	< 0.4	2.8	8.5	5.7	70.0
1352	DS3/D02_04-3	2.7	< 0.4	2.8	9.0	6.2	72.6
1353	DS3/D04_04-1	2.5	< 0.4	2.7	7.0	4.2	62.2
1354	DS3/D04_04-2	2.6	< 0.4	2.9	7.4	4.6	55.5
1355	DS3/D04_04-3	2.5	< 0.4	2.7	7.3	4.5	58.5
1356	DS3/D05_04-0	2.9	< 0.4	3.1	8.6	5.6	74.5
1357	DS3/D07_04-0	2.0	< 0.4	2.2	5.7	3.5	52.9
1358	DS3/D10_04-1	2.5	< 0.4	2.8	8.5	5.7	86.3
1359	DS3/D10_04-2	2.7	< 0.4	2.9	8.3	5.4	89.7
1360	DS3/D10_04-3	2.7	< 0.4	2.9	8.0	5.1	88.4
1361	DS3/D15_04-1	2.8	< 0.4	2.9	9.4	6.5	70.3
1362	DS3/D15_04-2	2.8	< 0.4	2.9	9.1	6.2	67.8
1363	DS3/D15_04-3	2.8	< 0.4	3.0	8.6	5.7	72.5
1364	DS3/D20_04-1	2.8	< 0.4	2.9	8.4	5.4	71.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1365	DS3/D20_04-2	3.0	1.0	4.0	8.0	4.0	69.8
1366	DS3/D20_04-3	2.8	< 0.4	3.0	8.1	5.1	70.3
1367	DS3/D45_04-0	3.5	0.8	4.3	10.5	6.2	67.4
1368	DS3/D70_04-0	3.7	0.9	4.6	10.5	5.9	67.1
1369	DS3/D00_05-0	2.6	0.5	3.1	9.6	6.5	88.6
1370	DS3/D02_05-1	2.6	< 0.4	2.7	8.9	6.2	67.7
1371	DS3/D02_05-2	2.7	< 0.4	2.9	8.8	5.9	71.7
1372	DS3/D02_05-3	2.7	< 0.4	2.8	8.2	5.4	73.9
1373	DS3/D04_05-1	2.5	< 0.4	2.7	8.5	5.7	78.0
1374	DS3/D04_05-2	2.7	< 0.4	2.9	7.3	4.3	89.9
1375	DS3/D04_05-3	2.7	< 0.4	3.0	7.7	4.7	73.1
1376	DS3/D05_05-0	2.8	< 0.4	3.0	8.5	5.5	73.4
1377	DS3/D07_05-0	2.9	< 0.4	3.1	7.5	4.4	69.1
1378	DS3/D10_05-1	2.6	< 0.4	2.8	8.2	5.4	86.4
1379	DS3/D10_05-2	2.6	< 0.4	2.9	8.7	5.8	85.0
1380	DS3/D10_05-3	2.6	< 0.4	2.9	8.9	6.0	83.8
1381	DS3/D15_05-1	1.1	< 0.4	1.3	7.5	6.2	69.4
1382	DS3/D15_05-2	1.0	< 0.4	1.2	6.2	5.0	67.2
1383	DS3/D15_05-3	1.0	< 0.4	1.2	6.7	5.4	66.6
1384	DS3/D20_05-1	< 0.2	< 0.4	0.3	5.6	5.3	74.1
1385	DS3/D20_05-2	< 0.2	< 0.4	0.3	4.6	4.3	72.0
1386	DS3/D20_05-3	< 0.2	< 0.4	0.3	5.3	5.0	75.1
1387	DS3/D45_05-0	0.5	< 0.4	0.7	7.2	6.6	77.0
1388	DS3/D70_05-0	< 0.2	< 0.4	0.3	8.0	7.8	94.8
1389	DS3/D00_06-0	2.6	0.8	3.3	7.3	3.9	92.7
1390	DS3/D02_06-1	2.5	1.0	3.4	8.6	5.2	84.1
1391	DS3/D02_06-2	2.4	0.7	3.1	8.3	5.2	85.7
1392	DS3/D02_06-3	2.4	0.7	3.2	8.3	5.1	89.9
1393	DS3/D04_06-1	2.4	0.7	3.1	8.0	4.9	94.8
1394	DS3/D04_06-2	2.4	0.6	3.0	8.1	5.0	91.8
1395	DS3/D04_06-3	2.3	< 0.4	2.5	8.7	6.2	93.4
1396	DS3/D05_06-0	2.6	0.7	3.2	7.1	3.9	90.2
1397	DS3/D07_06-0	1.8	0.4	2.1	5.0	2.8	64.4
1398	DS3/D10_06-1	2.4	< 0.4	2.6	9.7	7.1	100.1
1399	DS3/D10_06-2	2.5	0.8	3.3	9.6	6.4	100.8
1400	DS3/D10_06-3	2.4	0.6	3.0	9.5	6.5	98.2
1401	DS3/D15_06-1	2.5	< 0.4	2.7	9.0	6.4	86.1
1402	DS3/D15_06-2	2.6	0.6	3.2	9.2	5.9	85.2
1403	DS3/D15_06-3	2.6	0.5	3.1	9.0	5.9	88.2
1404	DS3/D20_06-1	2.4	< 0.4	2.6	8.5	5.9	83.4
1405	DS3/D20_06-2	2.3	< 0.4	2.5	8.8	6.3	86.4
1406	DS3/D20_06-3	2.3	< 0.4	2.5	8.5	6.0	87.0
1407	DS3/D45_06-0	0.7	< 0.4	0.9	6.7	5.8	86.0
1408	DS3/D70_06-0	< 0.2	< 0.4	0.3	6.4	6.2	88.2

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1409	DS3/D00_07-0	4.0	2.0	5.9	11.1	5.1	83.7
1410	DS3/D02_07-1	4.0	< 0.4	4.1	9.7	5.5	65.5
1411	DS3/D02_07-2	3.8	< 0.4	4.0	9.3	5.3	62.3
1412	DS3/D02_07-3	4.0	< 0.4	4.1	9.6	5.4	66.2
1413	DS3/D04_07-1	3.8	< 0.4	4.0	9.2	5.2	71.3
1414	DS3/D04_07-2	3.7	< 0.4	4.0	10.2	6.2	72.0
1415	DS3/D04_07-3	3.6	< 0.4	3.8	10.9	7.1	76.1
1416	DS3/D05_07-0	3.4	< 0.4	3.6	9.2	5.6	72.2
1417	DS3/D07_07-0	1.2	< 0.4	1.4	5.9	4.5	76.1
1418	DS3/D10_07-1	< 0.2	< 0.4	0.3	6.1	5.8	91.8
1419	DS3/D10_07-2	< 0.2	< 0.4	0.4	6.1	5.6	84.6
1420	DS3/D10_07-3	< 0.2	< 0.4	0.3	5.4	5.1	93.6
1421	DS3/D15_07-1	< 0.2	< 0.4	0.3	6.6	6.3	80.6
1422	DS3/D15_07-2	< 0.2	< 0.4	0.3	6.3	5.9	80.9
1423	DS3/D15_07-3	< 0.2	< 0.4	0.3	5.9	5.6	79.2
1424	DS3/D20_07-1	< 0.2	< 0.4	0.3	5.3	5.0	79.7
1425	DS3/D20_07-2	< 0.2	< 0.4	0.3	5.8	5.5	80.2
1426	DS3/D20_07-3	< 0.2	< 0.4	0.3	6.3	6.0	79.4
1427	DS3/D45_07-0	< 0.2	< 0.4	0.3	7.6	7.3	90.3
1428	DS3/D70_07-0	< 0.2	< 0.4	0.3	8.8	8.5	98.0
1429	DS3/D00_08-0	2.7	< 0.4	2.9	9.2	6.3	90.6
1430	DS3/D02_08-1	2.8	< 0.4	3.0	8.6	5.6	66.8
1431	DS3/D02_08-2	2.6	< 0.4	2.7	9.4	6.6	66.3
1432	DS3/D02_08-3	2.6	< 0.4	2.7	8.7	6.0	67.6
1433	DS3/D04_08-1	2.4	< 0.4	2.7	8.6	6.0	78.2
1434	DS3/D04_08-2	2.5	< 0.4	2.7	8.4	5.7	76.5
1435	DS3/D04_08-3	2.5	< 0.4	2.7	9.1	6.4	72.2
1436	DS3/D05_08-0	2.9	0.4	3.2	7.9	4.6	72.3
1437	DS3/D07_08-0	2.3	< 0.4	2.5	6.8	4.3	61.0
1438	DS3/D10_08-1	2.8	< 0.4	3.0	10.1	7.1	81.4
1439	DS3/D10_08-2	2.4	< 0.4	2.7	10.2	7.5	81.9
1440	DS3/D10_08-3	2.6	< 0.4	2.9	9.3	6.4	81.8
1441	DS3/D15_08-1	2.9	< 0.4	3.1	9.6	6.5	82.3
1442	DS3/D15_08-2	2.8	< 0.4	3.0	9.8	6.9	79.1
1443	DS3/D15_08-3	2.8	< 0.4	3.0	9.3	6.3	78.3
1444	DS3/D20_08-1	3.0	0.5	3.5	8.0	4.5	76.0
1445	DS3/D20_08-2	2.7	< 0.4	2.9	8.6	5.7	72.7
1446	DS3/D20_08-3	2.7	< 0.4	2.9	7.9	5.0	68.8
1447	DS3/D45_08-0	3.6	0.9	4.6	10.6	6.1	67.2
1448	DS3/D70_08-0	3.7	1.3	5.1	10.9	5.8	69.9
1449	DS3/D00_09-0	2.6	0.8	3.4	7.5	4.2	98.0
1450	DS3/D02_09-1	2.4	0.4	2.7	8.3	5.5	83.8
1451	DS3/D02_09-2	2.2	0.4	2.6	8.7	6.1	85.8
1452	DS3/D02_09-3	2.3	0.6	2.9	8.5	5.6	85.1

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1453	DS3/D04_09-1	2.2	< 0.4	2.5	9.0	6.6	89.6
1454	DS3/D04_09-2	2.4	0.6	3.0	8.2	5.2	88.0
1455	DS3/D04_09-3	2.2	< 0.4	2.5	8.6	6.1	88.1
1456	DS3/D05_09-0	2.7	0.6	3.2	7.3	4.1	94.3
1457	DS3/D07_09-0	2.1	< 0.4	2.3	6.5	4.2	50.1
1458	DS3/D10_09-1	2.5	< 0.4	2.7	9.8	7.1	103.5
1459	DS3/D10_09-2	2.4	0.7	3.1	9.2	6.2	110.4
1460	DS3/D10_09-3	2.2	< 0.4	2.4	9.7	7.3	102.6
1461	DS3/D15_09-1	2.6	< 0.4	2.8	9.4	6.6	96.0
1462	DS3/D15_09-2	2.4	< 0.4	2.6	9.7	7.1	98.8
1463	DS3/D15_09-3	2.6	< 0.4	2.8	9.1	6.3	92.2
1464	DS3/D20_09-1	2.4	< 0.4	2.6	8.5	5.8	84.4
1465	DS3/D20_09-2	2.5	< 0.4	2.7	8.3	5.6	84.4
1466	DS3/D20_09-3	2.6	< 0.4	2.8	8.3	5.5	79.2
1467	DS3/D45_09-0	3.7	0.6	4.3	9.0	4.6	91.7
1468	DS3/D70_09-0	3.0	0.6	3.6	7.5	3.9	80.3
1469	DS3/D00_10-0	2.7	5.0	7.6	13.2	5.6	83.4
1470	DS3/D02_10-1	2.6	4.9	7.5	11.2	3.6	65.1
1471	DS3/D02_10-2	2.7	4.8	7.5	11.9	4.3	64.0
1472	DS3/D02_10-3	2.6	4.8	7.4	11.7	4.3	60.4
1473	DS3/D04_10-1	2.5	4.0	6.5	13.2	6.7	81.0
1474	DS3/D04_10-2	2.7	5.3	8.0	12.1	4.1	86.8
1475	DS3/D04_10-3	2.5	4.7	7.2	11.9	4.7	78.3
1476	DS3/D05_10-0	2.9	4.8	7.7	12.2	4.5	76.4
1477	DS3/D07_10-0	2.7	4.4	7.2	11.9	4.8	70.0
1478	DS3/D10_10-1	2.7	5.0	7.7	14.6	6.9	98.3
1479	DS3/D10_10-2	2.6	4.8	7.4	13.9	6.5	93.6
1480	DS3/D10_10-3	2.6	4.9	7.5	14.2	6.6	91.4
1481	DS3/D15_10-1	2.9	5.9	8.8	14.9	6.1	75.7
1482	DS3/D15_10-2	2.9	5.7	8.6	14.0	5.5	73.4
1483	DS3/D15_10-3	2.9	5.6	8.5	14.3	5.8	83.0
1484	DS3/D20_10-1	3.0	5.7	8.6	12.8	4.1	69.2
1485	DS3/D20_10-2	2.8	4.9	7.7	12.5	4.7	67.3
1486	DS3/D20_10-3	2.9	5.5	8.4	13.0	4.6	69.1
1487	DS3/D45_10-0	3.6	5.3	8.9	16.1	7.1	71.6
1488	DS3/D70_10-0	3.7	5.9	9.5	15.8	6.2	69.0
1489	DS3/D00_11-0	2.7	< 0.4	2.9	9.1	6.2	87.3
1490	DS3/D02_11-1	2.6	< 0.4	2.7	8.2	5.5	60.2
1491	DS3/D02_11-2	2.7	< 0.4	2.8	6.7	3.9	59.2
1492	DS3/D02_11-3	2.6	< 0.4	2.7	7.2	4.5	60.1
1493	DS3/D04_11-1	2.7	< 0.4	2.9	9.1	6.1	91.8
1494	DS3/D04_11-2	2.5	< 0.4	2.7	8.6	5.9	74.1
1495	DS3/D04_11-3	2.5	< 0.4	2.7	9.1	6.4	79.6
1496	DS3/D05_11-0	2.9	< 0.4	3.0	8.2	5.2	73.3

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1497	DS3/D07_11-0	2.6	< 0.4	2.8	8.2	5.4	73.7
1498	DS3/D10_11-1	2.5	< 0.4	2.7	9.4	6.7	87.0
1499	DS3/D10_11-2	1.9	< 0.4	2.1	8.9	6.8	88.0
1500	DS3/D10_11-3	2.1	< 0.4	2.4	9.6	7.3	88.7
1501	DS3/D15_11-1	2.7	< 0.4	2.9	9.6	6.7	77.7
1502	DS3/D15_11-2	2.6	< 0.4	2.7	10.2	7.4	86.2
1503	DS3/D15_11-3	2.8	< 0.4	3.0	9.6	6.6	77.0
1504	DS3/D20_11-1	2.8	< 0.4	3.0	8.3	5.4	72.2
1505	DS3/D20_11-2	2.8	< 0.4	3.0	8.4	5.4	70.4
1506	DS3/D20_11-3	2.6	< 0.4	2.8	8.3	5.5	75.3
1507	DS3/D45_11-0	3.2	0.7	3.9	11.2	7.4	66.0
1508	DS3/D70_11-0	3.9	0.9	4.8	11.2	6.4	70.6
1509	DS3/D00_12-0	2.6	< 0.4	2.9	9.8	6.9	87.1
1510	DS3/D02_12-1	2.5	< 0.4	2.6	6.3	3.8	53.9
1511	DS3/D02_12-2	2.6	< 0.4	2.7	7.0	4.2	53.4
1512	DS3/D02_12-3	2.7	< 0.4	2.8	6.5	3.7	53.6
1513	DS3/D04_12-1	2.6	< 0.4	2.9	8.5	5.7	72.6
1514	DS3/D04_12-2	2.7	< 0.4	3.0	8.6	5.7	81.4
1515	DS3/D04_12-3	2.5	< 0.4	2.8	8.6	5.8	76.3
1516	DS3/D05_12-0	3.0	< 0.4	3.2	7.9	4.7	71.7
1517	DS3/D07_12-0	2.3	< 0.4	2.5	6.5	3.9	55.3
1518	DS3/D10_12-1	1.7	< 0.4	2.0	9.7	7.7	90.6
1519	DS3/D10_12-2	2.5	< 0.4	2.7	9.2	6.5	82.0
1520	DS3/D10_12-3	2.7	< 0.4	2.9	9.4	6.5	82.0
1521	DS3/D15_12-1	2.5	< 0.4	2.7	9.3	6.6	78.0
1522	DS3/D15_12-2	2.3	< 0.4	2.5	9.5	7.0	82.9
1523	DS3/D15_12-3	2.3	< 0.4	2.5	9.0	6.4	84.5
1524	DS3/D20_12-1	< 0.2	< 0.4	0.3	5.1	4.8	85.4
1525	DS3/D20_12-2	< 0.2	< 0.4	0.3	4.7	4.4	89.9
1526	DS3/D20_12-3	0.3	< 0.4	0.5	4.9	4.4	92.5
1527	DS3/D45_12-0	0.4	< 0.4	0.5	8.1	7.5	71.6
1528	DS3/D70_12-0	0.3	< 0.4	0.4	7.6	7.1	87.5
1529	DS3/D00_13-0	2.5	1.3	3.8	7.6	3.8	97.2
1530	DS3/D02_13-1	2.3	0.8	3.1	7.2	4.1	83.8
1531	DS3/D02_13-2	2.3	0.9	3.1	6.9	3.8	74.5
1532	DS3/D02_13-3	2.3	0.8	3.1	7.2	4.1	83.0
1533	DS3/D04_13-1	2.3	0.6	2.9	9.7	6.8	90.6
1534	DS3/D04_13-2	2.4	1.0	3.4	8.5	5.1	95.3
1535	DS3/D04_13-3	2.4	0.9	3.3	9.0	5.6	93.4
1536	DS3/D05_13-0	2.6	0.6	3.2	7.2	4.1	91.4
1537	DS3/D07_13-0	2.2	< 0.4	2.4	6.4	4.0	80.0
1538	DS3/D10_13-1	2.4	0.7	3.1	9.6	6.5	95.7
1539	DS3/D10_13-2	2.1	0.5	2.6	10.0	7.4	102.3
1540	DS3/D10_13-3	2.2	< 0.4	2.4	9.7	7.3	95.0

2) Continued.

Sample	Sample identification	TOxN	Ammonium	DIN	TDN	DON	DOC
1541	DS3/D15_13-1	2.6	0.7	3.3	9.6	6.3	88.8
1542	DS3/D15_13-2	2.6	0.5	3.1	9.7	6.7	88.4
1543	DS3/D15_13-3	2.7	0.4	3.1	9.6	6.5	88.5
1544	DS3/D20_13-1	2.3	< 0.4	2.5	8.6	6.1	98.8
1545	DS3/D20_13-2	2.3	< 0.4	2.4	8.3	5.9	94.8
1546	DS3/D20_13-3	2.0	< 0.4	2.2	8.3	6.1	96.1
1547	DS3/D45_13-0	0.6	< 0.4	0.8	6.5	5.7	80.3
1548	DS3/D70_13-0	0.4	< 0.4	0.5	7.5	7.0	88.3
1549	DS3/D00_14-0	4.0	1.7	5.7	11.2	5.5	83.3
1550	DS3/D02_14-1	3.7	< 0.4	3.8	8.1	4.3	55.3
1551	DS3/D02_14-2	3.8	< 0.4	3.9	8.5	4.6	53.7
1552	DS3/D02_14-3	3.7	< 0.4	3.8	8.1	4.3	54.1
1553	DS3/D04_14-1	3.8	< 0.4	4.0	10.3	6.3	84.1
1554	DS3/D04_14-2	3.8	< 0.4	4.0	9.3	5.3	81.2
1555	DS3/D04_14-3	3.9	< 0.4	4.2	10.5	6.3	92.1
1556	DS3/D05_14-0	3.6	< 0.4	3.8	9.5	5.6	76.2
1557	DS3/D07_14-0	1.2	< 0.4	1.4	6.4	5.0	66.0
1558	DS3/D10_14-1	< 0.2	< 0.4	0.2	6.3	6.1	90.6
1559	DS3/D10_14-2	< 0.2	< 0.4	0.2	6.7	6.5	86.8
1560	DS3/D10_14-3	< 0.2	< 0.4	0.3	6.3	6.0	88.2
1561	DS3/D15_14-1	0.3	< 0.4	0.5	7.3	6.9	87.5
1562	DS3/D15_14-2	< 0.2	< 0.4	0.3	7.6	7.3	94.2
1563	DS3/D15_14-3	< 0.2	< 0.4	0.3	7.4	7.1	86.7
1564	DS3/D20_14-1	< 0.2	< 0.4	0.3	5.7	5.4	99.4
1565	DS3/D20_14-2	< 0.2	< 0.4	0.3	5.8	5.5	92.6
1566	DS3/D20_14-3	< 0.2	< 0.4	0.3	5.9	5.6	96.2
1567	DS3/D45_14-0	0.6	< 0.4	0.8	9.2	8.4	85.6
1568	DS3/D70_14-0	0.4	< 0.4	0.5	9.7	9.1	98.7

< 0.2 and < 0.4 = less than the detection limit of UEA instrument

Appendix 4.2: Chlorophyll *a* concentrations of incubation experiments.

1) Incubation experiments in summer 2012.

Station	Chlorophyll *a* concentration (µg/L)							
	Before the start of the incubation		At the end of the incubation					
	Unfiltered	200 µm filtered	T1	T2	T3	T4	T5	T6
WG set 1	1.3	1.2	< 0.1	0.1	< 0.1	< 0.1	0.3	0.1
WG set 2	1.5	1.5	0.5	0.6	0.3	0.4	1.2	0.4
9 set 1	0.7	0.7	0.3	0.3	0.2	0.2	0.3	0.8
9 set 2	0.7	0.7	0.2	0.3	0.2	0.1	0.6	0.6
24 set 1	0.5	0.4	0.1	0.3	0.1	0.2	0.6	0.5
24 set 2	0.5	0.5	0.1	0.2	0.1	0.2	0.7	0.7

The detection limit of the measurement is 0.1 µg/L (UEA instrument).

2) Incubation experiments in autumn 2013, winter 2013 and spring 2014.

Station	Chlorophyll *a* concentration (µg/L)									
	Before the start of the incubation			At the end of the incubation						
	Unfiltered	200 µm filtered	1.0 µm filtered	T1	T2	T3	T4	T5	T6	T7
West Gabbard										
Autumn set 1	1.4	1.4	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	8.9	< 0.1	4.9
Autumn set 2	1.4	1.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	7.7	< 0.1	3.3
Mean	*1.4*	*1.5*	*na*	*na*	*na*	*na*	*na*	*8.3*	*na*	*4.1*
SD	*0.0*	*0.0*	*na*	*na*	*na*	*na*	*na*	*0.9*	*na*	*1.1*
Winter set 1	0.9	0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	7.6
Winter set 2	0.8	0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	6.7
Mean	*0.8*	*0.8*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*7.2*
SD	*0.0*	*0.0*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*0.6*
Spring set 1	2.0	2.0	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.6
Spring set 2	2.2	2.0	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.5
Mean	*2.1*	*2.0*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*0.6*
SD	*0.1*	*0.0*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*0.1*
Dowsing										
Autumn set 1	2.0	1.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.2	< 0.1	0.3
Autumn set 2	2.0	1.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.4	< 0.1	0.4
Mean	*2.0*	*1.8*	*na*	*na*	*na*	*na*	*na*	*1.3*	*na*	*0.4*
SD	*0.0*	*0.0*	*na*	*na*	*na*	*na*	*na*	*0.1*	*na*	*0.0*
Winter set 1	0.6	0.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	7.0
Winter set 2	0.7	0.8	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	7.6
Mean	*0.7*	*0.7*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*7.3*
SD	*0.1*	*0.1*	*na*	*na*	*na*	*na*	*na*	*na*	*na*	*0.4*
Spring set 1	2.2	2.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	4.8	< 0.1	0.7
Spring set 2	2.2	2.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2.9	< 0.1	1.1
Mean	*2.2*	*2.3*	*na*	*na*	*na*	*na*	*na*	*3.8*	*na*	*0.9*
SD	*0.0*	*0.0*	*na*	*na*	*na*	*na*	*na*	*1.4*	*na*	*0.3*

The detection limit of the measurement is 0.1 µg/L (UEA instrument).
Mean = mean concentration of duplicate incubation bottles (set 1 and set 2)
SD = standard deviation of duplicate incubation bottles (set 1 and set 2)
na = data is not available

Appendix 4.3: Initial mean inorganic nutrient concentration (µM) of incubated water in autumn 2013, winter 2013 and spring 2014.

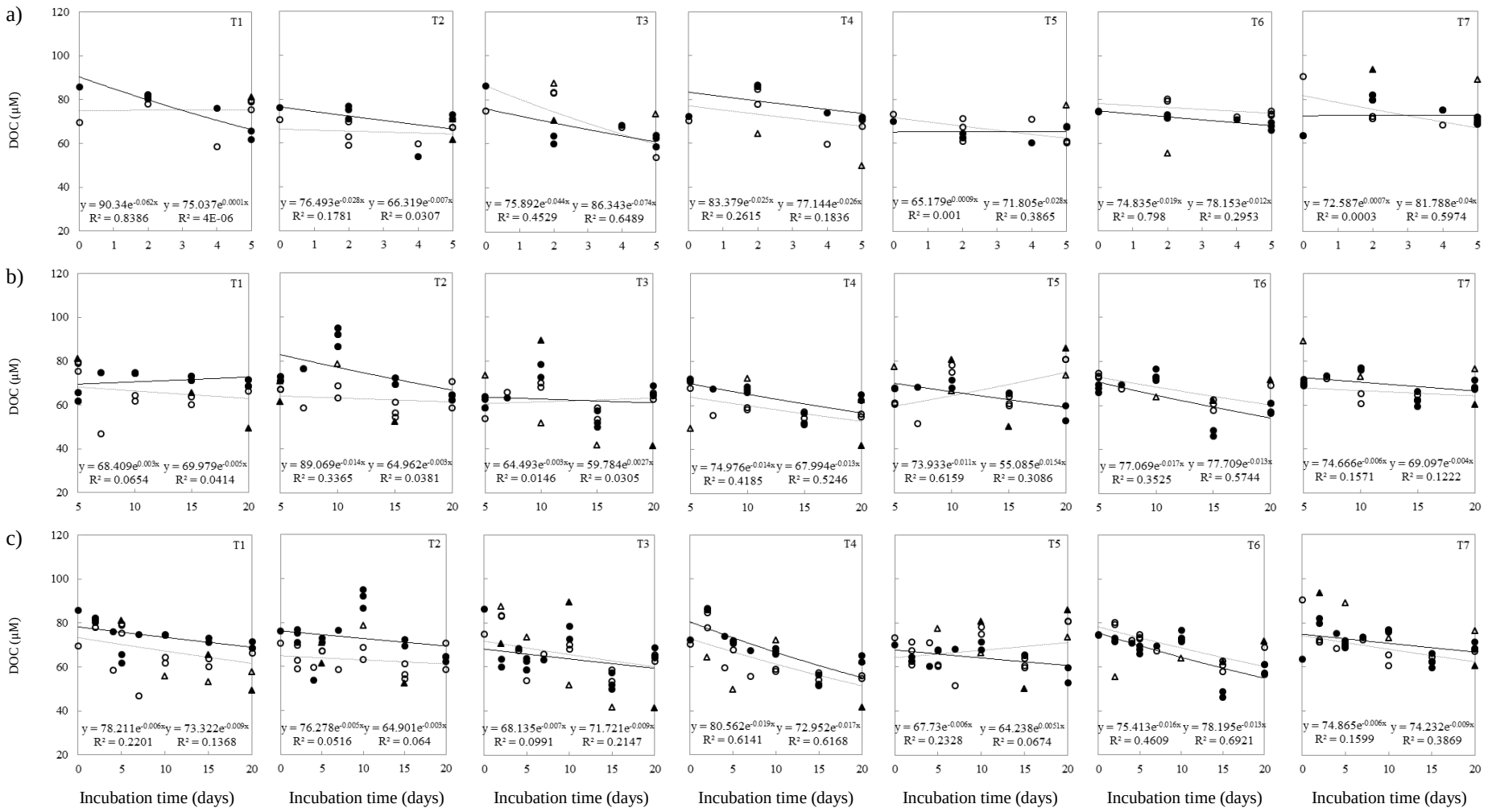
Nutrients	Station	Season	Concentration (Mean ± SD [a])						
			T1	T2	T3	T4	T5	T6	T7
Phosphate	WG	Autumn	0.6 ± 0.0	0.5 ± 0.0	0.4 ± 0.0	0.3 ± 0.3	0.6 ± 0.0	0.5 ± 0.0	0.5 ± 0.1
		Winter	0.4 ± 0.2	0.5 ± 0.1	0.5 ± 0.1	0.5 ± 0.0	0.5 ± 0.1	0.5 ± 0.0	0.5 ± 0.1
		Spring	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.1 ± 0.0
	DS	Autumn	0.3 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	0.7 ± 0.1	< 0.1 [b]	0.3 ± 0.0	0.2 ± 0.1
		Winter	0.5 ± 0.1	0.6 ± 0.0	0.5 ± 0.0	0.6 ± 0.0	0.6 ± 0.0	0.5 ± 0.0	0.4 ± 0.2
		Spring	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.4 ± 0.0
Silicate	WG	Autumn	4.7 ± 0.0	4.7 ± 0.3	1.4 ± 0.5	0.9 ± 0.4	5.0 ± 0.3	4.7 ± 0.4	4.4 ± 0.3
		Winter	3.7 ± 0.7	4.0 ± 0.5	3.6 ± 0.8	3.8 ± 0.0	4.2 ± 0.4	4.2 ± 0.2	3.9 ± 0.7
		Spring	2.4 ± 0.0	2.5 ± 0.1	2.2 ± 0.1	2.1 ± 0.0	2.3 ± 0.1	2.1 ± 0.1	2.2 ± 0.0
	DS	Autumn	1.3 ± 0.1	1.3 ± 0.1	1.4 ± 0.1	0.9 ± 0.1	1.0 ± 0.1	1.3 ± 0.0	1.3 ± 0.3
		Winter	2.9 ± 0.6	3.6 ± 0.1	3.0 ± 0.2	3.3 ± 0.1	3.7 ± 0.0	3.1 ± 0.1	2.8 ± 0.7
		Spring	3.3 ± 0.0	2.9 ± 0.2	2.9 ± 0.0	3.4 ± 0.6	2.9 ± 0.4	2.9 ± 0.2	3.1 ± 0.0

[a] SD is standard deviation of duplicate incubation bottles (set 1 and set 2) in each treatments (T1-T7).

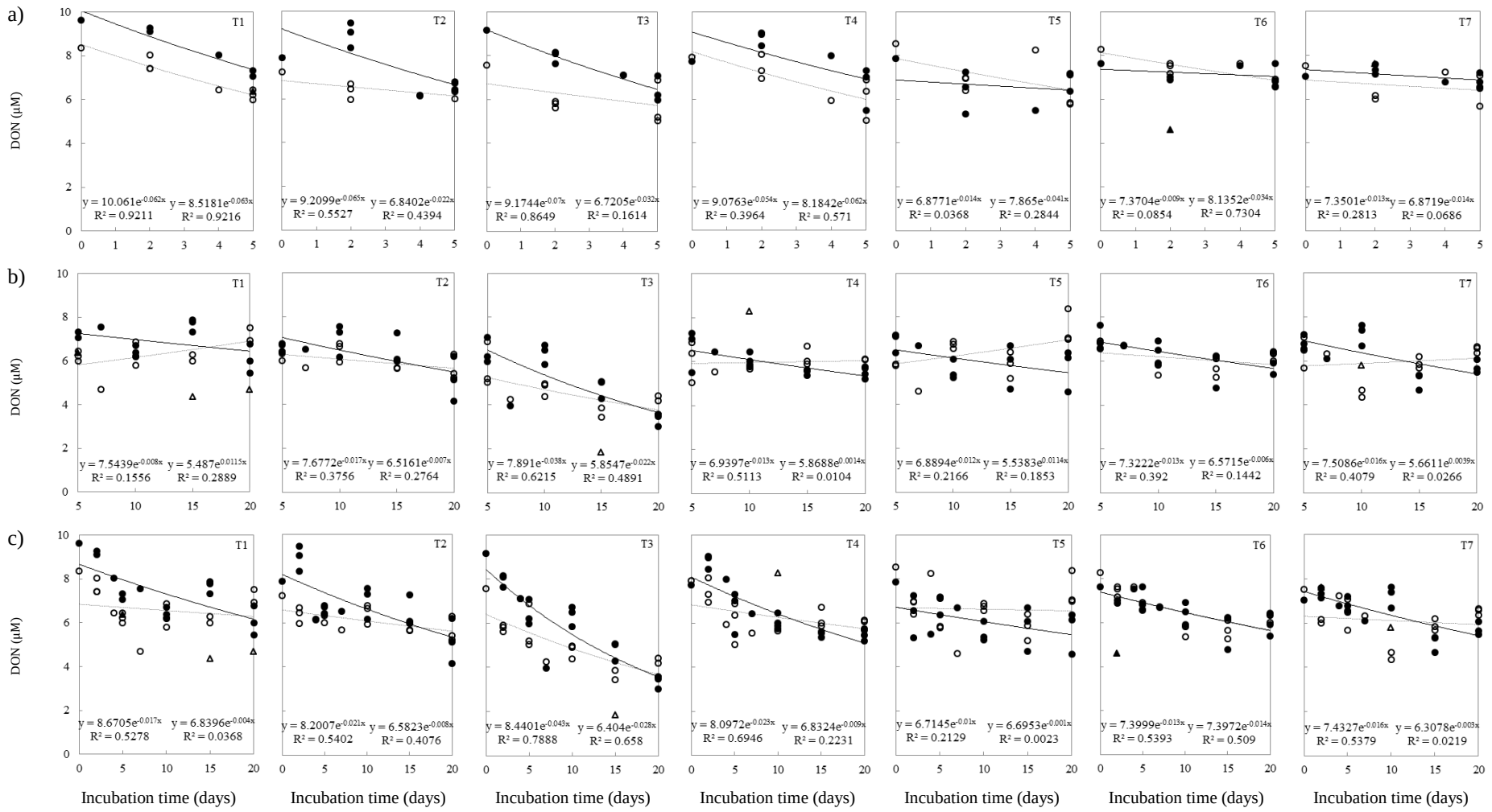
[b] the concentration below detection limit, the detection limit of the measurement is 0.1 µM (UEA instrument).

Appendix 4.4: Time courses of DOC and DON during the incubations with different treatments (T1-T7) sampled at West Gabbard and Dowsing stations in autumn 2013, winter 2013 and spring 2014.

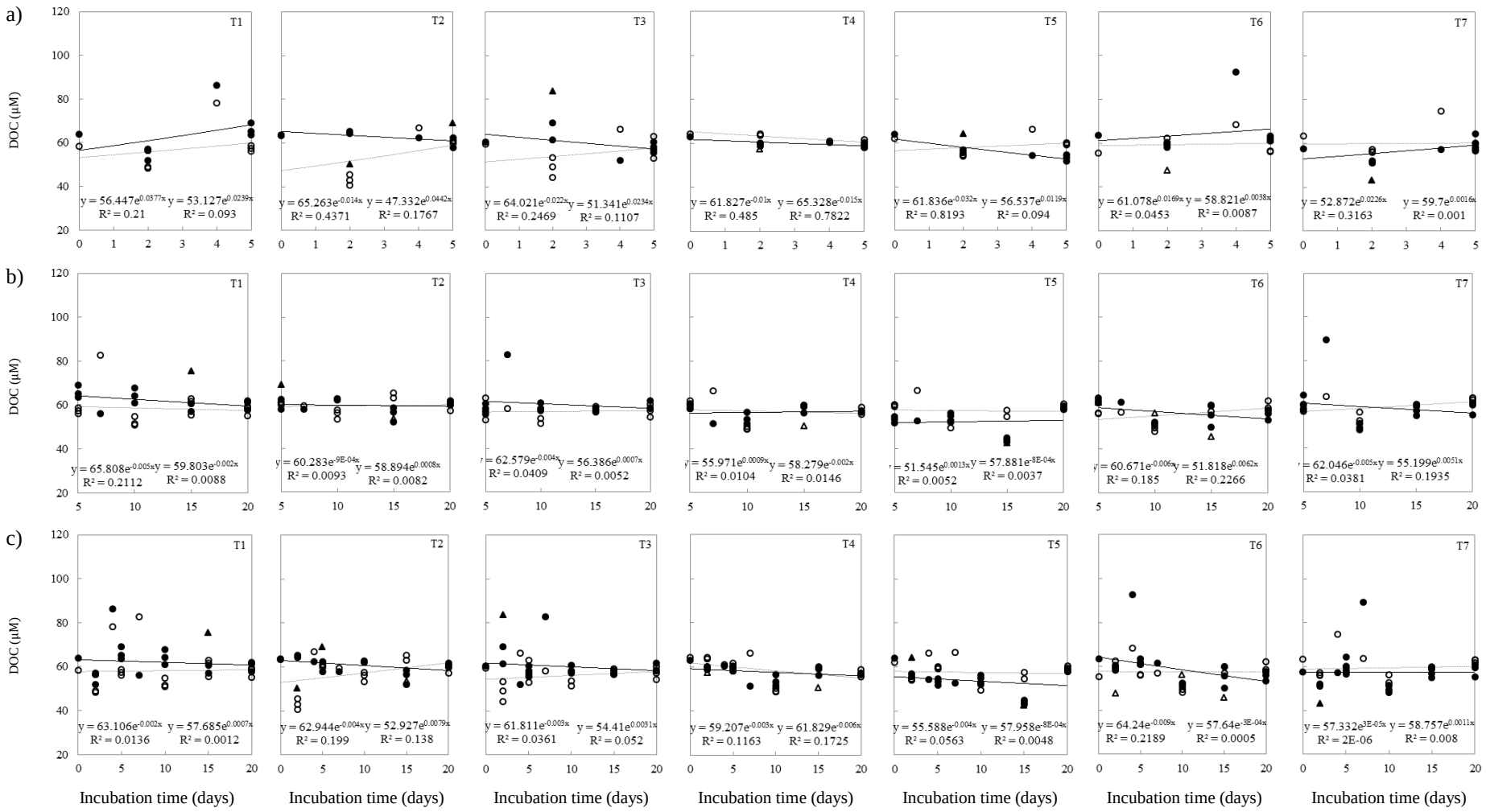
The results are presented in 1) to 10) as the following pages.



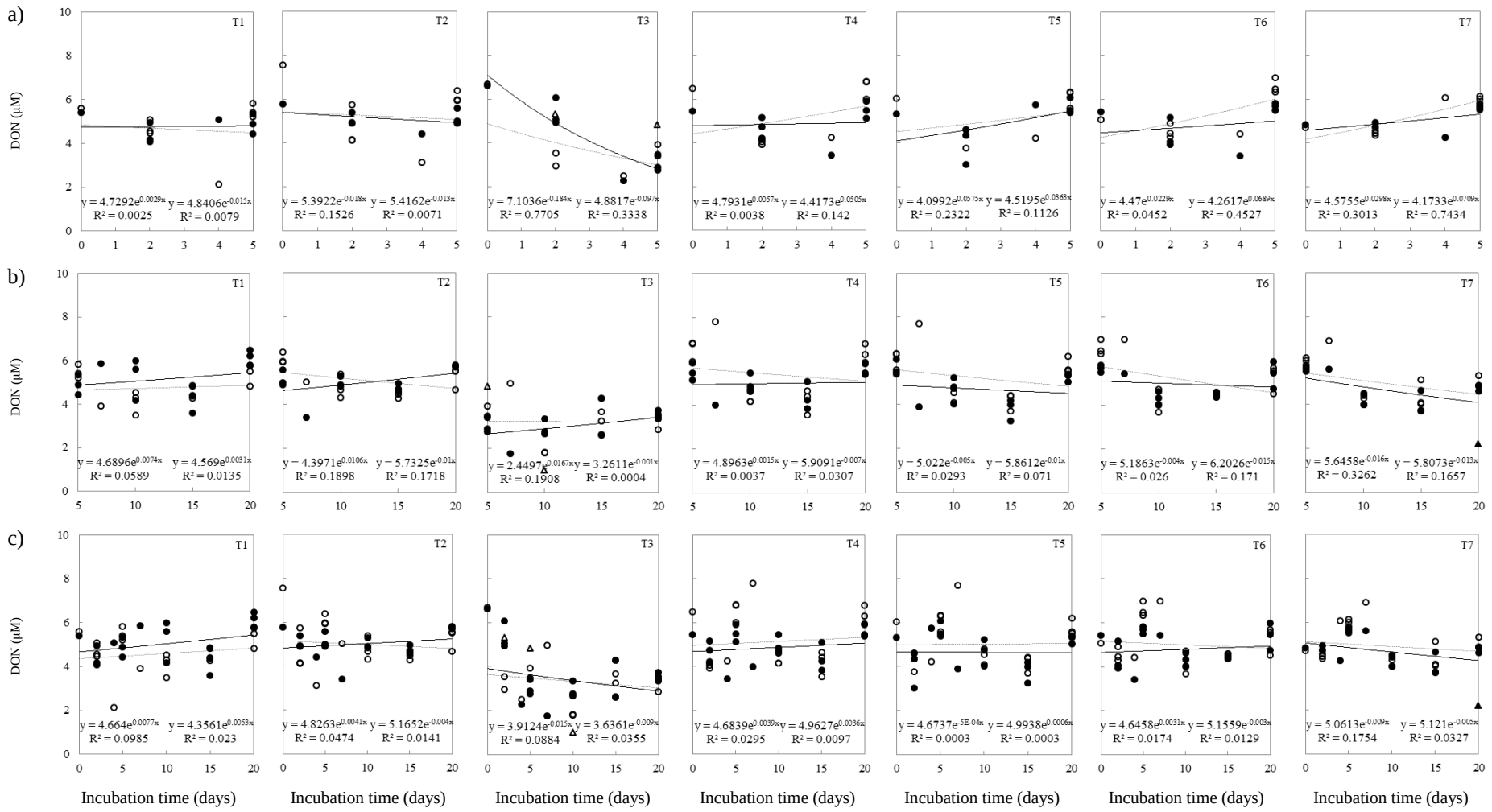
1) Time course of DOC during the incubations with different treatments (T1-T7) sampled at Dowsing station in autumn 2013 (DS1), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



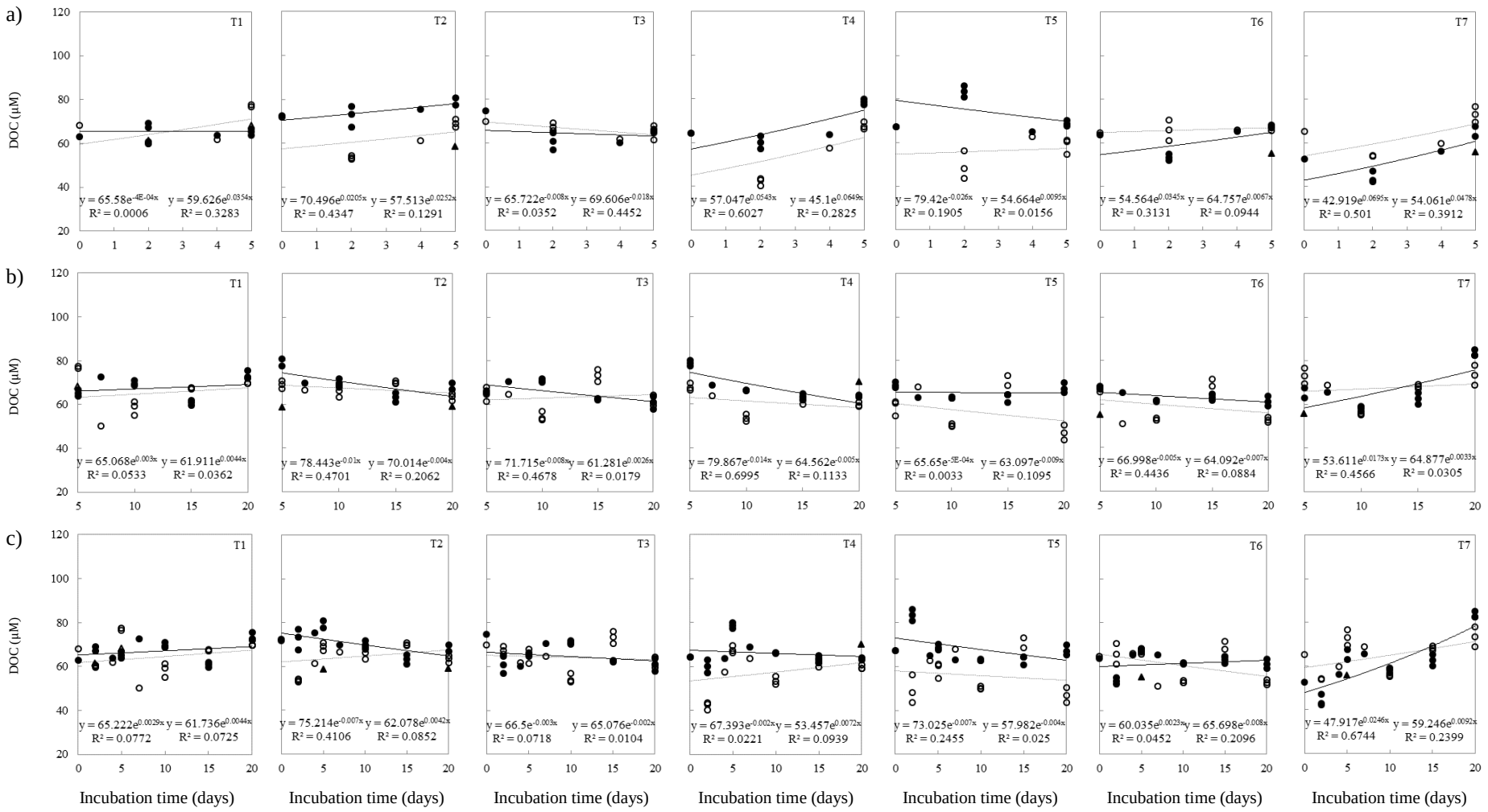
2) Time course of DON during the incubations with different treatments (T1-T7) sampled at Dowsing station in autumn 2013 (DS1), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



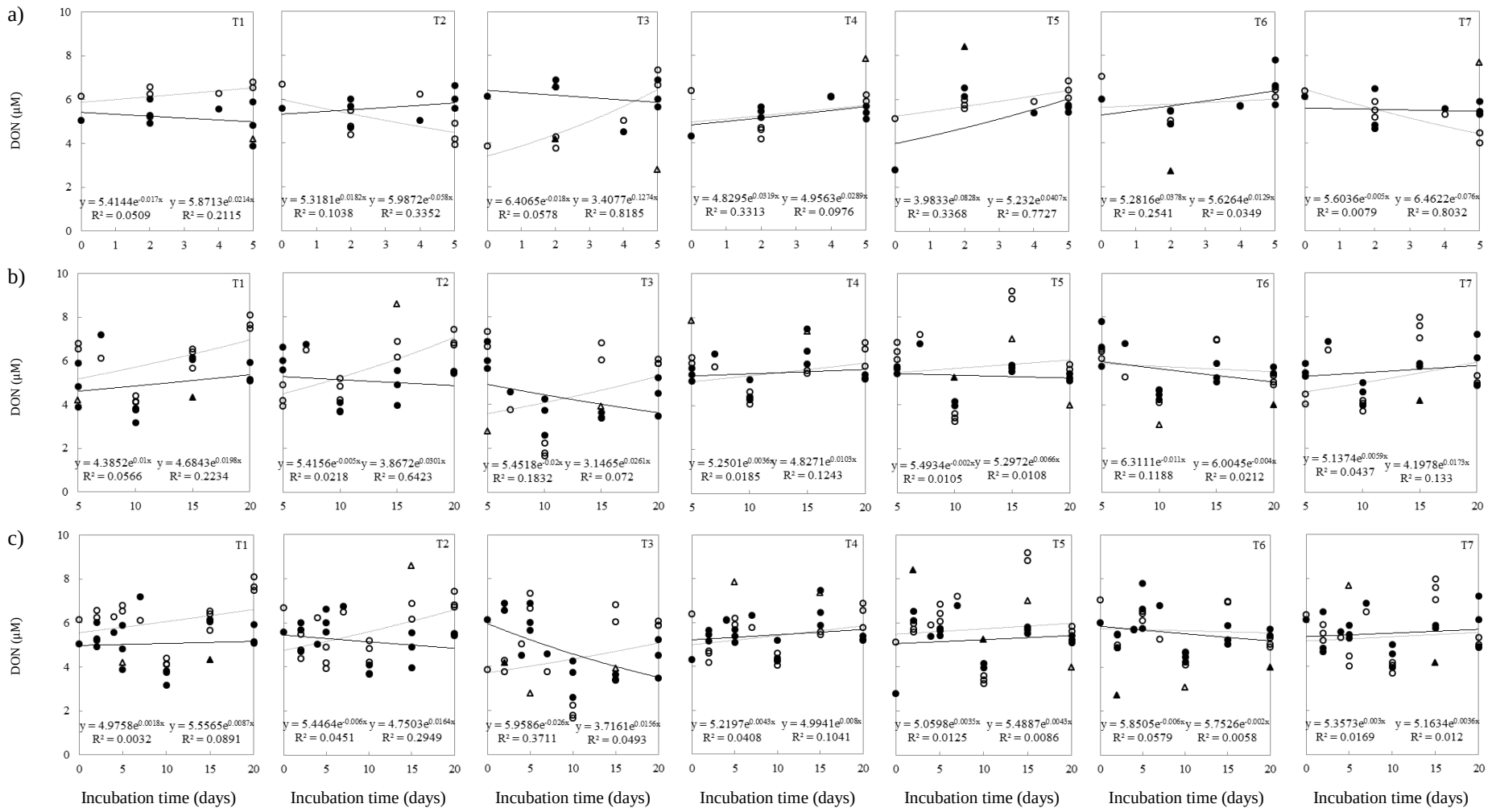
3) Time course of DOC during the incubations with different treatments (T1-T7) sampled at West Gabbard station in winter 2013 (WG2), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



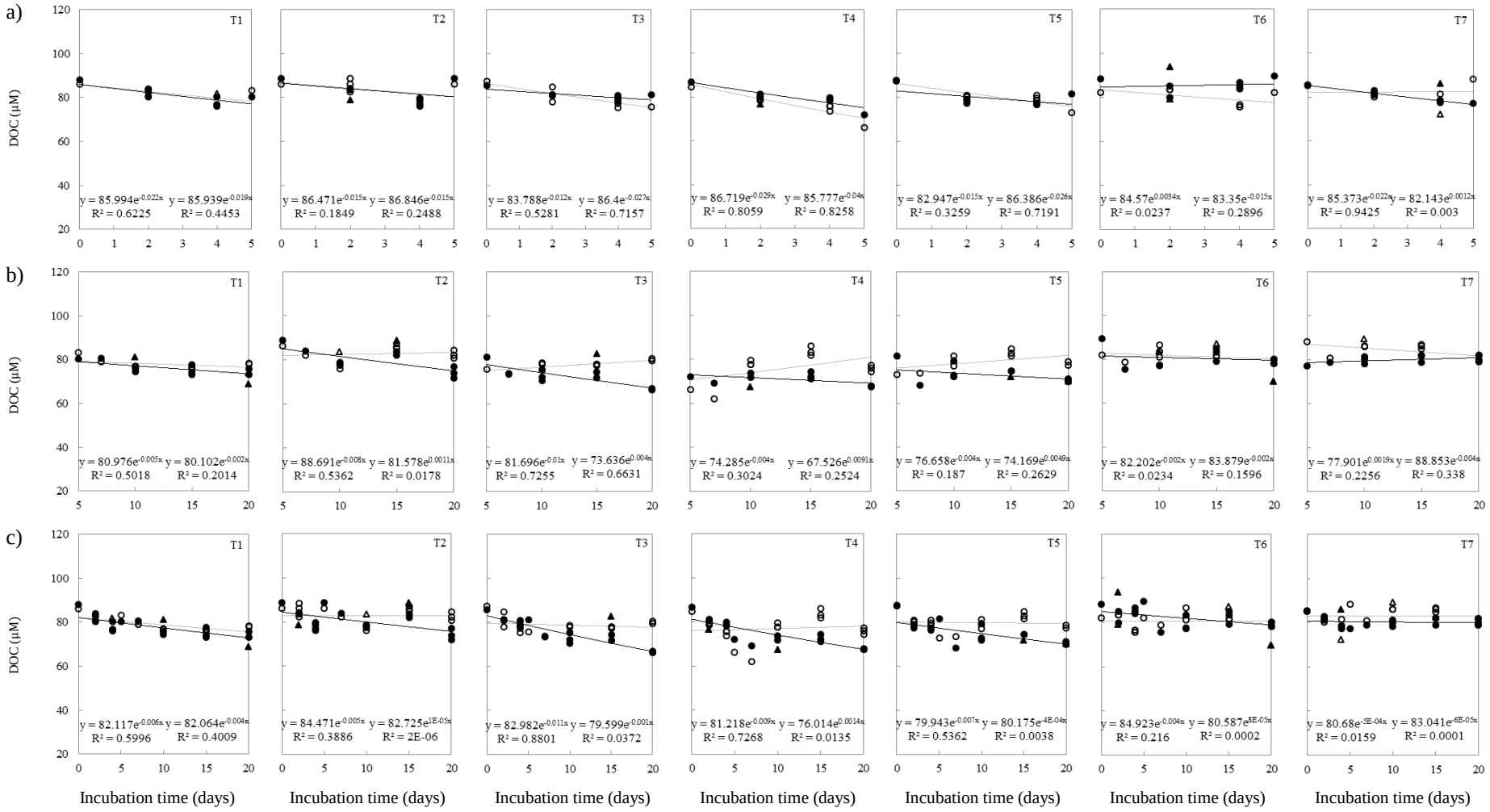
4) Time course of DON during the incubations with different treatments (T1-T7) sampled at West Gabbard station in winter 2013 (WG2), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



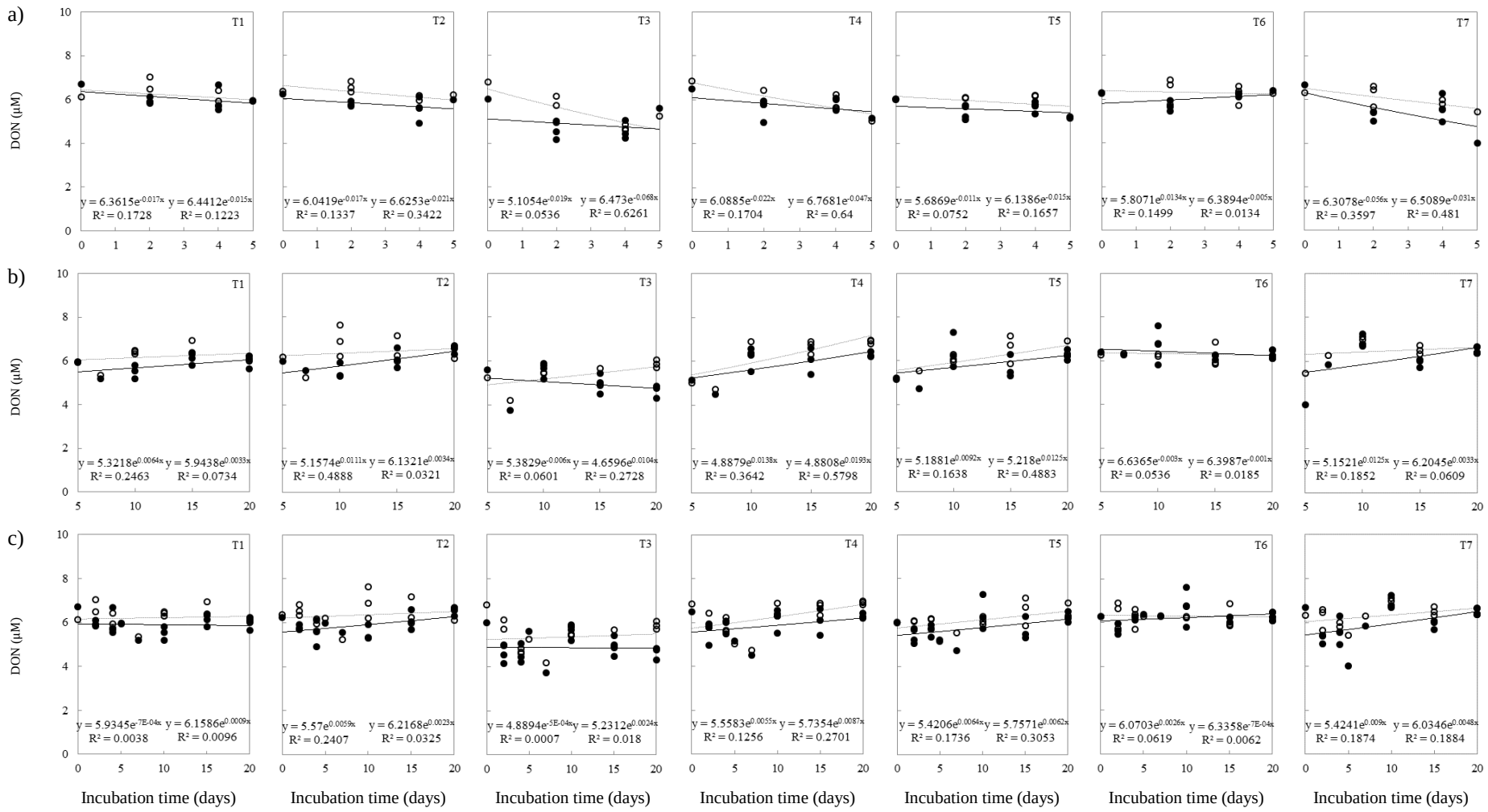
5) Time course of DOC during the incubations with different treatments (T1-T7) sampled at Dowsing station in winter 2013 (DS2), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



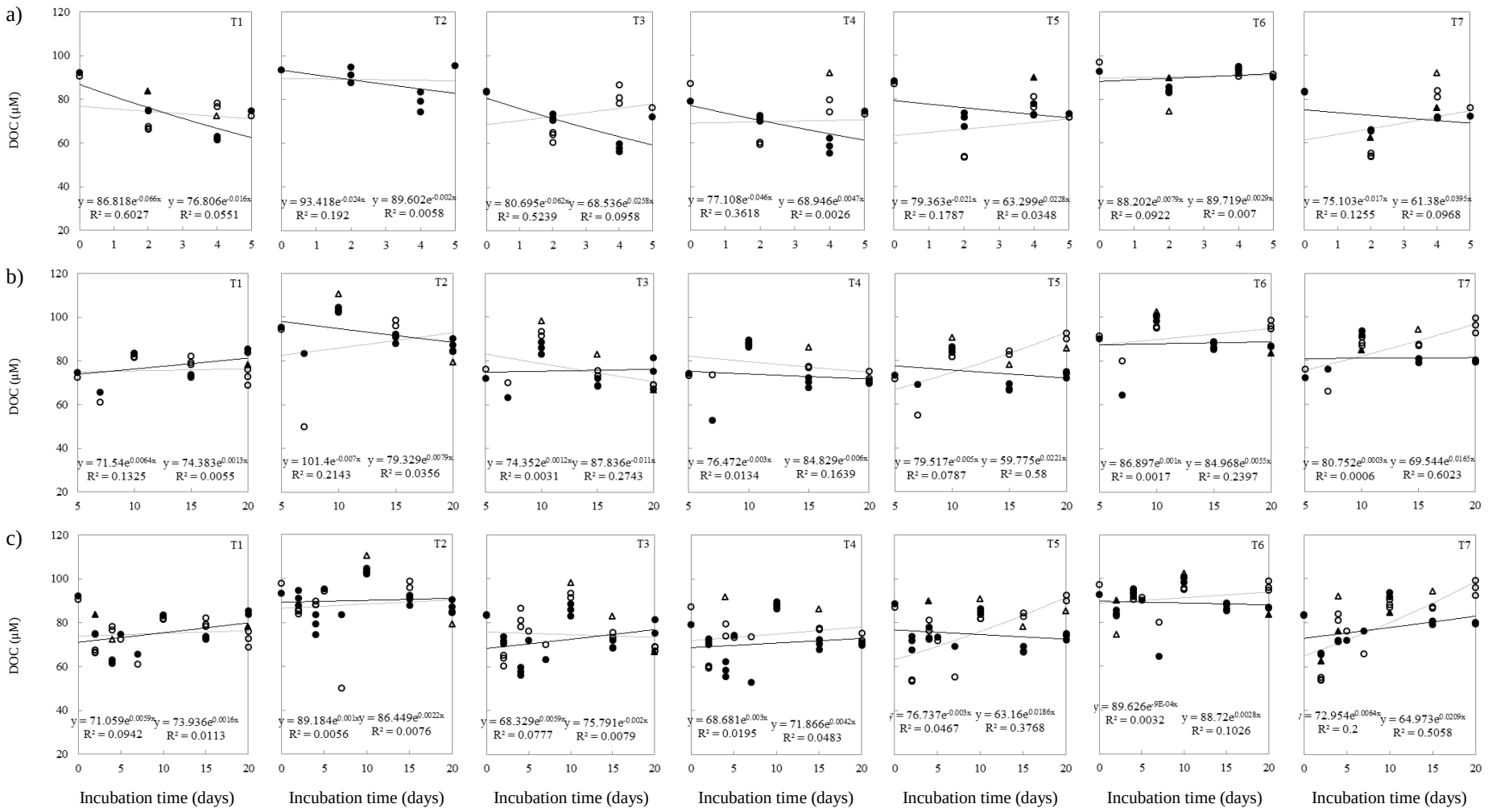
6) Time course of DON during the incubations with different treatments (T1-T7) sampled at Dowsing station in winter 2013 (DS2), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 5, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



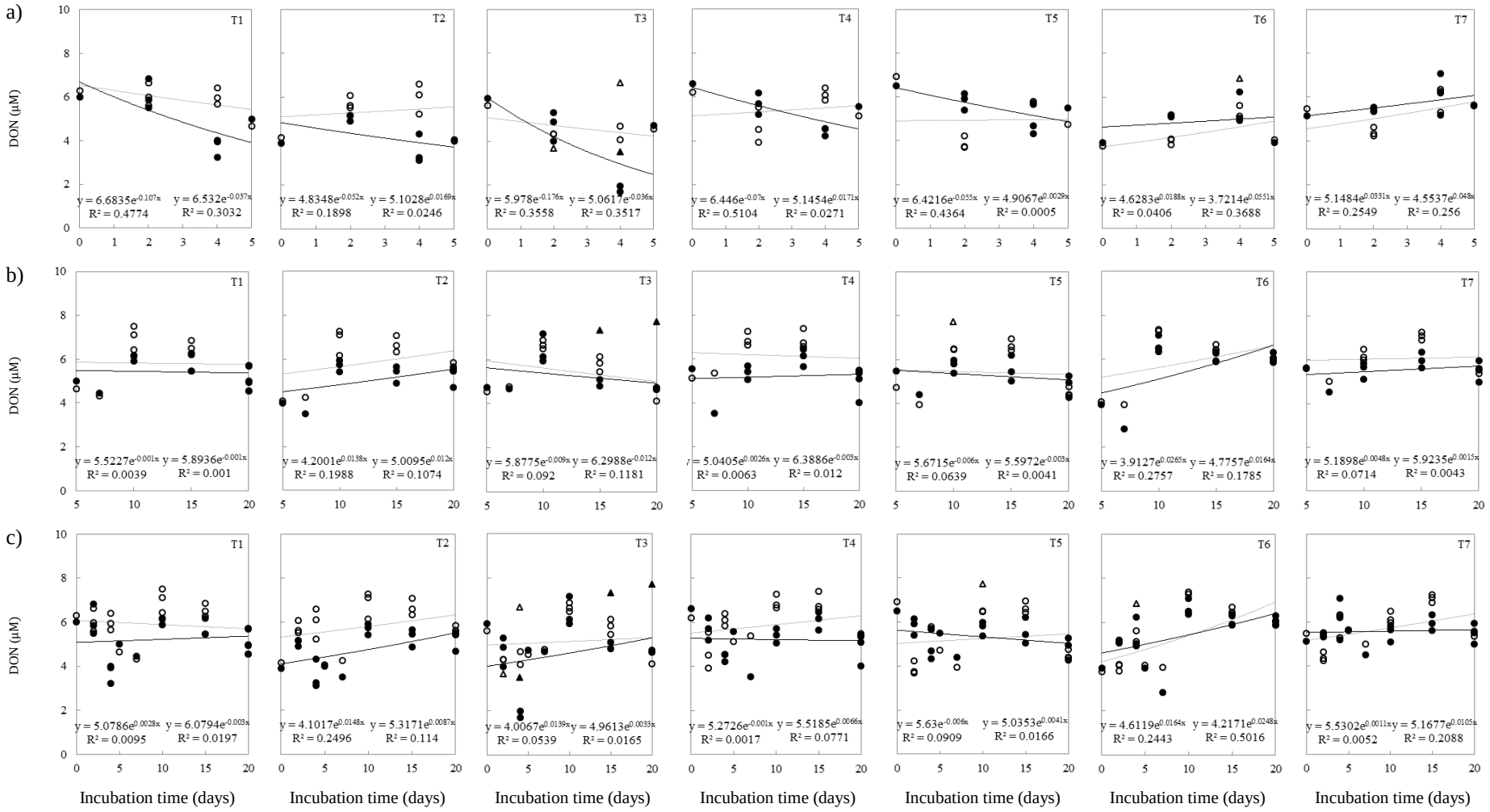
7) Time course of DOC during the incubations with different treatments (T1-T7) sampled at West Gabbard station in spring 2014 (WG3), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 4, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



8) Time course of DON during the incubations with different treatments (T1-T7) sampled at West Gabbard station in spring 2014 (WG3), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 4, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



9) Time course of DOC during the incubations with different treatments (T1-T7) sampled at Dowsing station in spring 2014 (DS3), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 4, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.



10) Time course of DON during the incubations with different treatments (T1-T7) sampled at Dowsing station in spring 2014 (DS3), the time period of incubation on day 0-5 (a), day 5-20 (b) and day 0-20 (c) in two duplicate bottles (set 1(filled dot, dark line) and set 2 (blank dot, grey line)). The line fitting by the exponential model. Three sub-samples of each sample were analysed on day 2, 4, 10, 15, 20. Where one sub-sample is substantially different from the others, it is excluded (triangles) from the exponential model.

Appendix 4.5: Rate constants (d^{-1}) obtained by fitting the exponential degradation (-) and production (+) of DOC and DON with incubation time at varying treatment (T1-T7) in two duplicate bottles (set 1 and set 2) in autumn, winter and spring.

Days	T	Set	k_{DOC} (d^{-1})						k_{DON} (d^{-1})					
			WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
0-5	1	1	-0.1037	-0.0619	0.0377	-0.0004	-0.0219	-0.0659	-0.0718	-0.0624	0.0029	-0.0166	-0.0175	-0.1074
	1	2	-0.1307	0.0001	0.0239	0.0354	-0.0188	-0.0155	-0.0919	-0.0632	-0.0153	0.0214	-0.0146	-0.0372
	2	1	-0.0939	-0.0283	-0.0136	0.0205	-0.0148	-0.0242	-0.0522	-0.0651	-0.0180	0.0182	-0.0166	-0.0522
	2	2	-0.0050	-0.0068	0.0442	0.0252	-0.0154	-0.0025	-0.0190	-0.0217	-0.0130	-0.0580	-0.0209	0.0169
	3	1	-0.0861	-0.0442	-0.0222	-0.0081	-0.0119	-0.0616	-0.0832	-0.0702	-0.1842	-0.0179	-0.0189	-0.1759
	3	2	-0.0297	-0.0735	0.0234	-0.0175	-0.0271	0.0258	-0.0532	-0.0319	-0.0973	0.1274	-0.0681	-0.0359
	4	1	-0.0457	-0.0248	-0.0097	0.0543	-0.0286	-0.0461	-0.0370	-0.0540	0.0057	0.0319	-0.0222	-0.0699
	4	2	-0.0358	-0.0257	-0.0152	0.0649	-0.0398	0.0047	-0.0504	-0.0622	0.0505	0.0289	-0.0470	0.0171
	5	1	-0.1006	0.0009	-0.0318	-0.0260	-0.0152	-0.0210	-0.0830	-0.0140	0.0575	0.0828	-0.0107	-0.0551
	5	2	-0.1022	-0.0282	0.0119	0.0095	-0.0260	0.0228	-0.0834	-0.0406	0.0363	0.0407	-0.0154	0.0029
	6	1	-0.0645	-0.0189	0.0169	0.0345	0.0034	0.0079	-0.0365	-0.0090	0.0229	0.0378	0.0134	0.0188
	6	2	-0.0453	-0.0116	0.0038	0.0067	-0.0145	0.0029	-0.0857	-0.0340	0.0689	0.0129	-0.0048	0.0551
	7	1	-0.0767	0.0007	0.0226	0.0695	-0.0216	-0.0169	-0.0395	-0.0135	0.0298	-0.0053	-0.0564	0.0331
	7	2	-0.1622	-0.0398	0.0016	0.0478	0.0012	0.0395	-0.1187	-0.0140	0.0709	-0.0757	-0.0306	0.0480
5-20	1	1	-0.0288	0.0030	-0.0050	0.0030	-0.0048	0.0064	-0.0592	-0.0079	0.0074	0.0100	0.0064	-0.0014
	1	2	0.0365	-0.0053	-0.0019	0.0044	-0.0023	0.0013	0.0035	0.0115	0.0031	0.0198	0.0033	-0.0012
	2	1	0.0029	-0.0144	-0.0009	-0.0104	-0.0083	-0.0068	-0.0151	-0.0168	0.0106	-0.0054	0.0111	0.0138
	2	2	0.0032	-0.0028	0.0008	-0.0036	0.0011	0.0079	0.0003	-0.0071	-0.0096	0.0301	0.0034	0.0120
	3	1	0.0111	-0.0028	-0.0035	-0.0078	-0.0098	0.0012	-0.0098	-0.0385	0.0167	-0.0204	-0.0062	-0.0088
	3	2	-0.0049	0.0027	0.0007	0.0026	0.0040	-0.0109	-0.0295	-0.0219	-0.0011	0.0261	0.0104	-0.0115
	4	1	0.0178	-0.0141	0.0009	-0.0140	-0.0036	-0.0032	-0.0052	-0.0131	0.0015	0.0036	0.0138	0.0026
	4	2	-0.0361	-0.0126	-0.0019	-0.0051	0.0091	-0.0063	-0.0544	0.0014	-0.0075	0.0103	0.0193	-0.0028
	5	1	-0.0076	-0.0113	0.0013	-0.0005	-0.0038	-0.0049	-0.0162	-0.0117	-0.0054	-0.0025	0.0092	-0.0056
	5	2	0.0165	0.0154	-0.0008	-0.0093	0.0049	0.0221	-0.0129	0.0114	-0.0096	0.0066	0.0125	-0.0025
	6	1	0.0074	-0.0174	-0.0061	-0.0048	-0.0016	0.0010	-0.0145	-0.0128	-0.0037	-0.0112	-0.0031	0.0265
	6	2	0.0074	-0.0127	0.0062	-0.0068	-0.0023	0.0055	-0.0063	-0.0058	-0.0153	-0.0044	-0.0012	0.0164
	7	1	0.0231	-0.0058	-0.0052	0.0173	0.0019	0.0003	-0.0011	-0.0164	-0.0162	0.0059	0.0125	0.0048
	7	2	0.0219	-0.0036	0.0051	0.0033	-0.0042	0.0165	-0.0038	0.0039	-0.0132	0.0173	0.0033	0.0015

Appendix 4.5: (continued).

Days	T	Set	k_{DOC} (d^{-1})						k_{DON} (d^{-1})					
			WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
0-20	1	1	-0.0247	-0.0063	-0.0019	0.0029	-0.0059	0.0059	-0.0497	-0.0171	0.0077	0.0018	-0.0007	0.0028
	1	2	0.0062	-0.0087	0.0007	0.0044	-0.0041	0.0016	-0.0071	-0.0043	0.0053	0.0087	0.0009	-0.0032
	2	1	-0.0032	-0.0047	-0.0037	-0.0075	-0.0055	0.0010	-0.0157	-0.0213	0.0041	-0.0058	0.0059	0.0148
	2	2	0.0037	-0.0030	0.0079	0.0042	0.0000	0.0022	0.0041	-0.0079	-0.0036	0.0164	0.0023	0.0087
	3	1	-0.0030	-0.0068	-0.0029	-0.0030	-0.0108	0.0059	-0.0131	-0.0430	-0.0152	-0.0264	-0.0005	0.0139
	3	2	-0.0113	-0.0089	0.0031	-0.0015	-0.0012	-0.0016	-0.0219	-0.0278	-0.0090	0.0156	0.0024	0.0033
	4	1	0.0047	-0.0189	-0.0028	-0.0022	-0.0092	0.0030	-0.0047	-0.0231	0.0039	0.0043	0.0055	-0.0010
	4	2	-0.0301	-0.0174	-0.0059	0.0072	0.0014	0.0042	-0.0431	-0.0086	0.0036	0.0080	0.0087	0.0066
	5	1	-0.0175	-0.0055	-0.0038	-0.0075	-0.0066	-0.0028	-0.0198	-0.0103	-0.0005	0.0035	0.0064	-0.0056
	5	2	-0.0057	0.0051	-0.0008	-0.0038	-0.0004	0.0186	-0.0121	-0.0011	0.0006	0.0043	0.0062	0.0041
	6	1	-0.0055	-0.0159	-0.0094	0.0023	-0.0037	-0.0009	-0.0129	-0.0135	0.0031	-0.0060	0.0026	0.0164
	6	2	-0.0024	-0.0131	-0.0003	-0.0084	0.0001	0.0028	-0.0151	-0.0137	-0.0032	-0.0018	-0.0012	0.0248
	7	1	0.0061	-0.0057	0.0000	0.0246	-0.0005	0.0064	-0.0101	-0.0157	-0.0087	0.0030	0.0090	0.0011
	7	2	-0.0021	-0.0087	0.0011	0.0092	-0.0001	0.0209	-0.0135	-0.0031	-0.0046	0.0036	0.0048	0.0105

WG1, DS1 = West Gabbard and Dowsing station in autumn 2013

WG2, DS2 = West Gabbard and Dowsing station in winter 2013

WG3, DS3 = West Gabbard and Dowsing station in spring 2014

Incubation time was extended to day 70 in spring 2014, but there is no significant different ($P > 0.05$) of the rate constant between this extend stage (day 20-70) and the second stage (day 5-20). Therefore, the rate constant of day 20-70 was not included in the table.

Appendix 4.6: Limits of detection of the individual rate constant for DOC and DON with incubation time at varying treatment (T1-T7) in two duplicate bottles (set 1 and set 2) in autumn, winter and spring.

Days	T	Set	limits of detection of the DOC rate constant [a]						limits of detection of the DON rate constant [a]					
			WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
0-5	1	1	0.0839	0.0243	0.0597	0.0153	0.0139	0.0478	0.0418	0.0183	0.0471	0.0585	0.0312	0.0917
	1	2	0.0349	0.0493	0.0609	0.0452	0.0188	0.0575	0.0546	0.0150	0.1401	0.0370	0.0319	0.0461
	2	1	0.0252	0.0544	0.0154	0.0209	0.0278	0.0405	0.1142	0.0478	0.0347	0.0436	0.0345	0.0881
	2	2	0.0361	0.0343	0.0779	0.0534	0.0219	0.0264	0.0793	0.0200	0.1257	0.0667	0.0237	0.0867
	3	1	0.0306	0.0434	0.0348	0.0345	0.0092	0.0480	0.0367	0.0227	0.0821	0.0647	0.0650	0.2117
	3	2	0.0354	0.0541	0.0541	0.0160	0.0140	0.0647	0.0500	0.0593	0.1375	0.0600	0.0429	0.0488
	4	1	0.0051	0.0340	0.0082	0.0360	0.0126	0.0500	0.0603	0.0544	0.0758	0.0370	0.0400	0.0559
	4	2	0.0285	0.0542	0.0072	0.0844	0.0149	0.0813	0.0532	0.0440	0.1014	0.0786	0.0288	0.0837
	5	1	0.0300	0.0220	0.0133	0.0437	0.0179	0.0403	0.0680	0.0583	0.0853	0.1040	0.0306	0.0511
	5	2	0.0570	0.0317	0.0301	0.0619	0.0133	0.0981	0.0543	0.0526	0.0833	0.0180	0.0281	0.1129
	6	1	0.0274	0.0078	0.0633	0.0457	0.0193	0.0222	0.0380	0.0264	0.0859	0.0579	0.0261	0.0748
	6	2	0.0299	0.0160	0.0405	0.0169	0.0204	0.0313	0.0611	0.0169	0.0618	0.0556	0.0334	0.0645
	7	1	0.0376	0.0404	0.0297	0.0620	0.0048	0.0447	0.0723	0.0176	0.0370	0.0488	0.0615	0.0462
	7	2	0.0313	0.0292	0.0426	0.0486	0.0205	0.1080	0.0861	0.0462	0.0340	0.0335	0.0259	0.0669
5-20	1	1	0.0158	0.0081	0.0062	0.0077	0.0036	0.0115	0.0245	0.0117	0.0179	0.0259	0.0075	0.0151
	1	2	0.0232	0.0181	0.0125	0.0143	0.0032	0.0117	0.0244	0.0120	0.0161	0.0234	0.0078	0.0244
	2	1	0.0171	0.0135	0.0062	0.0074	0.0055	0.0087	0.0184	0.0131	0.0132	0.0217	0.0076	0.0185
	2	2	0.0085	0.0095	0.0057	0.0042	0.0057	0.0310	0.0165	0.0069	0.0127	0.0142	0.0124	0.0231
	3	1	0.0140	0.0155	0.0104	0.0050	0.0043	0.0153	0.0159	0.0181	0.0207	0.0259	0.0164	0.0210
	3	2	0.0098	0.0108	0.0058	0.0115	0.0019	0.0135	0.0224	0.0142	0.0361	0.0625	0.0113	0.0210
	4	1	0.0117	0.0105	0.0055	0.0058	0.0038	0.0185	0.0182	0.0077	0.0147	0.0157	0.0121	0.0220
	4	2	0.0139	0.0085	0.0101	0.0086	0.0104	0.0100	0.0241	0.0089	0.0254	0.0182	0.0109	0.0171
	5	1	0.0232	0.0063	0.0112	0.0048	0.0061	0.0113	0.0284	0.0134	0.0186	0.0153	0.0139	0.0142
	5	2	0.0253	0.0163	0.0086	0.0161	0.0058	0.0154	0.0200	0.0145	0.0210	0.0423	0.0085	0.0277
	6	1	0.0275	0.0158	0.0077	0.0034	0.0077	0.0176	0.0169	0.0096	0.0136	0.0194	0.0087	0.0286
	6	2	0.0093	0.0069	0.0081	0.0131	0.0040	0.0069	0.0128	0.0086	0.0203	0.0188	0.0061	0.0235
	7	1	0.0032	0.0085	0.0157	0.0119	0.0023	0.0100	0.0096	0.0119	0.0147	0.0174	0.0175	0.0114
	7	2	0.0149	0.0069	0.0063	0.0114	0.0041	0.0095	0.0148	0.0150	0.0178	0.0279	0.0087	0.0154

Appendix 4.6: (continued).

Days	T	Set	limits of detection of the DOC rate constant [a]						limits of detection of the DON rate constant [a]					
			WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
0-20	1	1	0.0160	0.0066	0.0085	0.0051	0.0026	0.0098	0.0160	0.0086	0.0116	0.0164	0.0053	0.0142
	1	2	0.0227	0.0121	0.0103	0.0082	0.0027	0.0075	0.0152	0.0117	0.0172	0.0144	0.0048	0.0113
	2	1	0.0122	0.0109	0.0040	0.0048	0.0037	0.0064	0.0150	0.0098	0.0093	0.0134	0.0053	0.0128
	2	2	0.0059	0.0060	0.0102	0.0069	0.0034	0.0132	0.0122	0.0047	0.0149	0.0131	0.0062	0.0121
	3	1	0.0126	0.0114	0.0077	0.0054	0.0021	0.0105	0.0109	0.0111	0.0244	0.0178	0.0096	0.0324
	3	2	0.0073	0.0098	0.0067	0.0074	0.0029	0.0097	0.0149	0.0103	0.0261	0.0379	0.0088	0.0137
	4	1	0.0101	0.0077	0.0039	0.0074	0.0030	0.0105	0.0120	0.0077	0.0113	0.0104	0.0072	0.0124
	4	2	0.0087	0.0079	0.0069	0.0112	0.0058	0.0099	0.0163	0.0083	0.0181	0.0125	0.0072	0.0115
	5	1	0.0154	0.0055	0.0080	0.0066	0.0033	0.0066	0.0177	0.0099	0.0145	0.0166	0.0069	0.0089
	5	2	0.0202	0.0104	0.0062	0.0119	0.0036	0.0132	0.0149	0.0117	0.0152	0.0247	0.0047	0.0163
	6	1	0.0169	0.0092	0.0089	0.0055	0.0039	0.0086	0.0104	0.0064	0.0116	0.0130	0.0050	0.0144
	6	2	0.0088	0.0047	0.0071	0.0081	0.0034	0.0044	0.0110	0.0067	0.0139	0.0123	0.0061	0.0128
	7	1	0.0104	0.0070	0.0107	0.0088	0.0020	0.0071	0.0101	0.0073	0.0097	0.0118	0.0094	0.0074
	7	2	0.0178	0.0061	0.0062	0.0082	0.0028	0.0111	0.0148	0.0110	0.0124	0.0170	0.0050	0.0102

[a] Limits of detection of the rate constants in the table obtained by 2 times standard deviation (2*SD) of the individual slopes (the rate constant), the standard deviation of slope are calculated by using a least squares fit with Excel's LINEST function (the natural logarithm of the *y* values (*y* values = DOC or DON concentration) and *x* values (incubation time, day) are used).

WG1, DS1 = West Gabbard and Dowsing station in autumn 2013

WG2, DS2 = West Gabbard and Dowsing station in winter 2013

WG3, DS3 = West Gabbard and Dowsing station in spring 2014

Appendix 4.7: Mean rate constants (% d^{-1}) obtained by fitting the exponential degradation (-) and production (+) of DOC and DON with day 0-5 incubation time at varying treatment (T1-T7) in autumn, winter and spring. SE is standard errors.

T	Mean k_{DOC} (% d^{-1})						Mean k_{DON} (% d^{-1})					
	WG1	DS1	WG2	DS2	WG3	DS3	WG1	DS1	WG2	DS2	WG3	DS3
1	-11.72	-3.09*	3.08**	1.75**	-2.04	-4.07*	-8.18	-6.28	-0.62**	0.24**	-1.60**	-7.23*
2	-4.95*	-1.76**	1.53**	2.28**	-1.51**	-1.33**	-3.56**	-4.34	-1.55**	-1.99**	-1.88**	-1.77**
3	-5.79*	-5.88	0.06**	-1.28*	-1.95	-1.79*	-6.82	-5.11*	-14.07*	5.48*	-4.35*	-10.59**
4	-4.08	-2.53**	-1.52	5.96*	-3.42	-2.07**	-4.37**	-5.81*	2.81**	3.04**	-3.46*	-2.64*
5	-10.14	-1.37**	-1.00*	-0.82**	-2.06*	0.09**	-8.32	-2.73**	4.69**	6.18*	-1.30**	-2.61*
6	-5.49	-1.52*	1.03**	2.06**	-0.56**	0.54**	-6.11*	-2.15*	4.59*	2.54**	0.43**	3.70**
7	-11.95	-1.95*	1.21**	5.86*	-1.02*	1.13**	-7.91*	-1.37**	5.03*	-4.05*	-4.35*	4.06**
	Mean k_{DOC} (% d^{-1}) of all seasons and all stations (Mean ± SE)						Mean k_{DON} (% d^{-1}) of all seasons and all stations (Mean ± SE)					
1	-2.68 ± 2.14						-3.95 ± 1.51					
2	-0.96 ± 1.06						-2.52 ± 0.47					
3	-2.77 ± 1.01						-5.91 ± 2.72					
4	-1.23 ± 1.49						-1.74 ± 1.54					
5	-2.55 ± 1.55						-0.68 ± 2.18					
6	-0.66 ± 1.09						0.50 ± 1.65					
7	-1.12 ± 2.43						-1.43 ± 2.08					

* One of duplicate bottles (set 1 or set 2) was lower than the limits of detection.

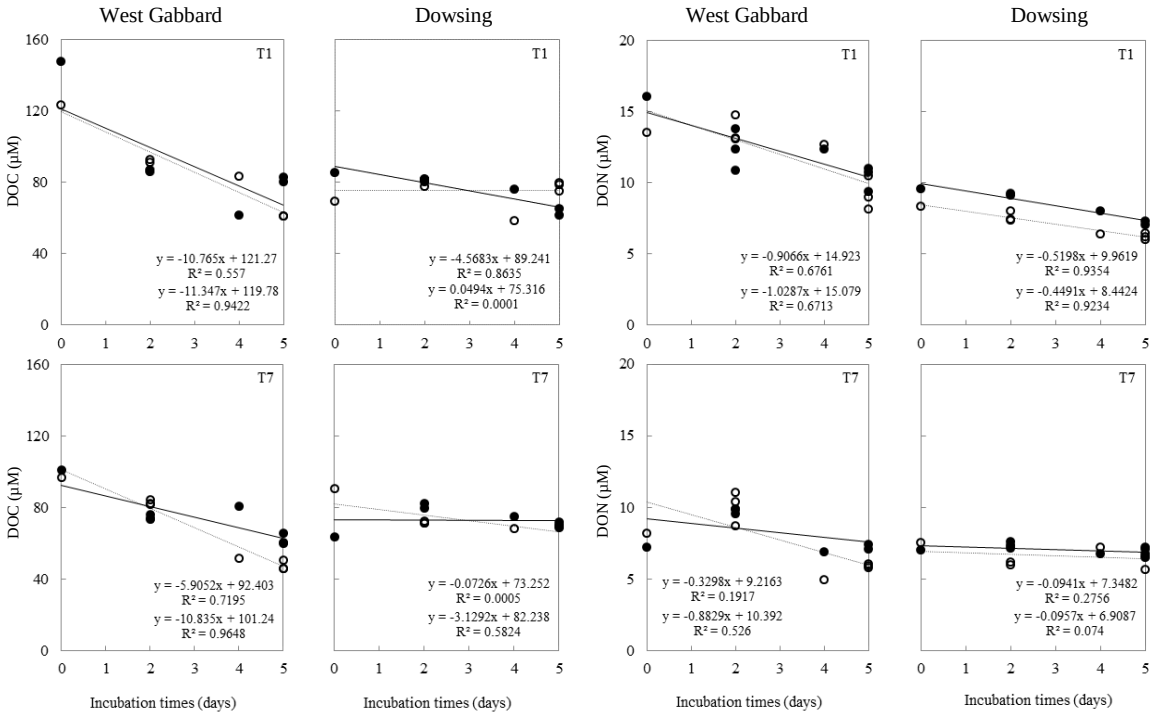
** Both two duplicate bottles (set 1 and set 2) were lower than the limits of detection.

WG1, DS1 = West Gabbard and Dowsing station in autumn 2013

WG2, DS2 = West Gabbard and Dowsing station in winter 2013

WG3, DS3 = West Gabbard and Dowsing station in spring 2014

Appendix 4.8: Summary of decay rates of incubation experiment (T1 and T7) in autumn 2013 using the linear regression analysis.



Decay rates of incubation experiments were recalculated in order to compare with the SmartBuoy. Rates were determined (recalculated) by the linear regression analysis with time (as the best fit line with the gradient yielded decay rate) using treatment 1 (T1) and treatment 7 (T7) of autumn 2013 incubation experiments with constant temperature at 15 °C. The time period of incubation on day 0 – 5 in two duplicate bottles included set 1 (filled dot, dark line) and set 2 (blank dot, grey line).

The gradient yielded decay rate of each bottle and the mean was reported in Table 4.8 (chapter 4)

Appendix 4.9: Rate constants and limits of detection of the rate constants in summer 2012.

1) Rate constants (d^{-1}) obtained by fitting the exponential degradation (-) and production (+) of DOC and DON with incubation time at varying treatment without antibiotics (T1, T3-T5) in two duplicate bottles (set 1 and set 2) in summer 2012.

Days	Treatment (T)	Set	k_{DOC} (d^{-1})			k_{DON} (d^{-1})		
			St. WG	St. 9	St. 24	St. WG	St. 9	St. 24
0-5	1	1	-0.01	-0.03	-0.06	0.01	0.05	-0.04
	1	2	-0.03	-0.06	-0.05	0.09	-0.06	-0.03
	3	1	-0.04	-0.05	0.02	-0.01	-0.03	-0.04
	3	2	-0.05	-0.03	0.01	0.07	-0.04	-0.05
	4	1	-0.02	-0.05	-0.04	-0.07	-0.01	-0.03
	4	2	-0.02	-0.02	-0.02	-0.01	-0.08	-0.05
	5	1	-0.07	-0.02	-0.04	-0.06	-0.12	0.01
	5	2	-0.01	-0.04	-0.05	0.02	-0.02	-0.05
5-20 [a]	1	1	-0.02			-0.04		
	3	1	-0.02			-0.01		
	4	1	-0.01			0.001 [b]		
	5	1	0.02			0.01		
0-20 [a]	1	1	-0.02			-0.03		
	3	1	-0.02			-0.01		
	4	1	-0.01			-0.01		
	5	1	0.01			-0.01		

St. = Sampling station

[a] The experiment was extended to day 20 at station WG set 1 only (see Figure 2.4 in chapter 2 for details).

[b] When the rate constant was less than 0.005 d^{-1}, it was presented in three decimal digits to be able to indicate a negative or positive value.

2) Limits of detection of the individual rate constant for DOC and DON with incubation time at varying treatment without antibiotics (T1,T3-T5) in two duplicate bottles (set 1 and set 2) in summer 2012.

Days	Treatment (T)	Set	limits of detection of the DOC rate constant [b]			limits of detection of the DON rate constant [b]		
			St. WG	St. 9	St. 24	St. WG	St. 9	St. 24
0-5	1	1	0.02	0.06	0.02	0.03	0.04	0.07
	1	2	0.01	0.01	0.02	0.12	0.02	0.09
	3	1	0.01	0.02	0.05	0.04	0.07	0.02
	3	2	0.02	0.02	0.04	0.12	0.07	0.03
	4	1	0.02	0.02	0.03	0.11	0.12	0.04
	4	2	0.01	0.03	0.01	0.10	0.03	0.06
	5	1	0.03	0.10	0.02	0.05	0.06	0.09
	5	2	0.01	0.06	0.02	0.05	0.06	0.04
5-20 [a]	1	1	0.01			0.03		
	3	1	0.01			0.02		
	4	1	0.004 [c]			0.01		
	5	1	0.01			0.02		
0-20 [a]	1	1	0.01			0.02		
	3	1	0.004 [c]			0.01		
	4	1	0.003 [c]			0.02		
	5	1	0.01			0.01		

[a] The experiment was extended to day 20 at station WG set 1 only (see Figure 2.4 in chapter 2 for details).

[b] Limits of detection of the rate constants in the table obtained by 2 times standard deviation (2*SD) of the individual slopes (the rate constant), the standard deviation of slope are calculated by using a least squares fit with Excel's LINEST function (the natural logarithm of the *y* values (*y* values = DOC or DON concentration) and *x* values (incubation time, day) are used).

[c] When limits of detection of the individual rate constant was less than 0.005, it was presented in three decimal digits to be able to indicate a negative or positive value.

St. = Sampling station

Appendix 4.10: Seasonal rate constant [a] of DOC and DON (k_{DOC} and k_{DON}, % d^{-1} ± SE) and related parameters (incubation temperature (°C) and initial concentration (µM ± SE, averaged all stations in each season)), the time period of incubation on day 0-5.

Treatments	Parameters		Summer 2012 (17 °C [b])	Autumn 2013 (15 °C [c])	Winter 2013 (7 °C [c])	Spring 2014 (11 °C [c])
T1 (Dark)	DOC	k_{DOC}	-4.11 ± 1.09	-7.41 ± 4.31	2.41 ± 0.67	-3.05 ± 1.02
		Initial Concentration	82.1 ± 3.7	106.8 ± 29.1	63.4 ± 2.1	89.3 ± 2.2
	DON	k_{DON}	0.21 ± 2.54	-7.23 ± 0.95	-0.19 ± 0.43	-4.41 ± 2.81
		Initial Concentration	6.0 ± 0.4	11.9 ± 2.9	5.6 ± 0.0	6.3 ± 0.1
T3 (Dark + N)	DOC	k_{DOC}	-2.54 ± 1.87	-5.84 ± 0.05	-0.61 ± 0.67	-1.87 ± 0.08
		Initial Concentration	84.3 ± 1.9	103.6 ± 23.0	66.2 ± 6.1	85.1 ± 1.5
	DON	k_{DON}	-1.75 ± 2.45	-5.96 ± 0.86	-4.30 ± 9.77	-7.47 ± 3.12
		Initial Concentration	5.4 ± 0.4	11.1 ± 2.8	5.8 ± 0.8	6.1 ± 0.3
T4 (Dark + P)	DOC	k_{DOC}	-2.67 ± 0.47	-3.30 ± 0.77	2.36 ± 3.60	-2.75 ± 0.67
		Initial Concentration	83.7 ± 2.3	87.1 ± 15.8	64.1 ± 0.3	84.5 ± 1.3
	DON	k_{DON}	-4.05 ± 0.12	-5.09 ± 0.72	2.92 ± 0.11	-3.05 ± 0.41
		Initial Concentration	6.1 ± 0.3	10.0 ± 2.1	5.7 ± 0.3	6.5 ± 0.1
T5 (T7) (Light)	DOC	k_{DOC}	-3.67 ± 0.40	-6.95 ± 5.00	3.54 ± 2.33	0.06 ± 1.07
		Initial Concentration	84.7 ± 4.0	87.8 ± 10.9	59.8 ± 0.8	84.4 ± 0.9
	DON	k_{DON}	-3.64 ± 1.55	-4.64 ± 3.27	0.49 ± 4.54	-0.15 ± 4.20
		Initial Concentration	5.9 ± 0.3	7.5 ± 0.2	5.5 ± 0.7	5.9 ± 0.6

SE =Standard errors

The rate constant with a negative value is net degradation, while a positive value is net production.

[a] Rate constants was averaged all stations in each season based on each treatment: treatment T1, T3 and T4 in summer 2012 was comparable to treatment T1, T3 and T4 in autumn 2013, winter 2013 and spring 2014,respectively; and treatment T5 in summer 2012 was similar to treatment T7 in autumn 2013, winter 2013, spring 2014. Note the experimental treatment details in chapter 2, section 2.3.2 and section 2.3.3.

[b] Average temperature of temperature range 16-19 °C onboard controlled by continuous flow of the online supply water.

[c] Constant temperature controlled by the control temperature room onboard and then the incubator at the UEA based laboratory.

Appendix 4.11: Seasonal rate constant (first five day) of DOC and DON (k_{DOC} and k_{DON}, % d^{-1} ± SE) and initial concentration (µM) for all treatment (T1-T7).

1) k_{DOC} and initial DOC concentration [a]

Treatment	Autumn 2013		Winter 2013		Spring 2014	
	Initial concentration	k_{DOC}	Initial concentration	k_{DOC}	Initial concentration	k_{DOC}
Station WG						
1	135.9	-0.12	61.2	0.03	87.2	-0.02
2	121.6	-0.05	63.6	0.02	87.4	-0.02
3	126.6	-0.06	60.0	0.00	86.5	-0.02
4	103.0	-0.04	63.8	-0.01	85.8	-0.03
5	130.0	-0.10	63.1	-0.01	87.7	-0.02
6	118.3	-0.05	59.5	0.01	85.2	-0.01
7	98.8	-0.12	60.6	0.01	85.4	-0.01
Station DS						
1	77.7	-0.03	65.5	0.02	91.5	-0.04
2	73.5	-0.02	72.2	0.02	95.7	-0.01
3	80.5	-0.06	72.3	-0.01	83.6	-0.02
4	71.3	-0.03	64.4	0.06	83.2	-0.02
5	71.6	-0.01	67.3	-0.01	87.8	0.00
6	74.5	-0.02	64.2	0.02	94.9	0.01
7	76.9	-0.02	59.0	0.06	83.5	0.01

[a] The mean value of duplicate incubation bottles
Incubation temperature was 15, 7 and 11 °C in autumn winter and spring, respectively
k_{DOC} (degradation (-) and production (+))

2) k_{DON} and initial DON concentration [a]

Treatment	Autumn 2013		Winter 2013		Spring 2014	
	Initial concentration	k_{DON}	Initial concentration	k_{DON}	Initial concentration	k_{DON}
Station WG						
1	14.8	-0.08	5.5	-0.01	6.4	-0.02
2	11.6	-0.04	6.7	-0.02	6.3	-0.02
3	13.9	-0.07	6.7	-0.14	6.4	-0.04
4	12.1	-0.04	6.0	0.03	6.7	-0.03
5	13.8	-0.08	5.7	0.05	6.0	-0.01
6	13.0	-0.06	5.3	0.05	6.3	0.00
7	7.7	-0.08	4.8	0.05	6.5	-0.04
Station DS						
1	9.0	-0.06	5.6	0.00	6.2	-0.07
2	7.6	-0.04	6.1	-0.02	4.0	-0.02
3	8.4	-0.05	5.0	0.05	5.8	-0.11
4	7.8	-0.06	5.4	0.03	6.4	-0.03
5	8.2	-0.03	4.0	0.06	6.7	-0.03
6	8.0	-0.02	6.5	0.03	3.8	0.04
7	7.3	-0.01	6.3	-0.04	5.3	0.04

[a] The mean value of duplicate incubation bottles
Incubation temperature was 15, 7 and 11 °C in autumn winter and spring, respectively
k_{DOC} (degradation (-) and production (+))