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1 Sedimentary and water column processes in the Oyster Grounds: A potentially
2 hypoxic region of the North Sea

3

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12

13 **Abstract**

14

15 The purpose of this research was to investigate the potential causes of low oxygen
16 levels in the bottom water of the Oyster Grounds region of the shallow southern North
17 Sea, an area which provides suitable conditions for low oxygen levels to develop. At
18 the end of the summer stratified period, relevant biogeochemical processes were
19 investigated using a combination of sedimentary and water column rate
20 measurements. Phytoplankton nitrate and ammonium uptake was measured
21 throughout the water column using ¹⁵N labelled isotopes and showed ammonium
22 uptake dominated in the upper and bottom mixed layer with a maximum 294.4 mol N
23 m⁻³ h⁻¹. In the deep chlorophyll maximum at the thermocline, primary production was
24 dominated by nitrate uptake, with an average of 35.0 mol N m⁻³ h⁻¹, relative to
25 ammonium uptake, with an average of 24.6 mol N m⁻³ h⁻¹. This high relative nitrate
26 uptake will in part result in exportable new production to the isolated bottom mixed
27 layer and sediments, as opposed to regenerated ammonium driven uptake. This
28 biomass export was indicated by significant benthic oxygen consumption rates in the
29 stratified region (782-1275 mol O₂ m⁻² h⁻¹) long after the end of the spring bloom.
30 The sediments were also an active net source of nitrate, ammonium, phosphate and

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1 silicate into the bottom mixed layer of 4.4, 8.4, 2.3 and 68.8 mol m⁻² h⁻¹ respectively.
2 The export of new production within the thermocline to the bottom mixed layer and
3 the consequent sediment oxygen consumption in the isolated bottom mixed layer in
4 the Oyster Grounds are expected to have contributed to the low bottom water oxygen
5 concentrations of 2.07 mg l⁻¹ (64.7 mol l⁻¹) measured. The long stratified period
6 associated with this low oxygen is predicted to occur more regularly in the future and
7 continued monitoring of this ecologically important region is therefore essential if the
8 causes of these potentially damaging low oxygen levels are to be fully understood.

9
10 **Keywords:** shelf sea; North Sea; hypoxia; phytoplankton; primary production;
11 sediment chemistry

12 13 **1. Introduction**

14
15 In the coastal regions of shallow shelf seas environmental problems due to increased
16 nutrient inputs have been a focus of research since the 1970s (Ryther and Dunstan,
17 1971). Problems due to these inputs are generally been studied in terms of either the
18 effects on nutrient load and stoichiometry on the development of harmful algal
19 blooms, e.g. *Phaeocystis pouchetii* in Dutch coastal waters (Peperzak, 2003), or the
20 development of low oxygen bottom water, e.g. the ‘dead zone’ in the Gulf of Mexico
21 (Rabalais et al., 2002). The latter is caused by the decomposition of increased primary
22 production due to excess nutrient loading, i.e. eutrophication, in bottom mixed layer
23 of the stratified water column with consequent oxygen consumption during
24 remineralisation. This low oxygen concentration may affect the fauna living in the
25 bottom water or in the sediments, e.g. demersal fish migration (Baden et al., 1990). In
26 general these effects occur when dissolved oxygen concentrations drop below 2mg O₂
27 l⁻¹ or 62.5 mol l⁻¹ (Diaz, 2001) and is defined as hypoxia, with a complete absence of
28 oxygen defined as anoxia (Diaz, 2001). There has been an increasing awareness of the
29 occurrence of anthropogenically induced hypoxia in large areas of stratified and
30 enclosed shelf seas, with substantial eutrophication-generated hypoxia also recorded
31 in the Baltic Sea (80,000 km²) (Conley et al., 2002) and the Black Sea (20,000 km²)
32 (Mee, 1992).

1 The North Sea has had few published studies on hypoxia and these have focussed on
2 coastal waters i.e. German Bight (summarised in Colijn et al. (2002)). The North Sea
3 is a shelf sea surrounded by some of the most heavily industrialised nations of
4 northern Europe - mainly Great Britain, The Netherlands, Belgium and Germany, and
5 has been shown to be strongly affected by anthropogenic activities evident from the
6 occurrence of phenomena such as fisheries decline (Cook et al., 1997). It has a total
7 area of 575,000 km² with the majority of the southern North Sea being relatively
8 shallow (~40m) and well-mixed year round, and with summer stratified areas in the
9 northern and central regions (Pingree et al., 1978) providing suitable physical
10 conditions for low oxygen conditions to potentially develop. Previous studies off
11 shore in the Oyster Grounds of the central stratified North Sea have shown decreasing
12 bottom water oxygen concentrations (Postma and Rommets, 1984; Peeters et al.,
13 1995) and although this region was not hypoxic, a recent report has also shown a
14 trend of decreasing oxygen levels (Boers, 2005). The Oyster Grounds is also a
15 temporary depocentre for sediments from the south-eastern North Sea (van Raaphorst
16 et al., 1998) and the shallow topography and stratified nature of this region combined
17 with potentially high nutrient concentrations and suitable sedimentary structure
18 therefore provide near ideal conditions for low oxygen levels to develop. In addition,
19 a recent study in the central North Sea, Weston et al. (2005) also showed that the
20 Deep Chlorophyll Maximum (DCM), present in similar stratified regions, to be a
21 major source of new production (Dugdale and Goering, 1967) after the spring bloom
22 and is therefore a potential source of biomass to the bottom waters.

23 The aim of this study was therefore to investigate sedimentary processes and
24 production in the DCM of the Oyster Grounds in terms of its potential to reduce
25 bottom water oxygen concentrations. This study involved the measurement of water
26 column and sedimentary nutrient uptake rates in addition to hydrographic profiles
27 along transects using a towed undulating conductivity, temperature and depth sensor
28 (CTD) throughout the western Oyster Grounds region.

29
30 *Figure 1*

31

32 **2. Materials and methods**

33

34 *2.1 Study area*

1

2 The Oyster Grounds, also called Oyster Ground, is a large, roughly circular,
3 depression in the central North Sea with its centre at 54° 30'N and 4° 30'E (Fig. 1). It
4 reaches a maximum depth of more than 50m at its centre and is bordered by the
5 shallower bathymetry of Dogger Bank, German Bight and Southern Bight. The
6 biologically enriched zone of the Frisian Front is situated on the southern edge of the
7 Oyster Grounds, in a sedimentary transitional zone where the seabed changes from the
8 sandy sediments of the Southern Bight to the muddy sediments of the Oyster Grounds
9 (Fig. 1). The Frisian Front is also in the transitional zone between the summer
10 stratified region of the deeper Oyster Grounds and the permanently well mixed
11 Southern Bight, as shown in figure 2, but is not a consistent feature in this region
12 (Baars et al., 1999). The onset of stratification in the central North Sea, of which the
13 Oyster Grounds is a part, is typically in May due to solar insolation and ends in mid-
14 October due to advective overturning from cooling (Tijssen and Wetsteyn, 1984).

15

16 *Figure 2*

17

18 In terms of marine nutrient input, at the southern edge of the Oyster Grounds there
19 are three sources of nutrients which converge from the West: continental coastal water
20 (CCW); Channel water (CW) and English coastal water (ECW). CCW is primarily
21 composed of riverine input from the continental Rhine and Meuse rivers and is
22 typically low in salinity and high in dissolved nutrients. CW is characterised by the
23 highest salinity in the region. ECW, made up primarily from riverine input from the
24 Thames, Wash and Humber, is typically of salinity 33 – 34 with elevated nutrients
25 compared that of the Channel water, but significantly lower than CCW. In the summer
26 stratified region the main source of nutrients to the upper mixed layer is central North
27 Sea water (CNSW), which originates from North Atlantic influx from the preceding
28 winter. Due to the bowl-like nature of the Oyster Grounds the thermal stratification
29 results in a bottom mixed layer which is broadly isolated from these external direct
30 inputs during the stratified period.

31

32 Stratification and bottom water isolation provide the physical conditions that are
33 necessary for low water oxygen to develop. The thermocline is also commonly within
34 the euphotic zone, i.e. >1% of surface irradiance, and results in the formation of a
DCM.

1

2 *2.2 Sampling strategy*

3

4 The sampling was carried out towards the end of the summer stratification in order
5 that any potential oxygen depletion would be at its maximum and also when input
6 from the DCM would be a source of biomass input to the bottom water. The cruise
7 was carried out on R/V 'Endeavour' during 27th September-3rd October 2003 with
8 process sites in the western Oyster Grounds at which water column primary
9 production, sedimentary denitrification, nutrient fluxes and oxygen consumption rates
10 were measured. One process station was in the year round well-mixed Frisian Front
11 (Station A) and 3 stations in the stratified region which formed the main focus of the
12 research (Fig. 1). In addition to sampling at process stations, a series of transects
13 provided measurement of physical, biological parameters at a high frequency in order
14 to allow these process sites to be understood as a part of the broader oceanographic
15 structure of the western region of the Oyster Grounds. An undulating CTD was used
16 to measure temperature, salinity and fluorescence along the whole of these transects.
17 Additional discrete stations along the transects were also sampled for a suite of
18 chemical parameters and chlorophyll *a*.

19

20 *2.3 Physical oceanography*

21

22 Measurements of temperature and salinity were carried out along the 7 separate
23 sampling transects (1-7; fig. 1) using both a towed oceanographic undulator fitted
24 with a Falmouth Scientific Inc. Integrated CTD (Maine, USA) and CTD rosette also
25 fitted with a Falmouth Scientific Inc. Integrated CTD (Maine, USA). The undulator
26 enables profiling from 4 m below the sea surface to 3 m above the seabed. A
27 comprehensive description of its use, calibrations and subsequent data analysis can be
28 found in Brown et al. (1996). The CTD rosette also had a fluorometer and a
29 photosynthetically active radiation (PAR) sensor (Li-cor, USA) attached. The
30 fluorometer enabled the DCM to be identified and sampled directly using Niskin
31 bottles (see section 2.4).

32 Salinity and density were calculated according to international standard procedures
33 for seawater (UNESCO, 1981) and were determined to a standard deviation of 0.01
34 for salinity.

1

2 *2.4 Chemical and biological survey*

3

4 Discrete samples were collected using a CTD rosette of 10 l Niskin bottles along
5 transects 1, 2 and 5 and at stations A-D (Fig. 1). Water samples were collected
6 throughout the water column for measurement of chlorophyll *a*, phaeopigments and
7 dissolved inorganic nutrients. For chlorophyll *a*, known volumes were filtered through
8 Whatman glass fibre (GF/F) filters in triplicate. Pigments were extracted in acetone
9 and analysis was carried out on board ship. A fluorometer (Turner Designs, USA) was
10 used to measure extracted pigment fluorescence, and phaeopigments after
11 acidification with HCl, following the method described by Tett (1987). The
12 fluorometer was calibrated using a solution of pure chlorophyll *a* (Sigma Chemical
13 Co.) with concentration being determined spectrophotometrically. The % error of
14 chlorophyll *a* analyses was < 2% relative to Turner certified reference material.
15 Samples were also taken in triplicate and analysed on board for nitrate and nitrite
16 (hereafter nitrate), ammonium, phosphate and silicate using a Skalar Autoanalyser
17 (The Netherlands) according to Kirkwood (1996). The detection limit for nitrate,
18 ammonium, phosphate and silicate analyses were 0.1 mol l⁻¹, 0.2 mol l⁻¹, 0.02 mol l⁻¹
19 and 0.1 mol l⁻¹ respectively. The % error for all nutrient analyses was < 5% relative
20 to Ocean Scientific International (U.K.) standards.

21 At four CTD stations (A-D; fig. 1) water column profile and sediment samples were
22 collected for further investigation using a CTD rosette. Light profiles were determined
23 using the PAR sensor attached to the CTD rosette prior to sampling. Discrete water
24 samples were collected using a CTD rosette of 10 l Niskin bottles. Samples for water
25 column phytoplankton nutrient uptake measurements were collected at 07-30 GMT.
26 Water samples were collected at selected depths throughout the water column for
27 measurement of chlorophyll *a*, nitrate, phosphate and silicate using an autoanalyser as
28 above. At one station (B; fig. 1) water column dissolved oxygen concentrations were
29 measured in both the upper mixed layer and bottom mixed layer in triplicate for 24h at
30 6h intervals. Samples were collected using the CTD rosette and analysed in triplicate
31 using a Sensoren Instrumente Systeme (Germany) end point detector and Metrohm
32 (Switzerland) Dosimat 665 Autotitrator according to (Williams and Jenkinson, 1982).
33 Oxygen samples at other stations were lost. Ammonium was determined at depths

1 sampled for nitrogen uptake measurements using a Jasco (Japan) fluorometer
2 according to Holmes et al. (1999). Fluorometric determination of ammonium resulted
3 in an improved detection limit compared to the colourimetric method with the
4 autoanalyser ($\sim 0.05 \text{ mol l}^{-1}$ compared to 0.5 mol l^{-1} , respectively). Intercalibration
5 for these methods showed comparable results $>1 \text{ mol l}^{-1}$ for the two methods used
6 (Results not shown). All nutrient and chlorophyll *a* analyses were in triplicate.

7

8 *2.5 Water column nutrient uptake rates*

9

10 Samples were collected from the CTD casts for nitrate and ammonium uptake
11 measurements at surface, 5 m, 15 m and bottom at station A (Fig. 1), at 5 m, in the
12 middle of upper mixed layer (UML), DCM associated with the thermocline and
13 bottom mixed layer (BML) for stations B and D, and at 5 m, in the mid UML, and
14 DCM for station C. The DCM was determined by inspection of the vertical profiles of
15 temperature and chlorophyll *a* fluorescence from a CTD cast. This profile was made
16 immediately before the water sample collection. All samples were pre-screened
17 through a 200 μm mesh to remove mesozooplankton.

18 For nitrate and ammonium uptake rates measurements 1 l seawater samples were
19 transferred to 1.2 l polycarbonate flasks and spiked with either ^{15}N -sodium nitrate (99
20 atom %: Isotec, USA) or ^{15}N -ammonium sulphate (98 atom %: Isotec, USA). Samples
21 were enriched by an estimated 10% of in situ nutrient concentration, subject to a
22 minimum addition of 0.1 mol N l^{-1} . Bottles from each depth were incubated in
23 triplicate at corresponding % surface light incident irradiance ($\pm 2\%$) respectively
24 using neutral density filters (Lee, U.K.). For light irradiances $<0.1\%$ samples were
25 incubated in the dark. Samples were incubated in deck based incubators at surface
26 seawater temperature using the online seawater supply for samples collected in the
27 UML or in well-mixed station A. Where samples were taken at the thermocline or
28 BML, samples were incubated in temperature controlled incubators to within $\pm 2^\circ\text{C}$
29 of in situ temperature. One 1 l seawater sample for both nitrate and ammonium uptake
30 from each depth was filtered immediately after isotope addition as a zero-time control.
31 All other samples were incubated for 3 h immediately after ^{15}N -nitrate or ^{15}N -
32 ammonium addition. After incubation, samples were filtered onto pre-combusted (4 h,
33 400°C) Whatman GF/F filters at low vacuum ($<50 \text{ mm Hg}$). All filters were dried

1 immediately after filtration (16 h, 40°C) and stored in clean Petri dishes at room
2 temperature. Particulate nitrogen and atom % N of filtrate was determined using a
3 Europa Scientific (U.K.) 20-20 continuous flow isotope mass spectrometer online
4 with an ANCA elemental analyser. Nitrogen uptake rates were then calculated using
5 the models of Dugdale and Goering (1967).

6

7 *2.6 Sedimentary process measurements*

8

9 Sediment samples and overlying water at each site were collected using a NIOZ box
10 corer (NIOZ, The Netherlands), which was deployed ~8 times to collect sediment for
11 sub-sampling. At each station 3 intact vertical sediment cores (40 cm long x 10 cm
12 i.d.) for sediment-water nutrient exchange (section 2.4.1) were taken and sealed at the
13 bottom with bungs, an additional three cores (50 cm long x 9 cm i.d.) for oxygen
14 uptake (section 2.4.2), and 8 small cores (25 cm long x 3.4 cm i.d.) for denitrification
15 experiments (section 2.4.3) were also taken from the box cores and sealed at the
16 bottom with bungs.

17

18 *2.6.1 Sediment-water nutrient exchange*

19

20 The overlying water in each of the core tubes was supplemented with water
21 collected by the CTD with Niskin bottles from near the seabed at the appropriate
22 station to a final volume of ~750ml. The cores were immediately placed in a
23 thermostatically controlled water bath at the temperature of the corresponding
24 overlying water and allowed to re-equilibrate for 1 h. The water overlying each core
25 was gently aerated and stirred to prevent oxygen depletion. An identical clear plastic
26 tube was incubated with ~750 ml of site water as a control. After re-equilibration,
27 sub-samples of the overlying water were removed by syringe at hourly intervals for
28 the first 2-5 h then two further samples were taken at 8 and 12 h. All subsamples were
29 immediately filtered through a 0.2 µm filter (Sartorius, Germany) prior to nutrient
30 analysis as above. Nutrient concentrations were corrected for the volume of overlying
31 water. The flux between the overlying water and sediment of each core was calculated
32 from the slope of the linear portion of the graph ($P < 0.05$) and converted to a flux.
33 The error on the nutrient flux associated with each individual core was defined by the

1 standard deviation of the linear regression analysis used to define the linear portion of
2 the graph and was <10%.

3

4 *2.6.2 Oxygen uptake rates*

5

6 The three oxygen uptake cores were stored completely submerged in aerated site
7 water at in situ temperatures for 4 hours for re-equilibration. These were subsequently
8 capped and completely water filled to exclude all air bubbles. The water column in
9 each core was stirred with an induction motor driving a magnetic follower (Rank
10 Brothers, U.K.) and a 20 ml mid-water column sample was then drawn off into a gas
11 tight syringe and gently transferred into a gas tight 12 ml Exetainer (Labco, UK) and
12 fixed for Winkler measurement of dissolved oxygen. Sediment-water oxygen uptake
13 rates were measured using dissolved oxygen electrodes (Strathkelvin Instruments
14 Ltd., U.K.) and data logging equipment as described by Nedwell and Trimmer (1996).
15 Oxygen uptake was recorded continuously for the 3 h incubation period.

16

17 *2.6.3 Denitrification rates*

18

19 Rates of denitrification, both coupled denitrification (D_n) and denitrification of
20 nitrate exchanged from the water column (D_w) were measured in the smaller cores
21 using the isotope pairing technique according to (Nielsen, 1992). ^{15}N labelled
22 $\text{Na}^{15}\text{NO}_3$ was added (nominal concentration $25\mu\text{M}$) to the water column of four
23 replicate cores. There were also four reference cores to which no isotope was added.
24 The water was gently stirred before a zero-time water sample for nutrient analysis was
25 taken and the core sealed using a rubber bung with a built-in magnetic follower. Care
26 was taken to avoid any air bubbles in the core. The cores were then incubated at in
27 situ temperature with stirring for 6 h. At the end of this time a two-way valve was
28 used to simultaneously introduce a nitrogen gas headspace (6 ml) and withdraw a T_f
29 nutrient sample (6 ml). Nutrient samples were filtered ($0.2\mu\text{m}$ Minisart Plus,
30 Sartorius, Germany) and then frozen at -20°C . The cores were then vigorously shaken
31 and placed on rollers for 10 min before a sample of the headspace was taken (4 ml)
32 and transferred through a septum to an inverted water filled 12 ml vial (Labco, U.K.),
33 with water venting to atmosphere through a small bore needle. Mass charge ratios for
34 $^{28}\text{N}_2$, $^{29}\text{N}_2$ and $^{30}\text{N}_2$ were analysed on an elemental analyser interfaced using a

1 continuous flow isotope ratio mass spectrometer (Flash EA 1112, Thermo-Finnigan,
2 Germany). Denitrification rates were calculated according to Nielsen (1992).

3

4 *Figure 3*

5

6 **3. Results**

7

8 *3.1 Physical oceanography*

9

10 The section (Fig. 3; section a) from the top of the Dogger Bank through station B to
11 station A showed three regions; well-mixed on the Dogger Bank (0 – 15 km),
12 stratified between 20 -120km, and well mixed inshore to the Dutch coast. The depth
13 of the bottom mixed layer (BML) in the stratified region was variable up to a
14 maximum of 15m above the seabed, while the upper mixed layer extended to 25 – 35
15 m depth. At the thermocline temperature gradients were strong with ~ 4°C change
16 over 3m vertically. Site A was situated in the well-mixed waters of the Frisian front,
17 and was the co-location meeting of the easterly extent of English coastal water,
18 English Channel water and fresher continental coastal water as evident from the
19 salinity (not shown) and density (Fig. 3). Section b (Fig. 3), which is orientated south
20 west – north east, showed well-mixed water to the south and the stratified region from
21 90km to the northern end of the section. In combination with section c (Fig. 3) and
22 fig. 4, showing bottom water density, there was a clear area of isolated bottom water
23 at the seabed of the Oyster Grounds region.

24

25 *Figure 4*

26

27 *3.2 Water column nutrient, chlorophyll a and dissolved oxygen*

28

29 In the surface waters of the CTD transect from the stratified Oyster Grounds (leg 2
30 and 5; fig. 1) to the well-mixed Frisian front (leg 1; fig.1) low concentrations (~ 0.1 –
31 0.5 mol l⁻¹) for nitrate, phosphate and ammonium were measured (Fig. 5). For
32 silicate, relatively higher concentrations were measured in surface waters up to a
33 maximum of 4.6 mol l⁻¹ (Fig. 5).

1

2 *Figure 5*

3

4 In the stratified region, all nutrient concentrations generally decreased to below
5 detection limits in the upper mixed layer. Nutrient concentrations increased both at the
6 thermocline and in the BML to maximum concentrations of nitrate (2.76 mol l^{-1}),
7 phosphate (0.78 mol l^{-1}), silicate (16.07 mol l^{-1}) and ammonium (3.60 mol l^{-1}). In the
8 stratified region chlorophyll *a* concentration was low or below detection limit in the
9 upper mixed layer and then increased at and below the thermocline ($1 - 1.5 \text{ g l}^{-1}$). In
10 the well mixed regions chlorophyll *a* concentrations ranged from $\sim 2 \text{ g l}^{-1}$ in the
11 deeper water to 5.8 g l^{-1} in the shallow water at the southernmost end of transect 1.
12 Although only transects 2 and 5 are shown they were indicative of the conditions for
13 all transects

14 Water column oxygen concentration measurements were only carried out at station
15 B with average concentrations over a 24h period of 2.07 mg l^{-1} (64.7 mol l^{-1}) and 5.43
16 mg l^{-1} (169.6 mol l^{-1}) in the bottom mixed layer (44m) and upper mixed layer (2m)
17 respectively.

18

19 *3.3 Sedimentary processes*

20

21 Significant rates of benthic oxygen uptake were measured at all sites ($P < 0.05$).
22 Rates of oxygen uptake (Table 1) ranged from $524 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ at station A to
23 $1275 \mu\text{mol O}_2 \text{ m}^{-2} \text{ h}^{-1}$ at station D. There were significant differences among the sites
24 (One-way ANOVA, $F = 5.87$, d.f. = 11, $P = 0.020$), station A had significantly lower
25 rates of uptake than station D (Tukey's post hoc test).

26 Rates of coupled nitrification-denitrification (D_n) were not significantly different
27 among the sites (One-way ANOVA, d.f. = 14, $F = 1.031$, $P = 0.416$) and ranged from
28 $2.6 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ at station C to $3.4 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ at station B (Table 1).
29 Denitrification supported by nitrate exchange from the overlying water (D_w) was
30 minimal (less than $1 \mu\text{mol N m}^{-2} \text{ h}^{-1}$) at all sites. A one way ANOVA showed a
31 significantly higher rate of D_w at station A at the Frisian Front (d.f. = 15, $F = 8.641$, P
32 = 0.003) (Tukey's post hoc test).

1 Sedimentary fluxes of nutrients from the sediment to the water column were highest
2 at station C for nitrate ($7.9 \text{ mol m}^{-2} \text{ h}^{-1}$), station A for nitrite ($0.4 \text{ mol m}^{-2} \text{ h}^{-1}$), station
3 A for ammonium ($39.7 \text{ mol m}^{-2} \text{ h}^{-1}$) and station D for silicate ($109.0 \text{ mol m}^{-2} \text{ h}^{-1}$)
4 (Table 1). The average for the stratified waters at stations B-D showed that there was
5 a flux of nitrate, phosphate, ammonium and silicate to the BML from the sediment
6 and overall was dominated by silicate.

7

8 *3.4 Water column nutrient uptake rates*

9

10 For station A, with a well-mixed water column, the uptake rates of ammonium and
11 nitrate showed a maximum at 5m of 19.9 and $55 \text{ mol m}^{-3} \text{ h}^{-1}$ respectively (Table 2).
12 For the remaining summer stratified stations (B-D) ammonium and nitrate uptake was
13 highest for all stations in the surface waters at station B (45.2 and $294.4 \text{ mol m}^{-3} \text{ h}^{-1}$,
14 respectively). Average uptake rates for the layers of the stratified water column
15 showed ammonium uptake dominated in the upper mixed layer and bottom mixed
16 layer, and nitrate uptake was highest and dominated in the DCM at the thermocline.

17

18 **4. Discussion**

19

20 *4.1 Weather pattern and water column structure*

21

22 The summer period of 2003 was characterised by calm and warm weather with sea
23 surface temperature in the Oyster Grounds an average of 2.7°C warmer for June -
24 August than the mean for the 1969 – 1993 (Bundesamt für Seeschifffahrt und
25 Hydrographie; <http://www.bsh.de/en>). The water column physical structure reflected
26 these conditions with moderate surface cooling and wind mixing resulting in strong
27 temperature gradients in the thermocline (Fig. 3; sections a and b). In combination
28 with the presence of sharp horizontal and vertical density gradients around the Oyster
29 Grounds (Fig. 3), this resulted in an isolated bottom mixed layer not influenced by
30 Channel Water or CCW. As a result of its offshore location, anthropogenic nutrient
31 inputs to the Oyster Grounds will also be lower than in other coastal regions (Fig. 2).
32 The nutrient concentrations are therefore broadly set at the onset of stratification
33 although sedimentary processes lead to a flux of regenerated nutrients (Table 1).

1 The stratified period ends with the break down of stratification generally occurring in
2 early October, due to the combination of advective overturning from cooling (Tijssen
3 and Wetsteyn, 1984) and storm events generating inertial motion (van Haren et al.,
4 2003).

5

6 *4.2 Sedimentary processes*

7

8 The situation of the Oyster Grounds as a temporal depocentre results in this region
9 playing an important role in biogeochemical cycling of carbon and nitrogen. Nitrate
10 and ammonium sedimentary flux rates were similar to a previous study in the Oyster
11 Grounds which measured positive fluxes of 13 ± 9 and $14 \pm 10 \text{ mol m}^{-2} \text{ h}^{-1}$ respectively
12 in August (Lohse et al., 1993). Although there are no recorded data for nitrite,
13 phosphate and silicate fluxes in the Oyster Grounds region, measurements of nutrient
14 fluxes for south western North Sea in October (SiO_2 $0 - \sim 30 \text{ mol m}^{-2} \text{ h}^{-1}$ (Sanders et
15 al., 2001)) and the Skaggeiak between March – September (NO_2^- $-0.9-0.2 \text{ mol m}^{-2} \text{ h}^{-1}$
16 1 ; PO_4^- $-15.1-60.2 \text{ mol m}^{-2} \text{ h}^{-1}$; and SiO_2 $0.0-0.16 \text{ mol m}^{-2} \text{ h}^{-1}$ (Hall et al., 1996))
17 showed a similar range.

18 The relative ratios of sedimentary N:P:Si flux demonstrates that in terms of Redfield
19 stoichiometry (Redfield et al., 1966) N was potentially limiting phytoplankton
20 primary production as has been shown for other regions of the North Sea (Riegman et
21 al., 1990). The silicate flux at all stations was considerably in excess of the equimolar
22 Si and N considered to be necessary for diatom growth (Justic et al., 1995). It would
23 also therefore be expected that there may be a different phytoplankton species
24 composition in the BML and DCM in relation to the SML where silicate
25 concentrations were low (Fig. 5).

26 The rates of denitrification (Table 1) were made before the introduction of a
27 technique allowing the measurement of rates of both denitrification and anaerobic
28 ammonium oxidation (anammox) (Trimmer et al., 2006). Anammox is significant in
29 some coastal sediments (for review see Dalsgaard et al. (2005)) and in these regions,
30 the use of the original isotope pairing technique of Nielsen (1992) can lead to an
31 overestimation of denitrification rates (Risgaard-Petersen et al., 2003). Rates of
32 denitrification reported here are therefore estimates of potential denitrification activity
33 with rates in the expected range for continental shelf regions (Seitzinger and Giblin,

1 1996) and similar to previous rate measurements in the Oyster Grounds in August of
2 $0.8 \text{ mol m}^{-2} \text{ h}^{-1}$ (Lohse et al., 1993) with denitrification in the Oyster Grounds
3 dominated by coupling with nitrification (Table 1).

4 The dominant denitrification pathway was coupled to the nitrification of porewater
5 ammonium, i.e. D_n , and therefore reduced potential ammonium flux. D_n represents
6 only 18% of total dissolved inorganic nitrogen (DIN) mineralization (nitrate flux +
7 ammonium flux + D_n), which is low compared to the D_n as a proportion of DIN
8 reported for the western Irish Sea (63%) (Trimmer et al., 1999). This is further
9 complicated in that if significant anammox were present, these estimates of D_n are
10 likely to be overestimates (Trimmer et al., 2006) making D_n as a proportion of DIN
11 lower still. The nitrite produced due to this pathway is also expected to be removed
12 from the water column due to the flux of nitrite into the sediments measured (Table
13 1).

14 Benthic oxygen consumption rates (Table 1) were typical for continental shelf
15 regions (Seitzinger and Giblin, 1996), although they were at the lower range of values
16 previously measured at the Frisian Front (van Raaphorst et al., 1990) which may be
17 expected since the Frisian Front is a region of enhanced sedimentation and benthic
18 production (van Raaphorst et al., 1992). It is this oxygen consumption which drives
19 the low bottom oxygen levels measured in combination with a source of biomass
20 input and stratification.

21 22 *4.3 Water column nutrient uptake rates*

23
24 Nitrate and ammonium uptake rates, for the whole water column, were in the range
25 $0.2\text{-}45.2$ and $2.2\text{-}249.4 \text{ mol m}^{-3} \text{ h}^{-1}$ respectively (Table 2) and are in agreement with
26 (Owens et al., 1990) who showed nitrate and ammonium uptake rates up to 80 and
27 $100 \text{ mol N m}^{-3} \text{ h}^{-1}$ for surface waters in this region during July. The f ratio is
28 commonly used to compare these uptake rates of ammonium and nitrate (Eppley and
29 Peterson, 1979) and gives an indication of the N uptake due to new production, i.e.
30 due to allochthonous nitrate sources, relative to regenerated production (Table 2). The
31 low f ratios in the surface waters are in agreement with Weston et al. (2004) which
32 showed f ratios ranging from 0.07-0.51 for the well-mixed region of the southern
33 North Sea for September. At the DCM, the average f ratio of 0.58 was high compared

1 to the average f ratio of 0.35 at a similar DCM close to the Dogger Bank (Weston et
2 al., 2005). The f ratio may be overestimated due to the omission of urea uptake
3 measurements (Riegman and Noordeloos, 1998) and water column nitrification (Yool
4 et al., 2007). Urea uptake is however not expected to significantly alter the overall
5 trends of nitrogen assimilation (Weston et al., 2004). The effect of nitrification in the
6 water column is difficult to quantify since there have been no measurements in the
7 North Sea and a limited number worldwide (Yool et al., 2007).

8 The clarity of the water column, stratification and the removal of nutrients in the
9 upper mixed layer (UML) results in the formation of a DCM at the thermocline and
10 hence continued new production throughout the summer. In the BML, high water
11 column ammonium uptake rates resulted from regenerated ammonium due to the
12 remineralisation of organic matter as shown by the ammonium flux from the
13 sediments (Table 1). By contrast, nitrate concentrations remained significantly higher
14 in the BML, which may be due to phytoplankton ammonium uptake repressing the
15 need for nitrate (Flynn, 1999). The regeneration of organic matter in the UML led to a
16 similar situation as in the BML with the production of ammonium due to
17 remineralisation of organic matter after the spring bloom leading to a dominance of
18 phytoplankton ammonium uptake.

19

20 *4.4 Low bottom water dissolved oxygen and its causes*

21

22 The measured bottom water dissolved oxygen concentration of 2.07 mg l^{-1} in
23 October 2003 in the centre of the Oyster Grounds was significantly lower than
24 published values with oxygen minima of $\sim 6\text{-}7 \text{ mg l}^{-1}$ in the BML in August 1976
25 (Postma and Rommets, 1984), $\sim 6.5 \text{ mg l}^{-1}$ in summer 1988 and $\sim 4.5 \text{ mg l}^{-1}$ in
26 summer 1989 (Peeters et al., 1995) and $\sim 3.2 \text{ mg l}^{-1}$ for September 2003 (Boers, 2005).
27 These low BML oxygen concentrations indicate the potential for this region to
28 develop hypoxia. In order for oxygen levels to decrease throughout the stratified
29 period, as shown by Boers (2005), there must be suitable i) physical conditions, ii)
30 biomass production, iii) nutrient input and iv) continued benthic oxygen consumption.
31 The occurrence of these conditions in the Oyster Grounds can be addressed as
32 follows:

33

1 i) The water column structure (section 4.1) shows how the bottom mixed layer is
2 isolated by strong gradients in the thermocline limiting the diffusion of oxygen into
3 the bottom mixed layer. Water mass transfer along the seabed is prevented by bottom
4 fronts, which are evident as sharp density contours (Fig. 3). Additionally, tidal
5 residuals are weak and do not act as a significant advective component (van Aken et
6 al., 1987).

7 ii) New biomass production, i.e. production that can be exported into the bottom layer,
8 has been shown to occur at the DCM by the high f ratio and nitrate uptake rates.
9 Consequently there was continuing net primary production even at the end of the
10 stratified growing period with the magnitude of the DCM new production previously
11 estimated to be equal to that of the spring bloom in the stratified regions of the
12 northern North Sea (Weston et al., 2005). In contrast to the DCM new production, the
13 continuous low primary production in the BML will not alleviate low bottom water
14 oxygen concentrations measured, since the production of oxygen due to primary
15 production in the BML will be compensated by oxygen uptake during sedimentary
16 remineralisation (Peeters et al., 1995).

17 iii) In order for the new production to occur, new (allochthonous) nutrients must drive
18 the production in the DCM. Nutrient input however has been shown to be provided
19 from sedimentary remineralisation with denitrification supported by nitrate uptake
20 ($\overline{A} v D_w 0.16 \text{ mol m}^{-2} \text{ h}^{-1}$ for BML nitrate) an order of magnitude less than the flux of
21 nitrate from the sediments therefore resulting in net nitrate flux. This flux would
22 therefore have supported the high nitrate in the BML (Fig. 5) and result in regenerated
23 production in the DCM. This flux would however be unable to fully support the
24 nitrate uptake rates measured in the DCM since nitrate uptake at the DCM averaged
25 $35 \text{ mol m}^{-3} \text{ h}^{-1}$ and nitrate flux was $4.5 \text{ mol m}^{-2} \text{ h}^{-1}$ into the BML for the stratified
26 stations. A significant proportion of the nitrate driven production at the DCM was
27 therefore new production which would result in oxygen consumption in the
28 sediments. Potential new N inputs due to atmospheric deposition would also drive
29 new production and potential new biomass input into the bottom waters but this
30 production would occur in the upper mixed layer (Spokes et al., 1993). These
31 atmospheric inputs would therefore not be expected to affect nitrate uptake rates in the
32 DCM.

1 iv) The significant measured rate of sedimentary oxygen consumption was expected
2 to be due to a recent input of ‘new’ organic matter to the sediments during the
3 stratified period, since a study in the western Irish Sea gyre (Trimmer et al., 1999)
4 showed that the impact of the spring bloom on benthic oxygen uptake only lasts a few
5 weeks. The remineralisation of this biomass will drive decreasing oxygen
6 concentrations in the BML long after the spring bloom, as was shown previously with
7 bottom water oxygen concentrations decreasing steadily to a minimum of 3.2 mg l^{-1}
8 throughout the stratified period (March – September) at the Oyster Grounds (Boers,
9 2005).

10
11 The continued new production in the thermocline at the DCM should therefore be
12 considered to be a significant driver of low oxygen bottom water concentrations in
13 this region. Although daily primary production in the DCM is low relative to the
14 spring bloom, the DCM occurs throughout the stratified period and can be expected to
15 have a similar magnitude of impact as the spring bloom on bottom oxygen levels.

16 17 *4.5 Consequences of low oxygen levels in the Oyster Grounds*

18
19 There have been a limited number of studies on low oxygen levels in the offshore
20 North Sea as outlined in Colijn et al. (2002). In addition, there have been no studies
21 on the ecosystem effects on the low oxygen concentrations in this region to the best of
22 our knowledge and this study has made no attempt to address this issue. This area is
23 however an important feeding ground for many demersal fish such as sole (*Solea*
24 *solea*) and plaice (*Pleuronectes platessa*), which are known to be affected by low
25 oxygen concentrations ($<3 \text{ mg l}^{-1}$) (Tyson and Pearson, 1991). While it is possible that
26 fish can employ avoidance tactics, relatively immobile shellfish and benthic fauna
27 may be impacted. For example, *Nephrops norvegicus* can be sensitive to water
28 column hypoxia, while adults can cope with a wide range of environmental variation
29 (except when hypoxic), the effect on juveniles is marked at relatively mild levels of
30 oxygen depletion ($<5 \text{ mg l}^{-1}$) (Baden et al., 1990). The benthic community
31 composition in the Oyster Grounds is likely to change if there are repeated large scale
32 low oxygen events.

33 Current climate change scenarios for the North Sea may also act to decrease bottom
34 water dissolved oxygen in this region in the future due to three main predicted

1 features: waters will be warmer by 2-3°C and therefore contain less dissolved oxygen
2 by 0.4mg l⁻¹; stratification will occur earlier, the period of stratification longer and of
3 greater geographic extent since the surface waters will warm up preferentially, and
4 summer storms will decrease (Hulme et al., 2002). The increase in stratification
5 period may therefore in turn increase the annual new production possible at the DCM
6 with the subsequent potential impacts on bottom water oxygen levels indicated by our
7 findings.

8

9 **5. Conclusion**

10

11 The Oyster Grounds region shows potential for low bottom oxygen levels due to the
12 isolation of a shallow bottom mixed layer and the remineralisation of the organic
13 matter produced during the spring bloom and also subsequently from new production
14 throughout the summer at the DCM until stratification breakdown. The offshore
15 regions of the North Sea are undersampled both in terms of addressing the extent of
16 low oxygen levels and also the relevant biogeochemical processes. There is therefore
17 a need for improved monitoring in such regions to determine the location and
18 development of low oxygen concentrations, and if necessary, its impact on the
19 benthos.

20

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22

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28

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15
16

1 Table 1

2 Sediment nutrient exchange rates (\pm SE; n=3) and sedimentary oxygen uptake (\pm SE; n=3) and denitrification (\pm SE; n=4) where D_w is
 3 denitrification supported by the uptake of nitrate from the overlying water and D_n is denitrification coupled to nitrification of porewater
 4 ammonium. All measurements are $\text{mol m}^{-2} \text{h}^{-1}$ and were made at bottom water temperature. For nutrient exchange rates, positive values indicate
 5 flux from sediment to water and negative values indicate from water to sediment. Average calculated for bottom mixed layer for station B-D
 6 (Station A was well-mixed). *For N:P:Si ratio $N^{\text{tot}} = \text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$ flux

Stn	NO_3^-	NO_2^-	NH_4^+	PO_4^-	SiO_2	* $N^{\text{tot}}:P:Si$	O_2 uptake	D_n	D_w
A	4.0 (± 2.0)	0.4 (± 0.1)	39.7 (± 8.8)	0.8 (± 0.8)	92.6 (± 16.7)	55.1: 1: 115.6	524.3 (± 63.4)	2.7 (± 0.7)	0.8 (± 0.2)
B	0.0 (± 0.0)	-7.7 (± 0.2)	11.4 (± 4.1)	2.9 (± 1.2)	58.9 (± 10.2)	1.3: 1: 20.3	996.5 (± 200.3)	3.4 (± 1.0)	0.15 (± 0.1)
C	7.9 (± 2.1)	-3.0 (± 0.2)	-4.2 (± 5.3)	1.0 (± 0.8)	38.6 (± 6.8)	0.7: 1: 38.6	782.1 (± 152.6)	2.6 (± 0.5)	0.07 (± 0.0)
D	5.6 (± 1.3)	-2.5 (± 0.1)	18.0 (± 6.7)	3.0 (± 0.7)	109.0 (± 15.0)	7.0: 1: 36.3	1275.1 (± 43.2)	2.8 (± 0.6)	0.26 (± 0.1)
Av	4.5	-4.4	8.4	2.3	68.8	3.7: 1: 29.9	1017.9	2.9	0.16

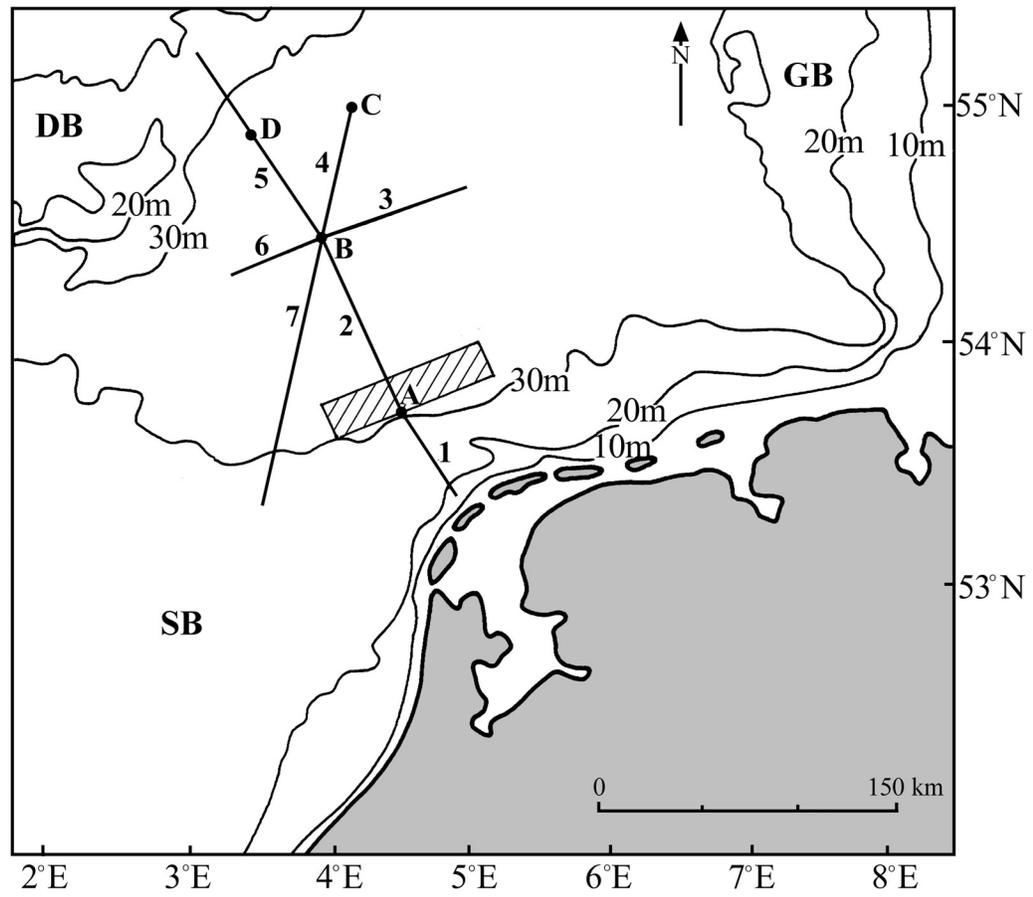
Table 2

Nitrate and ammonium uptake rates for stations A-D and f ratio for stations A-D where $f = \rho\text{NO}_3^- / (\rho\text{NO}_3^- + \rho\text{NH}_4^+)$ where ρ = uptake rate. Layers are well-mixed (WM, no stratification), surface of upper mixed layer (Surface), mid-upper mixed layer (UML), deep chlorophyll maximum (DCM) and bottom mixed layer (BML).

Station	Depth	Layer	NO_3^- uptake / $\mu\text{mol m}^{-3} \text{h}^{-1}$	SE (n-3)	NH_4^+ uptake / $\mu\text{mol m}^{-3} \text{h}^{-1}$	SE (n-3)	f ratio
A	0	WM	7.7	2.3	11.4	1.0	0.40
	5	WM	55	7.9	19.9	0.1	0.73
	15	WM	0.2	0.4	2.5	3.1	0.07
	36	WM	4.3	2.2	13.7	4.0	0.24
B	0	Surface	45.2	13.6	249.4	15.0	0.15
	15	UML	22.7	2.7	118.6	14.9	0.16
	34	DCM	32.0	2.5	30.0	0.9	0.51
	43	BML	6.4	2.8	25.1	7.1	0.20
C	0	Surface	2.6	0.9	4.2	0.1	0.38
	15	UML	1.3	0.2	11.9	1.7	0.09
	35	DCM	44.1	10.5	15.7	1.8	0.73
D	0	Surface	40.7	3.6	120.0	13.0	0.25
	15	UML	2.3	0.3	2.2	3.0	0.51
	29	DCM	28.9	2.1	28.0	7.0	0.51
	44	BML	4.5	2.5	16.0	7.0	0.22
		Average surface & UML	19.1		84.4		0.18
	Average DCM	35.0		24.6		0.58	
	Average BML	5.5		18.9		0.23	

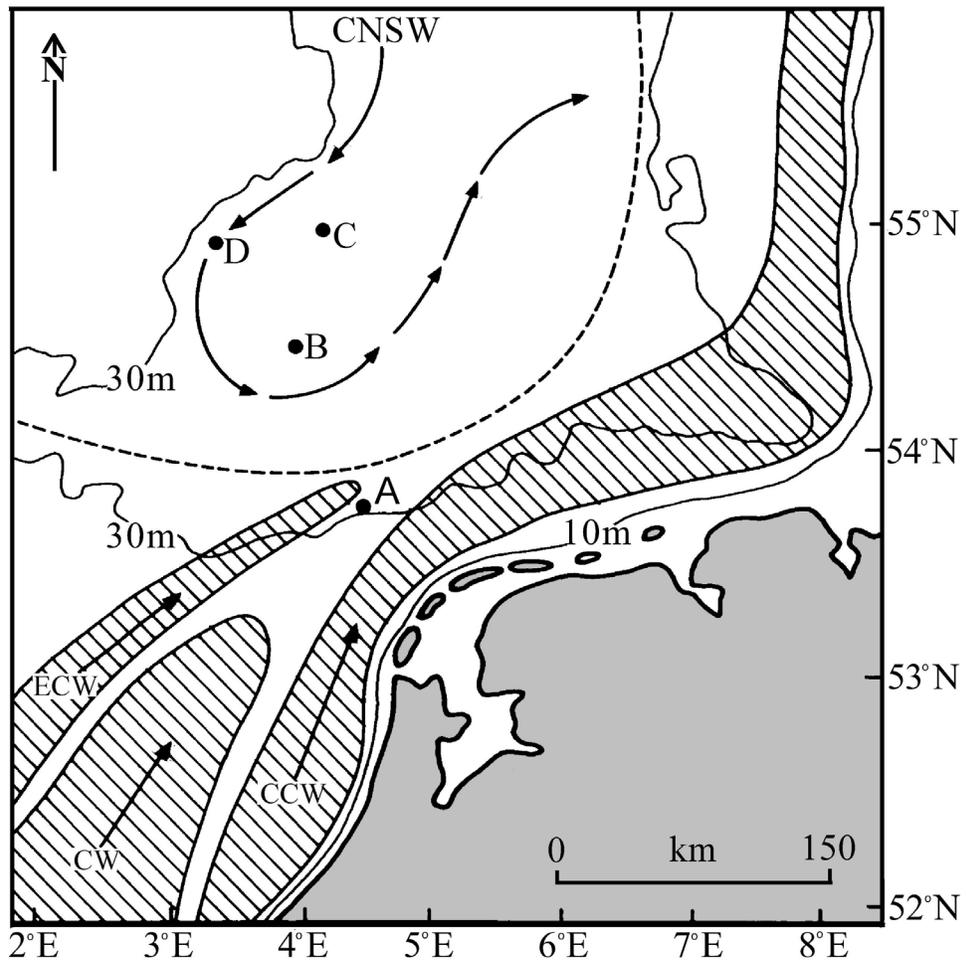
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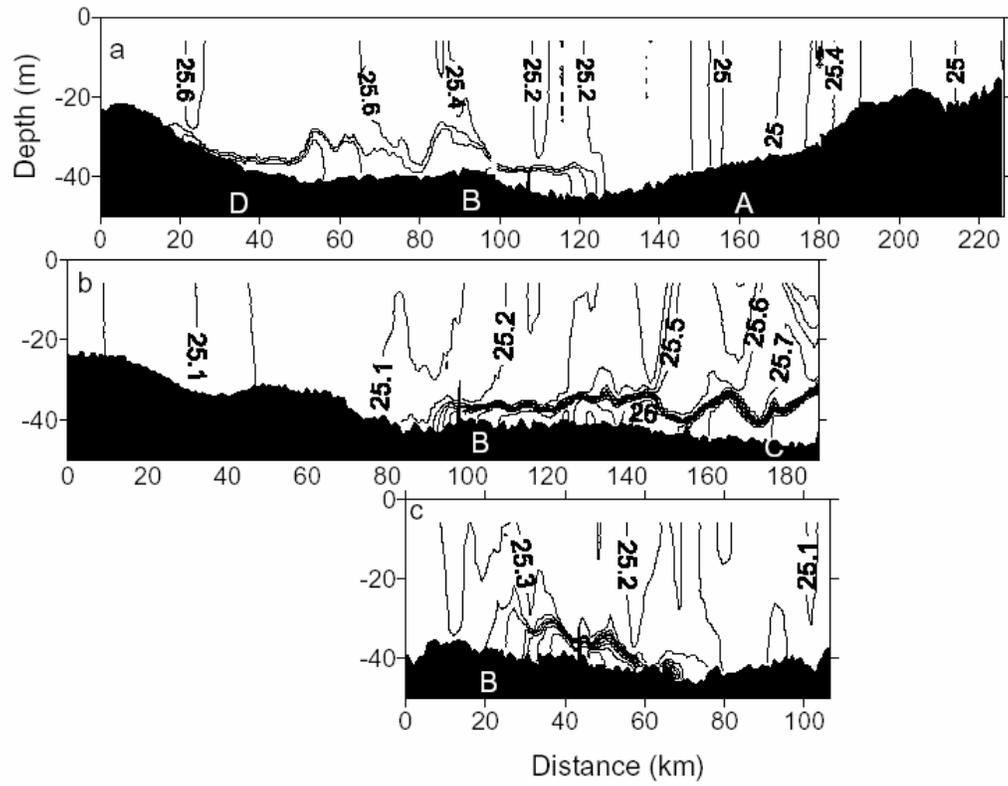
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2 Fig.1

ACCEPTED



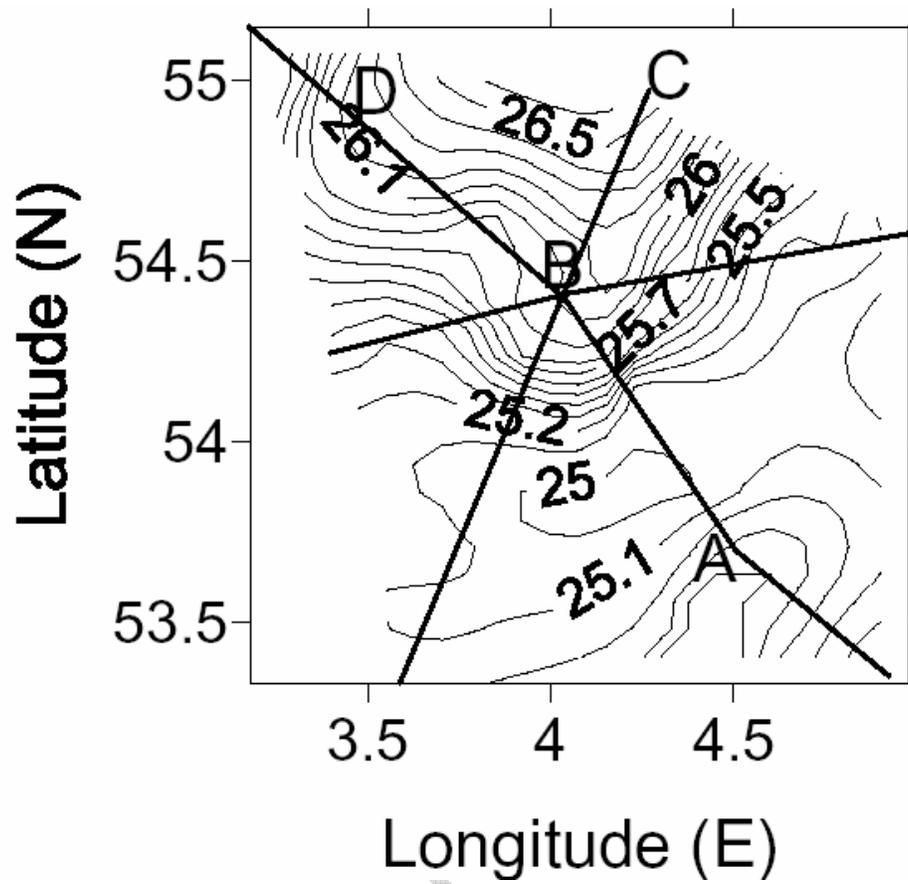
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2 Fig.2

ACCEPTED



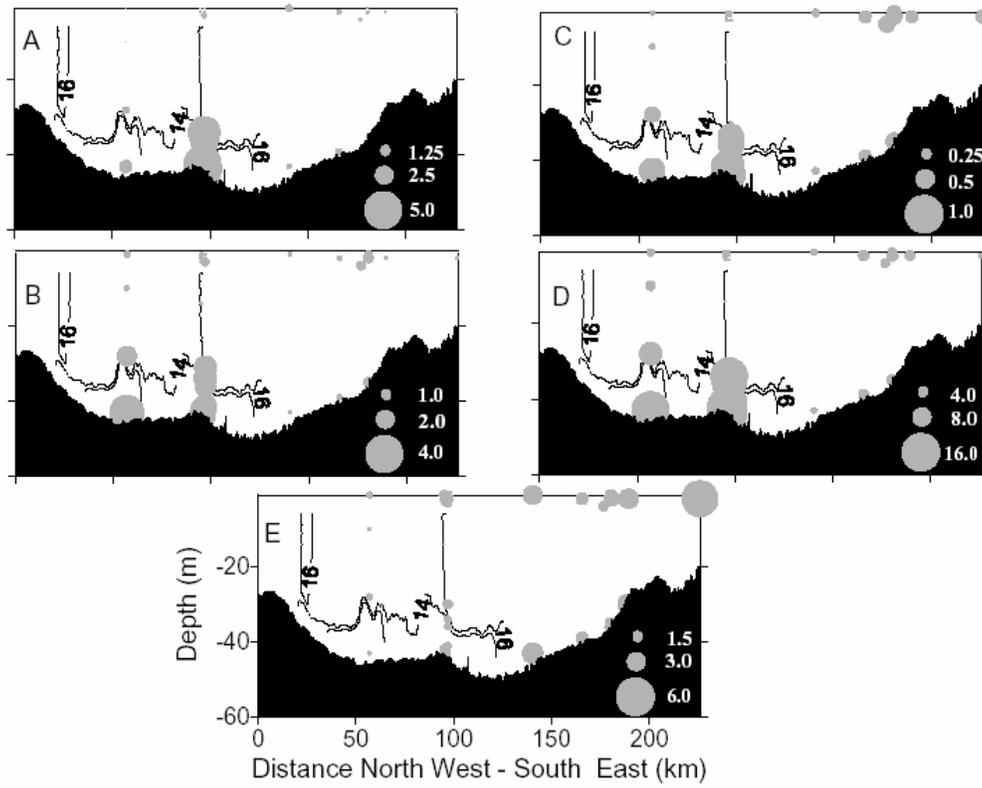
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2 Fig.3



1

2 Fig.4



1

2 Fig.5

3

4