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Seasonal benthic organic matter mineralisation measured by oxygen uptake and denitrification along a transect of the inner and outer River Thames estuary, UK

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ABSTRACT: Seasonal measurements of organic matter mineralisation by oxygen uptake and denitrification were carried out from July 1996 to March 1998 along a ~200 km transect of the River Thames estuary, UK. There was a distinct gradient of decreasing rates of organic matter mineralisation seaward, which was related to the concentration of suspended solids and sedimentary organic carbon (C) at each site. There was clear seasonality and highest rates of oxygen uptake (10 056 µmol O_2 m^{-2} h^{-1}) at the muddy sites, but lower rates and non-temperature-dependent oxygen uptake at the sandier sites. Denitrification, both that driven by nitrate from the overlying water (D_w) and that coupled to nitrification in the sediment (D_n), followed a similar trend to oxygen uptake, from negligible rates of approximately 1 µmol N m^{-2} h^{-1} for both D_w and D_n at the furthest offshore site, Site 12, to 11 407 and 8209 µmol N m^{-2} h^{-1}, respectively, at the inner muddy Site 1. The Thames estuary is heterotrophic and a very efficient organic C filter, trapping and remineralising 77% of its organic C input. Attenuation of fluvial nitrate loads was regulated by freshwater flow. Minimal attenuation (3%) occurred during peak flows (i.e. during periods of shortest freshwater flushing time) and >100% attenuation during periods of lowest freshwater flow (longest flushing times). Including the sewage treatment works (STWs) nitrate load in this calculation reduced the degree of attenuation of the nitrate load to, on average, 11%. Annual rates of D_w and D_n for an inner area of 125 km^2 were 112 and 85 Mmol N yr^{-1}, respectively, with a total rate of 196 Mmol N yr^{-1} (2744 t), which was equivalent to 9% of the total dissolved inorganic nitrogen (DIN) load for 1995-96. A mean denitrification rate (D_w) of 0.64 mol N m^{-2} yr^{-1}, based on measurements in 4 east coast estuaries, was used to estimate a total rate of denitrification for the entire area of UK east coast estuaries. The total rate of 0.81 Gmol N yr^{-1} represented 16% attenuation of the total fluvial discharge of nitrate (~6 Gmol N yr^{-1}) to the UK's east coast estuaries (1995-96) and hence a 16% reduction in the UK nitrate load to the North Sea.

KEY WORDS: Organic mineralisation · Oxygen uptake · Denitrification · Nutrient attenuation

INTRODUCTION

Estuaries are the major conduits between land and sea, through which flow the loads of soluble and particulate materials derived from the catchment area of each estuary. These loads may be derived from both leaching and run-off from the land and from atmospheric deposition within the catchment, each of which may have anthropogenic components. Estuaries act as traps for both particulate and dissolved organic loads, as well as mineral particles. Settlement of organic matter in turn stimulates benthic respiration and a remineralisation of organic material. Oxygen is rapidly depleted with depth in surface sediments and anoxic mineralisation proceeds via alternative electron acceptors. In nutrient-enriched estuaries nitrate is often abundant and may be respired and in turn lost as N_2 through denitrification (Nedwell 1975, Seitzinger et al. 1980, Billen et al. 1985, Law et al. 1991, Nielsen et al.

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1995, Nixon et al. 1996, Ogilvie et al. 1997, Trimmer et al. 1998).

Studies on benthic mineralisation in estuarine and coastal sediments have tended to be either spatially or temporally restricted (see Heip et al. 1995). Although both Kelley et al. (1990) and Middelburg et al. (1996) demonstrated gradients of decreasing mineralisation rates along estuaries, others have shown little variation between sediment sites (Hargrave & Philips 1981, Jørgensen & Sørensen 1985, Cammen 1991, Trimmer et al. 1998). Nowicki et al. (1997) reported denitrification data along an extensive gradient from Boston Harbour and Massachusetts Bay and did, at least for denitrification, show a clear relationship between sedimentary organic content and rates of mineralisation. However, their study did not include measurements of oxygen uptake by the sediment. The aim of the present study was to provide a detailed assessment (spatially and temporally) of mineralisation rates via oxygen uptake and denitrification along an estuarine and coastal gradient and to then use this data to assess the capacity of the Thames estuary as a biological filter for dissolved inorganic nitrogen (DIN) and organic C.

MATERIALS AND METHODS

Sample sites. The tidal Thames estuary covers an area of approximately 131 km^2 (Fig. 1) and is the 100 km stretch of the River Thames between Teddington Weir (landward), where it is 100 to 200 m wide, and Southend Pier (seaward), where it is 7 km wide. It drains a catchment of 14 000 km^2 with a population of 12 million people. Spring and neap tides at Southend are 6 and 3 m respectively (Environment Agency unpubl. public access data, Environment Agency Data Centre, Twirton, UK).

This study of the Thames estuary (Fig. 1) was divided into an inshore and an offshore transect visited between July 1996 and March 1998. Initially, from July 1996 to February 1997, in the inner Thames, 6 sites were visited between Mucking Flats (Site 4) and

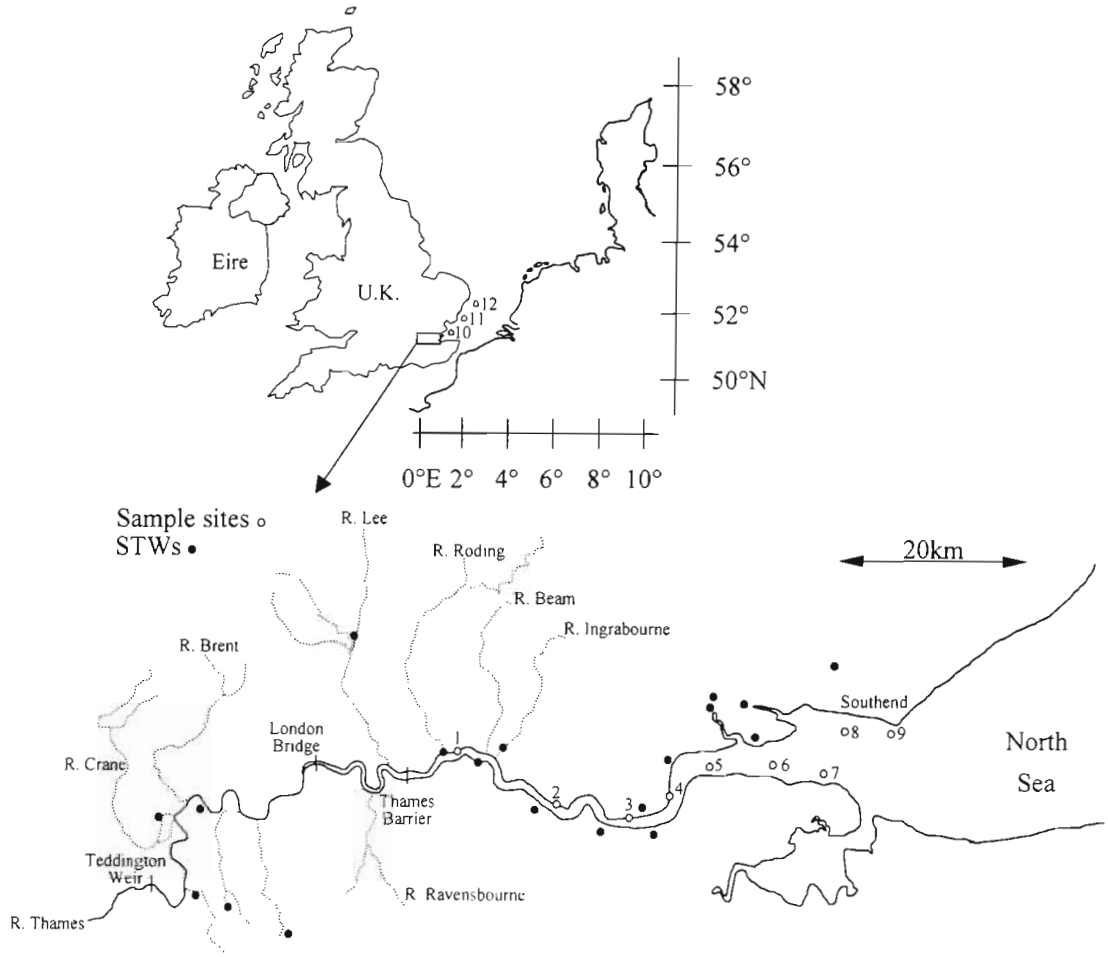

Fig. 1. Locations of the sample sites in both the inner and outer Thames transects. STWs: sewage treatment works

Southend (Sites 8 and 9). This was followed by a 3 mo crossover period of visiting 9 sites, when the transect was extended upstream to Beckton (Site 1), where the major sewage treatment works (STWs) serving London discharge. Finally, from August 1997 to March 1998, 6 sites were visited between Beckton and Southend. The inshore transect was visited with a small (15 man) hovercraft 2 h after high-tide (water depth over sediments at high-tide = 2 to 3 m). Sample site positions were determined using a global positioning system (GPS) to within ~100 m^2. The offshore transect extended from 16 km from Southend (Site 10, water depth at high-tide = 15 m) to the furthest extent of the Thames plume, 122 km offshore (Site 12, water depth at high-tide = 45 m) and was visited on board the RV 'Cirolina'. See Table 1 for locations and Table 2 for frequency and dates of visits.

Water column characteristics. Water samples (50 l) for core storage and analysis were collected by hand in plastic containers from each of the inner Thames sites. Bottom water samples (50 l) for storage of offshore sediment cores (see below) were collected using Niskin bottles mounted on a CTD rosette sampler. Subsamples of water (20 ml) were taken from each inner estuary site for nutrient analysis, filtered (0.2 µm Minisart Plus™, Sartorius UK Ltd) and fixed with mercuric chloride solution (200 µl, 0.2% w/v; Kirkwood 1992). Additional water samples were taken for salinity (200 ml) and chlorophyll (500 ml) analyses. The water and air temperatures at each site were measured with a mercury thermometer and the air pressure for the survey day recorded. Similar samples were taken at the offshore sites directly from the Niskin bottles mounted on the CTD and analysed immediately. All nutrient analyses (NO_3^-, NO_2^-, NH_4^+, SiO_3 and PO_4^{3-}; Kirkwood 1996) were carried out using a continuous flow autoanalyser (Skalar, SA4000, De-Breada, The Netherlands). Salinity was measured using a salinometer (Autosal, Guildline, USA). Suspended loads were measured by filtering known volumes of water through preweighed glass fibre filters (5 cm diameter, GF/F, Whatman Ltd, UK), drying and reweighing. Chlorophyll was measured by filtering between 0.1 and 0.25 l through GF/F glass fibre filters and extracting in neutralised 90% acetone for 24 h at 4°C in the dark. Measurements of extracted chlorophyll fluorescence (Tett 1987) were made (before and after acidification with 8% hydrochloric acid to distinguish phaeopigments) using a fluorometer (Turner Designs Model 10).

Sediment collection and storage. At each site in the inner Thames, sediment samples were collected by hand in approximately 50 cm of water. At the offshore sites, sediment samples were first collected using a NIOZ cylindrical box corer (31 cm inner diameter [i.d.], Netherlands Institute for Sea Research). The box corer collected 30 to 50 cm of sediment and 15 to 25 l of site water; any cores that had drained were discarded and the box corer was redeployed. Three large sediment cores (~30 cm deep) and overlying water (1 l) were collected to measure benthic oxygen uptake at each location using Perspex core tubes (65 cm long × 8 cm i.d.), each sealed at the bottom with a silicon rubber bung. Smaller sediment cores (~10 cm deep) and overlying water (~100 ml) were collected to measure benthic denitrification at the same time using small perspex core tubes (20 cm long × 3.4 cm i.d.), each sealed with a rubber bung. Cores from the inner sites were transported back to the laboratory usually within 3 h. All cores were then stored open and submerged in aerated site water at the *in situ* temperature until required (<2 to 12 h). The upper part of the inner Thames estuary suffers from a dissolved oxygen sag (Fig. 2). Therefore, storing the cores in aerated site water would have affected the *in situ* conditions and this would have been most dramatic at Sites 1 to 4, where the mean *in situ* dissolved oxygen levels were between 55 and 70% of air saturation.

Sediment characteristics. Sediment cores (30 cm × 6 cm i.d.) were taken at each site, to a depth of at least 15 cm and sealed at both ends with rubber bungs. Sediment porosity, particle size distribution, organic C, total nitrogen (N) and chlorophyll concentrations were measured at 1 cm depths on extruded samples down to 10 cm. Porosity was determined from the dry weights and wet weights of known volumes of sediment. Particle size distribution was measured by re-suspending each 1 cm slice in deionised water using an ultrasonic water bath and wet sieving through a range of stainless steel meshes (2000, 1000, 500, 250, 125 and 63 µm pore sizes). Each fraction was then collected, re-dried and re-weighed. Particle size was expressed as a percentage of the total dry weight. Each sample for C and N analysis was homogenised with hydrochloric acid (5 ml, 1 M) to remove carbonate, and after re-drying subsamples (20 mg) were analysed for their organic C and N contents with a CHN analyser (model 2400, Perkin-Elmer Ltd, Norwalk, Connecticut, USA) calibrated with standard acetanilide (71.09% C, 10.36% N). Sediment chlorophyll pigments were extracted (2:1 sediment volume to acetone) and measured as described above. Sediment temperatures were measured with a mercury thermometer inserted into the surface sediment layer.

Sediment biological rate measurements. ***Oxygen uptake:*** The 3 large core tubes were capped and completely water-filled to exclude air bubbles. A mid-column water sample (20 ml) was then drawn off into a gas-tight syringe, gently transferred to an Exetainer (12 ml Labco Ltd, High Wycombe, UK) and fixed for Winkler analysis of dissolved oxygen. The water col-

umn in each tube was stirred with an induction motor driving a magnetic follower (Rank Brothers Ltd, Cambridge, UK) at 300 rpm (Nedwell & Trimmer 1996). The rates of benthic O_2 uptake were measured using dissolved O_2 electrodes (model 1302, Strathkelvin Ltd, Glasgow, UK) coupled to a 6 channel O_2 meter (Essex Electronics Centre, Colchester, UK). The multi-channel O_2 meter was connected to a computer (V.I.P computers, UK) with data analysis software (Notelog®, Garrat Consultants, Colchester, UK) which logged, displayed and analysed the data. The on-screen computer logging enabled the oxygen concentration in the water column to be continuously monitored and statistically analysed for linearity with respect to time. Significant rates of oxygen uptake ($p < 0.05$) could usually be determined within 1 to 4 h. Triplicate incubation chambers containing only site water (500 ml), with no sediment present, were treated and incubated as above, to act as controls for water column remineralisation processes in the absence of sediment/water exchange.

Denitrification measured by isotope pairing: The 9 small sediment cores were used to measure denitrification rates using the $^{15}NO_3^-$ isotope pairing technique of Nielsen (1992). Six of the nine cores were spiked by addition of $^{15}NO_3^-$ (10 mM $Na^{15}NO_3^-$ [99.3 atom%, Europa, Crewe, UK]) into the overlying water and left to equilibrate for 0.5 h (Rysgaard et al. 1995). A prerequisite of the isotope pairing technique is a uniform mixing of the $^{14}NO_3^-$ and $^{15}NO_3^-$ isotopes throughout the denitrification zone (Nielsen 1992), which could have been a problem at the outer sites with a deeper oxic layer. In order to test for this we added $^{15}NO_3^-$ at a range of concentrations (5 to 40 µM), and if the calculated rates of coupled denitrification proved to be subsequently independent of the concentration of $^{15}NO_3^-$ added, this was taken as good evidence for uniform mixing (Nielsen 1992, Nielsen & Glud 1996). Once this had been proven cores were amended at the higher concentration of 40 µM $^{15}NO_3^-$ to minimise the underestimation of denitrification (Nielsen & Glud 1996). At the inner, higher nitrate sites enrichment of the NO_3^- pool was usually about 30% (Rysgaard et al. 1995).

Water samples (2 ml), collected from all core tubes to determine the initial $^{14}NO_3^-$:$^{15}NO_3^-$ ratio in the water overlying the treatment cores, were filtered and preserved prior to analyses (see above). The sediment in the 3 reference cores was then gently mixed into a slurry with the overlying water and a sample (20 ml) carefully drawn off into an Exetainer (12 ml Labco Ltd, High Wycombe, UK) containing $ZnCl_2$ solution (500 µl, 25% w/v) and sealed. The $^{15}NO_3^-$ enriched cores were sealed and incubated in the dark at the *in situ* temperature, with gentle stirring (~60 rpm) of the water column for 2 to 6 h. The on-screen data logging in the parallel oxygen uptake cores ensured that the concentration of oxygen in the overlying water never fell below 80% of air saturation (see above). Following incubation, the $^{15}NO_3^-$ enriched cores were processed as the reference cores.

All the slurry samples were sent to the National Environmental Research Institute, Silkeborg, Denmark, to be analysed for abundance and concentration of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$ on a gas chromatograph coupled to a dual inlet isotope ratio mass spectrometer (Europa Instruments, Crewe, UK). Denitrification rates were calculated according to Nielsen (1992).

Calculation of freshwater flushing times, nutrient loads and attenuation. The Thames estuary was subdivided into 2 main sections according to the type of bathymetric data available (H. R. Wallingford Ltd, UK)—Section 1: Teddington Weir to Westminster Bridge and Section 2: Westminster Bridge to Southend Pier. Section 1 was subdivided into 25 sectors, each 1000 m long. The cross-sectional area of each sector (given at 0.5 m depths) was multiplied by its length (1000 m) to give the volume of water within each sector at mid-tide. Section 2 was subdivided into 75 sectors, each 1000 m long. The width of the channel at 1.5 m intervals above or below chart datum (at mid-tide) was then used to construct a series of trapezia. The volume of water within each sector was calculated by multiplying the area of each trapezium (i.e. cross-sectional areas) by the length of each box (i.e. 1000 m) and summing the volume of all sectors.

Monthly (1992 to 1997) axial surveys of chlorinity (*Cl*) (Environment Agency unpubl. public access data) at discreet sampling sites along the estuary were used to assign a salinity (*S*) value to each sector, using Knudsen's formula:

$$S‰ = 0.030 + (1.805 \times Cl‰)$$

The volume of freshwater within each sector was then calculated using:

$$\text{freshwater } (m^3) = \text{total volume of sector } (m^3) \times [1-(S°/S^1)]$$

Where $S°$ is the salinity value assigned to each sector and S^1 is the salinity of the offshore coastal water outside the estuary, in this case 35‰ for the southern North Sea.

Seasonal variations in freshwater flushing times for the Thames estuary were calculated by dividing the seasonal freshwater volumes by seasonal freshwater flows; taken as the sum of flows from the River Lee, River Roding and the River Thames flowing over Teddington Weir (Environment Agency unpubl. public access data).

Nutrient loads (monthly averages for 1995-96) for the Thames and all the UK east coast estuaries (The Wick in Scotland to The Medway in England) were calcu-

lated by multiplying fluvial freshwater flows by nutrient concentrations (Harmonised Monitoring data, Department of the Environment, Transport and the Regions). Axial suspended solid and dissolved oxygen profiles (expressed as distance from London Bridge) along the Thames estuary (1993 to 1998) were provided by the Environment Agency (unpubl. public access data); sampling was usually within 2 to 3 d of our own sampling dates. The fluvial and STWs organic C loads to the Thames estuary are based on the most recent available data (Environment Agency unpubl. public access data) and are made up of average concentration data and average flow data for all data available to date from 11 rivers (81% being the Thames flowing into the estuary at Teddington), 16 STWs and 9 trade discharges (only 1 of which contributes more than 1% of the total organic C budget).

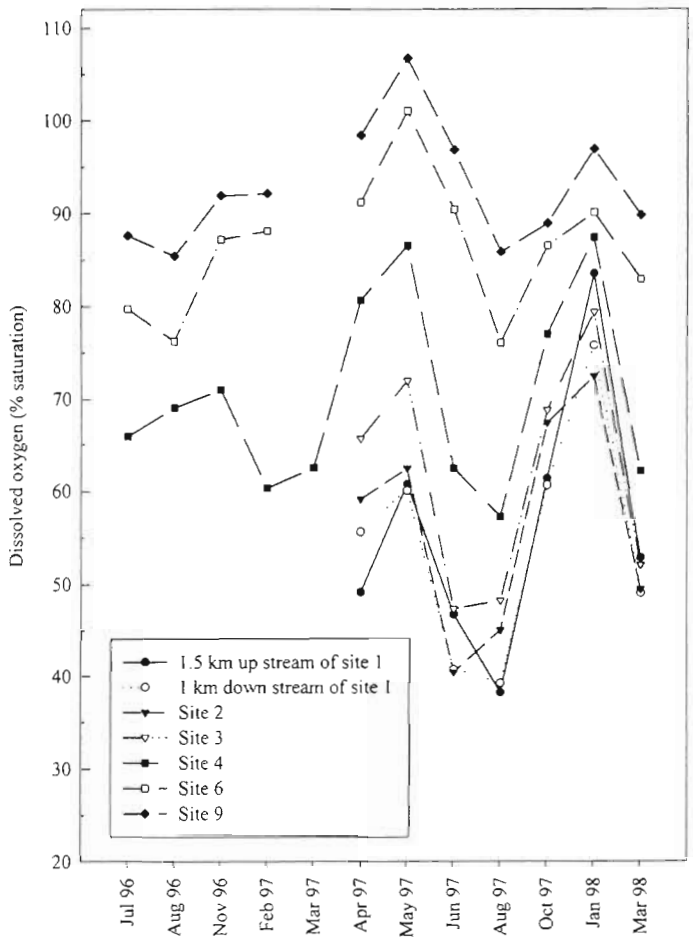

Fig. 2. Water column dissolved oxygen (% of air saturation). Point samples collected by the Environment Agency (unpubl. public access data) within 2 to 3 d of this study's sampling date

RESULTS

Water column characteristics

Dissolved oxygen increased down the inner estuary (Fig. 2), with minimum saturation (with respect to air) either side of Site 1 (mean 55 ± 4% SE, n = 14) and maximum saturation at Site 9 (92 ± 2% SE, n = 12). Dissolved oxygen increased at all sites during late spring (May 1997) and mid-winter (January 1998). Maximum nitrate concentrations were measured at the head of the transect at Site 1 (range 511 to 797 µM, mean = 611 µM), decreasing downstream to 0.6–9 µM (mean = 4 µM) at Site 12. Average chlorophyll concentrations did not vary significantly along the inner estuary; increasing from only 4 µg l^{-1} (range 1.3 to 7.3 µg l^{-1}) at Site 1, to a peak of 8 µg l^{-1} (range 3.5 to 23 µg l^{-1}) at Site 7 and then decreasing to 1.5 µg l^{-1} (range 0.6 to 2.9 µg l^{-1}) at Site 9. Maximum off-shore spring chlorophyll concentrations of 18.6 and 12.8 µg l^{-1} were measured at Sites 10 and 12, respectively. Salinity increased from 2.1 ± 0.2‰ (SE, n = 45, 5 yr mean) at London Bridge to 31.7 ± 0.7‰ (SE, n = 57, 5 yr mean) at Southend. The outer transect sites (Sites 10 to 12) were essentially fully marine, with salinity varying (by a few ‰) from around 34.4‰ at Site 10 to around 35‰ at Site 12.

Suspended loads initially increased down the estuary to 81 ± 3.8 mg l^{-1} (SE, n = 218, 5 yr mean) 18 km downstream from London Bridge, where both the major Beckton and Crossness STWs discharge (Fig. 3). Suspended loads then decreased further downstream until the broad high-tide turbidity maximum was reached, between 35 and 53 km downstream around the Tilbury Basin mudflats, where suspended loads peaked at 90 ± 5.6 mg l^{-1} (SE, n = 219, 5 yr mean). Suspended loads decreased again further seaward to their lowest values for the inner estuary at Southend of 28 ± 2.9 mg l^{-1} (SE, n = 58, 5 yr mean). There was then a third turbidity peak at Site 10 of 34 ± 2.7 mg l^{-1} (SE, n = 127) followed by a steady decrease seaward out to Site 12 (3.8 mg l^{-1} ± 0.3 SE, n = 96).

Sediment characteristics

From Site 1 seaward along the transect there was a general increase in particle size until, offshore, the sediments were dominated by fine and medium sands (Table 1). Porosity and organic C were greatest at the muddy sites (Sites 1, 4 and 5), decreasing in proportion

to each other ($p < 0.05$) seaward along the transect (Fig. 3). The lowest C:N ratios were also recorded at the 3 muddy sites. Although a C:N ratio of 12:1 was recorded at the offshore Site 12, the percent total N was probably below the limit of detection (0.02%) and the value of the ratio therefore suspect.

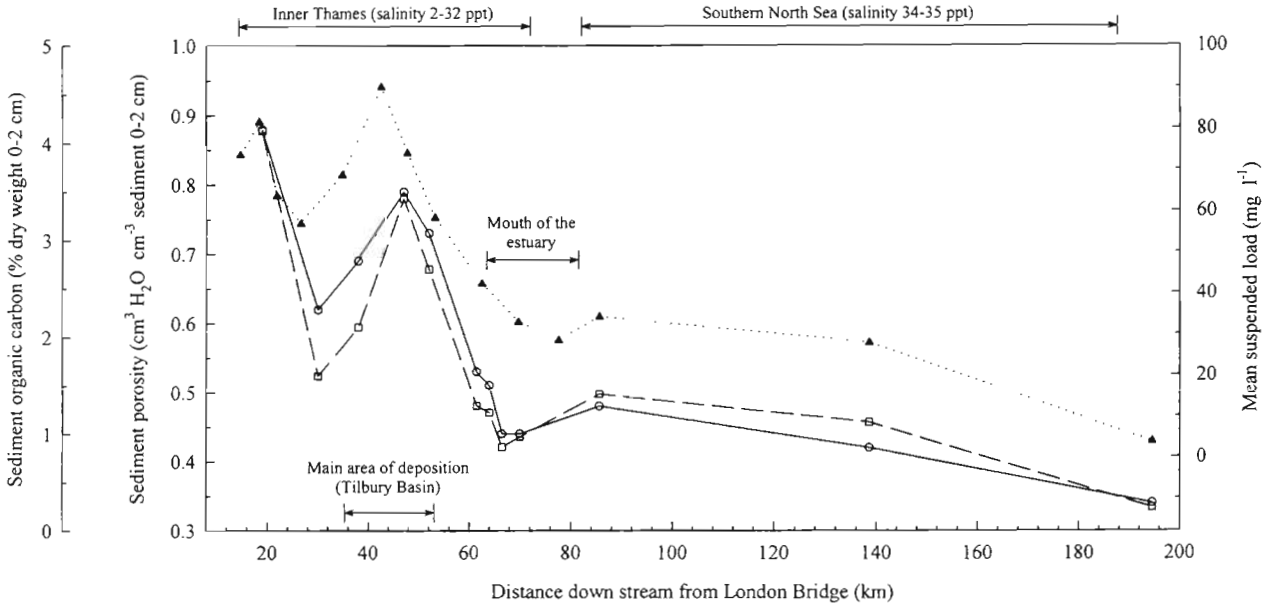

Fig. 3. Sediment porosity (○) and organic carbon (□); mean of all measurements for all sites from July 1996 to March 1998. Suspended load (▲); 18 to 80 km: 5 yr mean (Environment Agency unpubl. public access data), 80 to 200 km: mean of 6 surveys from July 1996 to April 1997

Table 1. Site locations and sediment characteristics for the 12 sites investigated on 6 occasions. Particle size measured once in May 1996 for inner Sites 4 to 10, July 1996 for outer Sites 1 to 3 and April 1997 for inner Sites 11 to 13

Site[a]	Location N	Location E	Particle size[b] 0–10 cm (≥50% w/w)	Porosity[c] 0–2 cm (cm^3 H_2O cm^{-3} sed.)	Organic C[d] 0–2 cm (% dry wt)	Total N[e] 0–2 cm (% dry wt)	C:N ratio 0–2 cm (% dry wt)
Inner							
1 (TH 11)	51° 31' 07	0° 07' 47	Silts/clays	0.88	4.13	0.35	12:1
2 (TH 12)	51° 27' 76	0° 16' 47	Very fine sands	0.62	1.60	0.10	16:1
3 (TH 13)	51° 27' 09	0° 22' 12	Very fine sands	0.69	2.10	0.07	30:1
4 (TH 9)	51° 28' 80	0° 26' 46	Silt/clays	0.79	3.43	0.23	15:1
5 (TH 5)	51° 29' 20	0° 31' 50	Silt/clays	0.73	2.70	0.18	15:1
6 (TH 10)	51° 29' 49	0° 35' 10	Very fine sands	0.53	1.29	0.05	26:1
7 (TH 4)	51° 29' 47	0° 38' 50	Fine sands	0.51	1.22	0.05	24:1
8 (TH 7)	51° 31' 28	0° 40' 83	Very fine–fine sands	0.44	0.86	≤0.02	43:1
9 (TH 8)	51° 31' 56	0° 44' 44	Very fine sands	0.44	0.97	≤0.02	49:1
Outer							
10 (TH 1)	51° 30' 80	0° 58' 00	Very fine sands–silt/clays	0.48	1.41	0.05	28:1
11 (TH 2)	51° 48' 00	1° 35' 00	Fine sands	0.42	1.12	≤0.02	56:1
12 (TH 3)	52° 00' 00	2° 20' 00	Medium sands	0.34	0.24	≤0.02	12:1

[a]Sites have been renumbered sequentially for clarity but the original TH number is given for cross reference to other JoNuS project papers
[b]Wentworth classification (Tait 1981): medium sands, 500 to 250 µm; fine sands, 250 to 125 µm; very fine sands, 125 to 63 µm; silt/clays, <63 µm
[c]CV 4%
[d]CV 14%
[e]CV 18%

Chlorophyll concentrations in the surface 0 to 1 cm sediment layer showed no significant variation along the inner estuary (mean 27 mg chl *a* m^{-2}) and showed no significant seasonal variation, apart from a small peak in May (mean 62 mg chl *a* m^{-2}).

Sediment rate measurements

Oxygen uptake

There was a broad range of sedimentary oxygen uptake rates along the transect (Table 2), from 507 µmol O_2 m^{-2} h^{-1} at the furthest offshore Site 12 to 10 056 µmol O_2 m^{-2} h^{-1} at the inner muddy Site 4. The overall trend of mean rates is illustrated in Fig. 4A. ANOVA indicated significant inter-site variation for rates of oxygen uptake on each occasion ($p \leq 0.05$). However, post hoc Tukey analysis showed very few significant ($p \leq 0.05$) inter-site differences from Sites 6 to 12 but a consistent peak in oxygen uptake at the inner muddy sites. ANOVA indicated significant seasonal differences in oxygen uptake rates at each site ($p \leq 0.003$). However, the clearest seasonal trends (i.e. significant correlation with seasonal temperature) and highest rates of oxygen uptake were at the muddy sites, whilst lower and non-temperature-dependent oxygen uptake rates were recorded at the sandier sites (Fig. 5). There was a significant positive correlation ($p < 0.001$) between overall average rates of oxygen uptake and sedimentary organic C content along the transect.

Denitrification

The calculated rates of coupled denitrification from the initial trial at the outer Sites 10 to 12 proved to be

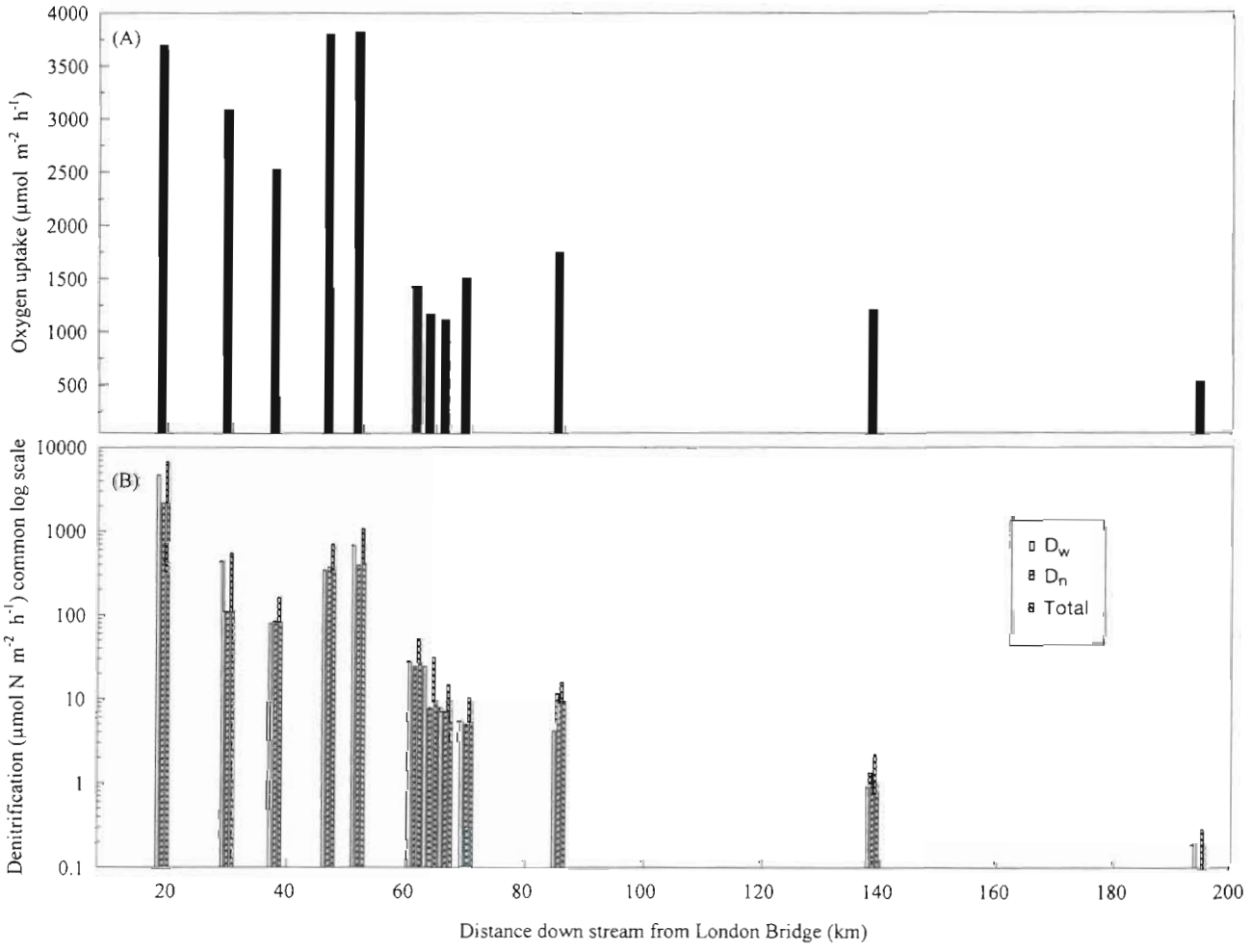

Fig. 4. Mean rates of (A) oxygen uptake and (B) denitrification at each site for all samples collected along the Thames transect

Table 2. Sedimentary rates of oxygen uptake and denitrification (D_w and D_n) for each site in the Thames estuary, numbers in brackets are standard errors, n = 3 and 6 respectively. Note standard errors of <1 are not shown. All rates are μmol O_2 or N m^{-2} h^{-1}

Site	Jul 96	Aug 96	Oct 96	Nov 96	Feb 97	Mar 97	Apr 97	May 97	Jun 97	Jul 97	Aug 97	Oct 97	Jan 98	Mar 98
Inner														
1 O_2							2870	3562	7485		3113	1740	2427	4721
							(256)	(142)	(1037)		(184)	(578)	(184)	(449)
1 D_w							11407	2311	398		4389	2047	6626	5757
							(1259)	(586)	(67)		(296)	(280)	(855)	(337)
1 D_n							8209	2428	558		437	138	301	2991
							(486)	(293)	(89)		(98)	(57)	(144)	(290)
2 O_2							2610	2495	6304		2884	1391	3220	2792
							(383)	(318)	(1205)		(538)	(405)	(434)	(20)
2 D_w							418	43	235		98	36	2240	58
							(129)	(11)	(66)		(21)	(4)	(1035)	(7)
2 D_n							385	15	0		38	16	271	63
							(114)	(4)			(7)	(5)	(108)	(5)
3 O_2							1671	2924	2957		5384	1632	1527	1647
							(360)	(237)	(830)		(186)	(389)	(140)	(82)
3 D_w							156	30	80		93	74	39	85
							(46)	(7)	(10)		(24)	(17)	(5)	(10)
3 D_n							157	21	145		47	19	100	116
							(32)	(6)	(57)		(9)	(6)	(38)	(14)
4 O_2	4313	6022		2387	1415	1546	2574	3714	6443		5486	2736	4301	4789
	(283)	(1439)		(101)	(104)	(221)	(186)	(511)	(1307)		(504)	(121)	(509)	(1008)
4 D_w	310	243		183	333	1646	741	123	109		124	165	96	58
	(26)	(30)		(63)	(20)	(423)	(163)	(25)	(29)		(22)	(30)	(19)	(12)
4 D_n	213	334		173	227	1816	962	81	158		151	53	215	90
	(23)	(39)		(39)	(37)	(557)	(198)	(11)	35		(33)	(11)	(44)	19
5 D_n	4328	10056		1772	1489	1412	5358	2625	4379					
	(714)	(1326)		(326)	(273)	(78)	(727)	(140)	(914)					
5 O_2	217	99		48	193	569	3261	986	178					
	(28)	(17)		(6)	(119)	(285)	(519)	(172)	(18)					
5 D_w	238	264		71	324	275	1513	187	284					
	(12)	(41)		(4)	137	(166)	(440)	(36)	50					
6 O_2	1798	836		1006	502	500	955	2407	2220		3680	539	1502	1843
	(255)	(74)		(127)	(182)	(1)	(197)	(451)	(428)		(413)	(45)	(70)	(243)
6 D_w	35	7		74	59	18	0	0	11		103	11	19	8
	(5)	(1)		(22)	(20)	(8)			(4)		(9	(1)	(9)	(1)
6 D_n	45	15		110	67	0	0	0	19		0	14	17	8
	(6)	(4)		(34)	(19)				(6)			(1)	(5)	
7 O_2	1277	1636		932	620	490	705	2147	823					
	(95)	(393)		(47)	(48)	(122)	(117)	(485)	(453)					
7 D_w	35	54		27	4	27	14	17	17					
	(1)	(11)		(7)	(1)	(2)	(9)	(7)	(6)					
7 D_n	25	16		22	0	0	0	0	0					
	(2)	(1)		(3)										
8 O_2	1358	1306		566	558	535	697	672	1004		2500	1576	1136	1248
	(266)	(63)		(80)	(207)	(23)	(175)	(101)	(214)		(161)	(540)	(85)	(142)
8 D_w	35	11		0	2	0	3	7	15		14	5	0	4
	(9)	(2)					(2)	(1)	(2)		(3)	(2)		(1)
8 D_n	35	14		0	5	0	0	11	0		10	9	0	4
	(3)	(2)			(1)			(1)			(3)	(1)		(1)
9 O_2	2242	3956		553	898	410	689	1137	2264					
	(552)	(449)		(59)	(125)	(32)	(250)	(308)	(1393)					
9 D_w	17	18		1	2	0	0	1	6					
	(2)	(4)							(1)					
9 D_n	16	12		1	1	0	0	0	11					
	(4)	(3)							(3)					

Table 2. (continued)

Site	Jul 96	Aug 96	Oct 96	Nov 96	Feb 97	Mar 97	Apr 97	May 97	Jun 97	Jul 97	Aug 97	Oct 97	Jan 98	Mar 98
Outer														
10 O_2	2325		1383				1058			2278				
	(425)		(252)				(58)			(233)				
10 D_w	5		5				3			4				
			(1)											
10 D_n	27		9				5			7				
	(2)		(1)				(1)			(1)				
11 O_2	1481		1480				473			1458				
	(129)		(27)				(77)			(368)				
11 D_w	2		1				2			0				
11 D_n	1.3		4				0			2				
			(1)											
12 O_2	541		609				507			1427				
	(136)		(35)				(59)			(127)				
12 D_w	0		0				1			0				
12 D_n	0		0				0			0				

independent of the concentration of $^{15}NO_3^-$ added, which was taken as good evidence for a uniform mixing of the $^{14}NO_3^-$ and $^{15}NO_3^-$ isotope pools.

Denitrification, both that driven by nitrate from the overlying water (D_w) and that coupled to nitrification in the sediment (D_n) (Table 2), followed a trend along the transect similar to that of oxygen uptake, from negligible rates of approximately 0 to 1 µmol N m^{-2} h^{-1} for both D_w and D_n at the furthest offshore site, Site 12, to maximum values of 11407 and 8209 µmol N m^{-2} h^{-1}, respectively, at the inner muddy Site 1. The overall trend of mean values is illustrated in Fig. 4B. ANOVA indicated significant inter-site variation for rates of D_w and D_n on each occasion ($p \leq 0.038$), with significantly higher rates consistently being measured at the muddy sites. ANOVA indicated significant seasonal variation ($p \leq 0.004$) in the rates of D_w (except Site 3, $p = 0.142$) and D_n (except Sites 3 and 7, $p = 0.090$ and 0.105, respectively) measured at each of the sites. The average rates of both D_w and D_n were significantly ($p < 0.05$) positively correlated with the sediment organic C content along the transect. There was a significant positive correlation ($p < 0.001$) between the overall average rates of D_w and overall average NO_3^- concentrations for all sites along the transect. However, this relationship was strongest ($r = 0.92$ compared with $r = 0.53$) at Sites 6 to 12, with a sediment organic C content of <1.5% (dry wt). The D_w fraction dominated denitrification at the majority of the inner sites, with a maximum

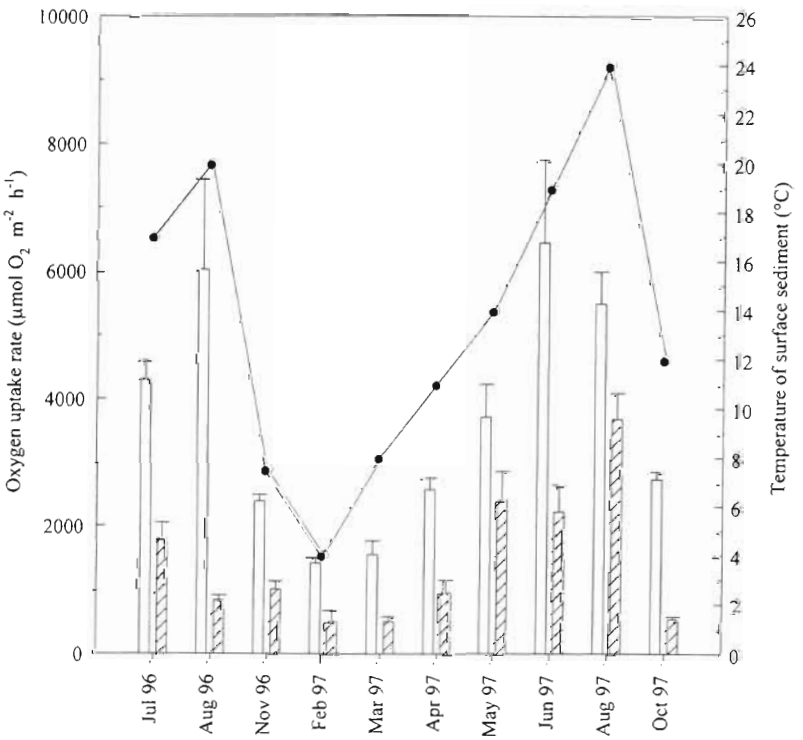

Fig. 5. Oxygen uptake rates at a muddy site (Site 4, open bars), and a sandy site (Site 6, hatched bars) together with the sediment temperature (●). Bars indicate standard error, n = 3

C delivered to the Thames estuary from either STW or fluvial discharge was deposited and remineralised before the mouth of the estuary at Southend. Zwolsmann (1994) also estimated that 60% of the fluvial sediment discharge to the Thames estuary was retained within the estuary.

The average area-normalised rate of organic C mineralisation in the Thames estuary (21 mol C m^{-2} yr^{-1}) was similar to that measured in the Great Ouse (29 mol C m^{-2} yr^{-1}, Trimmer et al. 1998). Extrapolating the combined average area-normalised rate (25 mol C m^{-2} yr^{-1}) to the entire estuarine area of the UK (6×10^9 m^2) suggests that 150 Gmol C (1.8×10^6 t) is recycled back to the atmosphere each year. The annual estuarine production of CO_2 in the UK is, therefore, comparable to that produced from agriculture, shipping, civil aircraft and railways, i.e. 1×10^6 t each, respectively (Digest of Environmental Statistics 1997). The recycling of fixed C back to atmospheric CO_2 by estuarine sediments further emphasises the significance of estuaries as biological filters, not only of DIN loads but also of particulate and dissolved organic C.

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