A diagenetic model discriminating denitrification and dissimilatory nitrate reduction to ammonium in a temperate estuarine sediment

B. A. Kelly-Gerreyn[1,*], M. Trimmer[2], D. J. Hydes[1]

[1]**Southampton Oceanography Centre, Waterfront Campus, European Way, Southampton SO14 3ZH, United Kingdom**
[2]**School of Biological Sciences, Queen Mary College, University of London, London E1 4NS, United Kingdom**

ABSTRACT: A diagenetic model is presented which considers nitrate reduction by both denitrification and Dissimilatory Nitrate Reduction to Ammonium (DNRA). This work builds on an existing model (Kelly-Gerreyn et al. 1999; Mar Ecol Prog Ser 177:37–50). Previous models have assumed nitrate reduction to be solely due to denitrification. This paper questions the reliability of this assumption in coastal areas and suggests that DNRA can account for a high proportion of nitrate reduction. Data from a North Sea estuary (the lower Gt. Ouse, Norfolk, UK) containing high nutrient concentrations (mean 406 µM NO_3^-) are used to derive a relationship between temperature and the proportioning of nitrate reduction driven by nitrate from the overlying water into denitrification and DNRA. The relationship is assumed to apply to total nitrate reduction. The result is a function which shows that DNRA and denitrification occur at all temperatures but that DNRA is the favoured pathway at the extremes of the observed temperatures (<14 and >17°C) while denitrification is favoured only in a narrow range of temperatures (14 to 17°C). The mechanism is probably an adaptive response of different nitrate-reducing bacteria to temperature. This temperature relationship is implemented in the model and used to successfully simulate both observed rates of uncoupled denitrification (4 to 228 µmolN m^{-2} h^{-1}), denitrification fuelled by nitrate in the overlying water (D_w), and calculated rates of DNRA fuelled by nitrate in the overlying water ($DNRA_w$) (measured nitrate flux – measured D_w rate). In contrast, standard diagenetic formulae for nitrate reduction (i.e. by denitrification only) cannot satisfactorily reproduce the D_w rates observed in these sediments. It is concluded that temperature is an important controlling factor for partitioning nitrate reduction into DNRA and denitrification in the lower Gt. Ouse sediments. This temperature effect implies that during an extended warm summer in temperate estuaries receiving high nitrate inputs, nitrate reduction may contribute to, rather than counteract, a eutrophication event. Diagenetic models of the nitrogen cycle in coastal areas should include DNRA.

KEY WORDS: Diagenesis model · Denitrification · Dissimilatory nitrate reduction to ammonium · Temperature

INTRODUCTION

A number of diagenetic models have been developed in recent years (Boudreau 1995, Soetaert et al. 1996, Kelly-Gerreyn et al. 1999) to help improve understanding of sedimentary biogeochemical processes. Some models (Wang & Van Cappellan 1996) are more complex than others (Kelly-Gerreyn et al.

1999) in terms of the number of processes considered, and yet their underlying formulae for any particular process are the same. In this respect, the nitrogen cycle in all of these models consists of nitrate and ammonium, denitrification and nitrification. Intermediate nitrogenous compounds are neglected mostly due to lack of adequate data. In all of the models mentioned so far, nitrate reduction is treated as denitrification (whether directly coupled to ammonium oxidation as in Soetaert et al. 1996 or not). However, the alternative

*E-mail: b.kelly-gerreyn@soc.soton.ac.uk

Table 1. Percentage contribution of Dissimilatory Nitrate Reduction to Ammonium (DNRA) to sedimentary nitrate reduction at different locations around the world (ABT = Acetylene Blockage Technique)

%	Location	Method	Source
7–3	Coastal/Estuarine (Tokyo Bay), Japan	^{15}N assay + ABT	Koike & Hattori (1978)
56	Coastal/Marine (Limfjorden), Denmark	^{15}N assay + ABT	Sørensen (1978)
5–30	Coastal/Intertidal, New Zealand	^{15}N assay + ABT	Kaspar (1983)
40–70	Coastal/Estuarine, Japan	^{15}N assay + ABT	Nishio et al. (1983)
0–18	Coastal, New Zealand (South Island)	^{15}N assay + ABT	Kaspar et al. (1985)
65–90	Estuarine (Norsminde Fjord), Denmark	ABT	Jørgensen & Sørensen (1985)
32	Coastal/Marine, The Netherlands	^{15}N assay + ABT	Goeyens et al. (1987)
70	Estuarine (Norsminde Fjord), Denmark	ABT	Jørgensen & Sørensen (1988)
4–21	Estuarine (Norsminde Fjord), Denmark	^{15}N assay + ABT	Jørgensen (1989)
97	Coastal (Hiroshima Bay), Japan	ABT + estimate of nitrification	Kim et al. (1997)
54	Estuarine (Lower Gt. Ouse), UK	ABT	Trimmer et al. (1998)
98	Coastal Lagoon, France	^{15}N assay + ABT	Gilbert et al. (1998)

pathway which converts nitrate to ammonium can be a greater component of nitrate reduction in coastal sediments (e.g. Gilbert et al. 1998, Trimmer et al. 1998). This latter component is called Dissimilatory Nitrate Reduction to Ammonium (DNRA).

The ecological significance of these 2 competing processes is that denitrification leads to a loss of nitrogen from the ecosystem while DNRA retains nitrogen in the preferred form for biological uptake. While denitrification has received much attention (e.g. Seitzinger 1988, Middelburg et al. 1996, Hydes et al. 1999), some research, but no modelling, has been carried out on DNRA (e.g. Cole & Brown 1980, Sørensen 1978). Table 1 shows that DNRA (measured using ^{15}N assay techniques and/or estimated from measurements of

both denitrification using the acetylene blockage technique and nitrate exchange at the sediment water interface) can account for a high proportion of the total nitrate reduction that takes place in sediments. Sørensen (1978) has shown that in organic-rich sediments, DNRA may account for up to one third of the total carbon oxidation.

Microbes capable of nitrate reduction are widely distributed in nature (Cole & Brown 1980, Tiedje 1988). Hence, any restriction to nitrate reduction will probably be related to environmental conditions that regulate the process rather than to a lack of microorganisms. Consequently, any model of nitrate reduction must account for the effect of the regulating factors. These include temperature (King & Nedwell 1984,
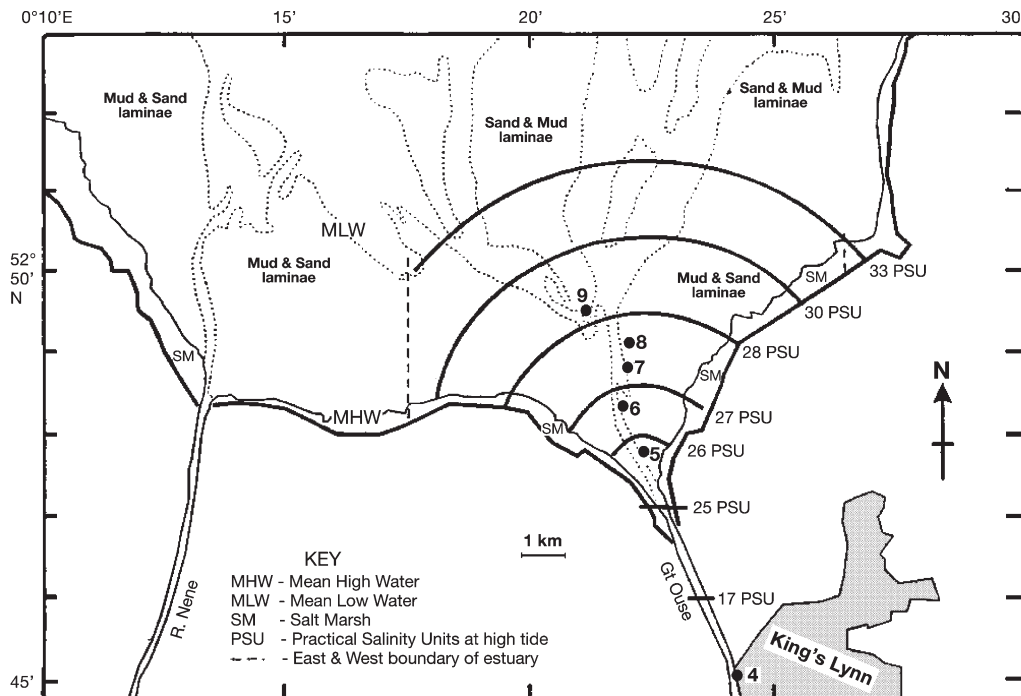

Fig. 1. Location of the 6 sites (4 to 9) in the lower Gt. Ouse (reproduced from Trimmer et al. 1998)

Ogilvie et al. 1997a), the labile carbon:nitrate ratio (Rehr & Klemme 1989), pH (Kim et al. 1997) nitrate concentrations (King & Nedwell 1987) and the type of organic substrate used (Herbert 1982).

The aim of this work is to develop a diagenetic model with a more complete description of nitrate reduction by including DNRA. Data, collected as part of the JoNuS (Joint Nutrient Study) programme, from a major UK North Sea estuary (the lower Gt. Ouse, Norfolk), are used to build on an existing diagenetic model (Kelly-Gerreyn et al. 1999). The central hypothesis tested in this work is the idea that temperature is an important factor in controlling the proportioning of nitrate reduction into denitrification and DNRA in the lower Gt. Ouse sediments.

OBSERVATIONAL BASIS FOR MODEL

The lower Gt. Ouse is a temperate latitude North Sea estuary containing high concentrations of nitrate (up to 830 µM). A full description of the estuary and its sediment characteristics are found in Trimmer et al. (1998). Hence, only a brief description including some results is given here. Fig. 1 shows the location of the sample sites (Sites 4 to 9, Trimmer et al. 1998) visited 11 times between April 1994 and April 1995. Note that Site 4 is King's Lynn in the lower Gt. Ouse, the same Site 4 referred to in Nedwell & Trimmer (1996) and in Kelly-Gerreyn et al. (1999). Table 2 outlines the sediment characteristics for the 6 sites of interest.

All sites were visited at low tide and remained submerged at all times. Sediment water nutrient exchange and oxygen uptake (core incubations), rates of denitrification fuelled by nitrate from the overlying water column, D_w (acetylene blockage technique), sediment temperature, organic content, porosity, and water column nutrients were measured for each visit to the sites. The methodology is described by Nedwell & Trimmer (1996) and by Trimmer et al. (1998).

Sediment temperature ranged from 5 to 22°C over the season. These sediments were consistent sinks for nitrate (mean across all sites: 310 µmol m^{-2} h^{-1}) and

consistent sources of ammonium (mean across all sites: 270 µmol m^{-2} h^{-1}). Benthic oxygen demand was significantly correlated (p < 0.05) with temperature. D_w rates varied between 4 and 228 µmolN m^{-2} h^{-1} across the sites and accounted for less than half (46%) of the annual flux of nitrate to the sediment. Nitrate reduction (DNRA plus denitrification) accounted for up to 5 and 25% of the total annual organic carbon mineralisation respectively. The remainder of the carbon oxidation was assumed to be mediated by oxygen and sulphate.

MODEL DESCRIPTION, EQUATIONS AND ASSUMPTIONS

A detailed description of the basic model is given in Kelly-Gerreyn et al. (1999). Briefly, this is a one-G (Berner 1980) type reaction-diffusion model which describes the sediment column as a 1D vertical system of 150 equally sized adjoining boxes totalling a depth of 15 cm. The model variables, O_2, NO_3^-, NH_4^+, SO_4^{2-}, and S^{2-} are calculated from data-imposed steady state concentrations of total organic carbon (TOC) which is assumed to be evenly distributed in the sediment as in Kelly-Gerreyn et al. (1999). All model assumptions are the same as those in Kelly-Gerreyn et al. (1999). The model processes are nitrification, sulphide reoxidation and carbon respiration via oxygen, nitrate and sulphate. Organic carbon mineralisation produces ammonium, sulphate reduction produces free sulphide, and nitrate reduction produces N_2 gas.

Nitrate reduction has been extended (see below) to account for DNRA and is the main subject of this paper. Model equations are similar to those in Table 2 of Kelly-Gerreyn et al. (1999) but have been modified to take in to account temperature changes. To do this an Arrhenius-type temperature function of the form

$$Q_{10}\text{fact} = e^{0.07(\text{Temperature} - 20)} \qquad (1)$$

multiplies each reaction term of each model equation (see Table 2 in Kelly-Gerreyn et al. 1999). This temperature effect assumes a Q_{10} of 2.

Table 2. Sediment characteristics of the 6 sites in the lower Gt. Ouse (taken from Trimmer et al. 1998). FS = fine sand (250–125 µm); VFS = very fine sand (125–63 µm); S/C = sand/clay (<63 µm). Values are mean ± SE

Site	Particle size (>50% w/w)	Water content	Porosity (cm^3 H$_2$O cm^{-3} sed.)	Organic C (% dry wt)	Total N (% dry wt)	C:N ratio (mol:mol)
4	VFS	0.23 ± 0.01	0.38 ± 0.01	0.10 ± 0.01	0.02 ± 0.01	5
5	S/C	0.33 ± 0.03	0.57 ± 0.03	0.78 ± 0.23	0.07 ± 0.02	13
6	VFS	0.21 ± 0.01	0.38 ± 0.01	0.21 ± 0.03	0.02 ± 0.00	17
7	S/C	0.44 ± 0.03	0.61 ± 0.02	2.23 ± 0.35	0.14 ± 0.02	19
8	S/C	0.26 ± 0.02	0.45 ± 0.03	0.44 ± 0.17	0.03 ± 0.01	18
9	FS	0.39 ± 0.09	0.56 ± 0.02	0.36 ± 0.08	0.06 ± 0.02	8

BOUNDARY CONDITIONS, INITIALISATION AND IMPOSED DATA

In the absence of porewater data, a zero flux bottom boundary condition is imposed for all model variables (note the difference for ammonium in the upper Gt. Ouse sediments where the bottom boundary condition was fixed by measurements, see Table 4 of Kelly-Gerreyn et al. 1999). This assumes that all reactive organic carbon has been respired at the depth of the model domain. Top boundary values at the sediment-water interface (SWI) for oxygen, nitrate and ammonium are the mean (triplicates) core incubation concentrations in the water column during the incubation period. For all model runs, free sulphide levels are set to zero in the water column. Sulphate concentrations in the water column are calculated from salinity assuming conservative mixing from an end-member concentration of 28.23 mM SO_4^{2-} (Wilson 1975) at 35 salinity. At Sites 5 to 9 the salinity range of 25 to 29 yields sulphate concentrations of 20.17 to 23.39 mM SO_4^{2-}, respectively. As the model is insensitive to this range in sulphate concentrations a mean sulphate concentration of 21.78 mM SO_4^{2-} is used as the top boundary condition at Sites 5 to 9. At low tide, salinity at Site 4 was always approximately 1. Consequently, the sulphate top boundary concentration is calculated as 0.81 mM at Site 4. Measured TOC concentrations (see Table 2) are imposed in each model box and assumed to be evenly distributed with depth. No porewater measurements were made in these sediments and so initial concentrations of each model variable (O_2, NO_3^-, NH_4^+, SO_4^{2-} and S^{2-}) are set to the same value in each model box (i.e. uniform concentrations with depth). Preliminary runs (not shown) show that the model outcome was not sensitive to the initial conditions of these solutes.

TEMPERATURE AND PROPORTIONING OF NITRATE REDUCTION INTO DENITRIFICATION AND DNRA

For the purposes of the analysis that follows, nitrate reduction, denitrification and DNRA refer to the components of these processes which are fuelled by nitrate from the overlying water column. Consequently, to avoid confusion, the terms NR_w (nitrate reduction fuelled by nitrate from the overlying water), D_w and $DNRA_w$ will be used from here on. All other references to nitrate reduction, denitrification and DNRA are for total rates (i.e. the sum of rates fuelled by nitrification and by incoming nitrate from the overlying water column). Hence, it is assumed that the flux of nitrate to the sediment is equivalent to the rate of NR_w, where $NR_w = D_w + DNRA_w$. This assumption is justified by the findings (Trimmer et al. 1998) that at all sites, the nitrate fluxes (90% of which were directed into the sediment) were significantly correlated (p < 0.05) with both the rates of D_w and the ammonium effluxes (r = 0.47), the strongest correlation being at Site 7 (r = 0.78). This suggests a strong link between the nitrate flux and both D_w and $DNRA_w$ and supports the opening statements and assumptions of this section. Rates of nitrification can therefore be assumed to be negligible or in constant proportion with nitrate reduction. Furthermore, as nitrification is inhibited by the acetylene blockage technique used here, the effect of nitrification on the following calculations is, at best, minimal.

Linking the measurement of D_w with the contemporaneously measured nitrate flux enables a description of the partitioning of NR_w into $DNRA_w$ and D_w. Dividing D_w by the nitrate flux gives the proportion (P_D) of NR_w due to D_w. It follows that the remaining proportion (P_{DNRA}) is due to $DNRA_w$. Thus,

$$P_D = D_w / \text{nitrate flux to the sediment} \qquad (2)$$

and

$$P_{DNRA} = 1 - P_D \qquad (3)$$

Note that this calculation is valid only if the flux of nitrate is directed towards the sediment. As mentioned above, the lower Gt. Ouse sediments, with few exceptions (only 10% of the 112 measurements of nitrate fluxes were directed from the sediment to the water column), were consistent sinks for nitrate. The range of P_D values derived in this way is between 0.04 and 0.92 when all sites are considered (see Table 3). This large range indicates considerable variation in the proportioning of NR_w into $DNRA_w$ and D_w. Fig. 2 shows the relationship between temperature and P_D at Sites 4 to 9. Note that because of either a lack of measurement at a particular temperature and/or a flux of nitrate out of the sediment, not all sites have P_D values at every temperature.

The values of P_D show some variation between sites. However, an overall pattern in the behaviour of P_D with temperature is discernible. Statistical analysis (1-way ANOVA tests) shows that there is no significant difference (p = 0.89) in the means between sites, but that there is a significant difference (p = 0.04) between temperatures when sites are grouped together. This suggests a correlative link between temperature and the partitioning of NR_w into D_w and $DNRA_w$. It also suggests that the mean effect of temperature on NR_w partitioning is the same at each site. Note that the lowest mean P_D value (0.28 ± 0.16 [SE]) occurs at Site 7, which has the highest C:N ratio (19, Table 2), while the highest mean P_D (0.49 ± 0.14 [SE]) occurs at Site 4, which has the lowest C:N ratio (5, Table 2). Measurements of total organic carbon and total organic nitrogen at other times in the year were not significantly

Table 3. Rates of uncoupled denitrification (D_w), fluxes of nitrate (N_f) across the sediment water interface and values for P_D (=D_w /N_f, see text) at the 6 sites in the lower Gt. Ouse. (cnp = calculation not possible; nm = not measured; units = µmolN m^{-2} h^{-1}; negative value = flux to sediment)

Temp. (°C)	Month	Site 4			Site 5			Site 6			Site 7			Site 8			Site 9		
		N_f	D_w	P_D	N_f	D_w	P_D	N_f	D_w	P_D	N_f	D_w	P_D	N_f	D_w	P_D	N_f	D_w	P_D
5	Jan 95	432.95	21	cnp	nm	nm	cnp	nm	nm	cnp	−227.24	30	0.13	nm	nm	cnp	−115.65	9	0.08
7	Apr 94	−154.61	18	0.12	−8.55	47	5.50	161.20	42	cnp	−1149.58	50	0.04	−1081.12	91	0.08	−27.75	15	0.54
9	Nov 94	−251.08	81	0.32	−399.37	60	0.15	575.00	19	cnp	−1070.64	84	0.08	383.77	40	cnp	−211.83	8	0.04
14	May 94	−184.20	158	0.86	−300.09	176	0.59	−327.13	174	0.53	−433.21	228	0.53	−474.86	121	0.25	−121.30	88	0.73
17	Aug 94	−165.08	131	0.79	nm	nm	cnp	nm	nm	cnp	−68.68	63	0.92	−343.83	32	0.09	nm	nm	cnp
22	Jul 94	−288.31	106	0.37	−149.90	166	1.11	−218.41	19	0.09	−290.68	60	0.21	−56.41	37	0.66	−30.31	4	0.13

different (Trimmer 1997). Consequently it is assumed that there is no correlation between C:N ratio and nitrate reduction partitioning (see 'Discussion'). With the exception of Site 8, the overall effect of temperature on P_D is to yield highest values at temperatures between 14 and 17°C and lowest values at the extremes of the observed temperature (5 and 22°C). On the basis of the aforementioned significant correlations (p < 0.05) between the nitrate fluxes and both the rates of D_w and the ammonium effluxes, it is assumed from hereon that this temperature relationship holds for total nitrate reduction, i.e. D_w + coupled nitrification-denitrification (D_n) + DNRA$_w$ + coupled nitrification-DNRA (DNRA$_n$). Hence, the function P_D indicates that in the lower Gt. Ouse sediments, colder (<14°C) and warmer (>17°C) temperatures favour DNRA and moderate (14 to 17°C) temperatures favour denitrification. This effect is well illustrated by the variation with temperature in the mean P_D (Fig. 2). The exceptions to the general behaviour are found at Site 9 (P_D = 0.54 at 7°C) and at Site 8 (P_D = 0.66 at 22°C). These are caused by large values of D_w relative to the nitrate flux. It is not possible to explain why these exceptions exist.

To implement this behaviour into the model, it is necessary to derive a function from this data set. The function requires a form which follows the mean P_D at all sites (Fig. 2). Fitting yields a slightly right-skewed, bell-shaped curve which has the form:

$$\mathrm{Fit}P_D = Ae^{-\left(\frac{T_{opt}-T}{\sigma}\right)^2} \tag{4}$$

where T_{opt} is the optimum temperature for selection of D_w (i.e. highest P_D), T is the temperature, σ is the standard deviation of the temperature and A is a coefficient that is derived by fitting Eq. (4) to the pooled data. The mean P_D (Fig. 2) suggests T_{opt} = 16°C. Given σ = 6.09, A is calculated numerically with the statistical software package SYSTAT, yielding A = 0.65. Fig. 3 shows the fit of Eq. (4) to the pooled data of calculated P_D values for all sites. The fit has the correlation r^2 = 0.42 and closely resembles the mean P_D which is repeated in Fig. 3 for comparison purposes. Given that there is a significant difference (p = 0.04, see above in this section) in the mean P_D between temperatures, there is sufficient reason to have confidence in the use of Eq. (4).
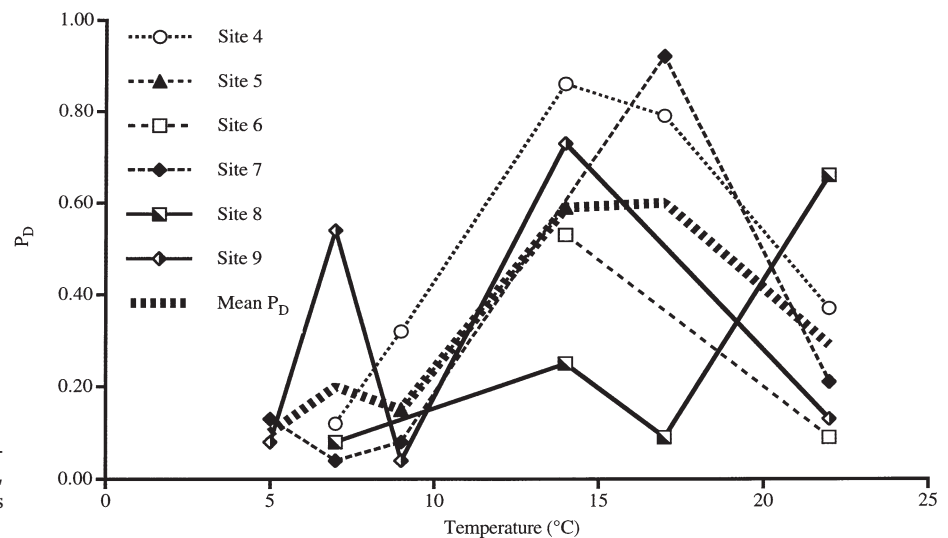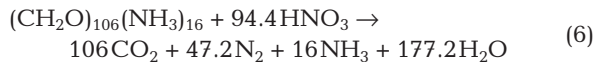

Fig. 2. Relationship of P_D (temperature selection in nitrate reduction, see text) with temperature at 6 sites in the lower Gt. Ouse sediments
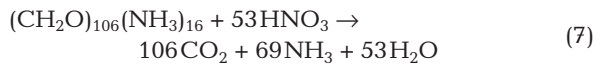
IMPLEMENTATION OF EQ. (4) INTO THE MODEL

The model equation for carbon oxidation via nitrate (SuboxMin) is

$$\text{SuboxMin} =$$

$$k_{NO_3} \times [\text{TOC}] \underbrace{\left(\frac{NO_3}{NO_3 + Ks_{NO_3}} \right)}_{NO_3^- \text{ limitation}} \underbrace{\left(1 - \frac{O_2}{O_2 + Ks_{inhO_2}} \right)}_{O_2 \text{ inhibition}} \times Q_{10}\text{fact} \quad (5)$$

where T is temperature, TOC is total organic carbon, Ks_{NO_3} is the half saturation constant for nitrate limitation, Ks_{inhO_2} is the half saturation constant for oxygen inhibition, k_{NO3} is the first order rate constant and the units are in mmolC m^{-3} d^{-1}. All parameter values used in this model (except for k_{NO_3}) and their definitions are shown in Kelly-Gerreyn et al. (1999). Multiplying Eq. (5) by Eq. (4) yields a formula that, according to the temperature, determines what proportion of total nitrate reduction follows DNRA and denitrification. However, Eq. (5) needed modification to account for the stoichiometric conversion of TOC to either dinitrogen gas (denitrification) or to ammonium (DNRA). Using

$$(CH_2O)_{106}(NH_3)_{16} + 94.4\,HNO_3 \rightarrow$$
$$106\,CO_2 + 47.2\,N_2 + 16\,NH_3 + 177.2\,H_2O \quad (6)$$

and

$$(CH_2O)_{106}(NH_3)_{16} + 53\,HNO_3 \rightarrow$$
$$106\,CO_2 + 69\,NH_3 + 53\,H_2O \quad (7)$$

for denitrification and DNRA, respectively, yields stoichiometric ratios (γ) of 0.4 (mole of N_2 produced per mole of carbon oxidised via nitrate) and 0.65 (mole of NH_3 produced per mole of carbon oxidised via nitrate and per mole of nitrate ammonified), respectively.
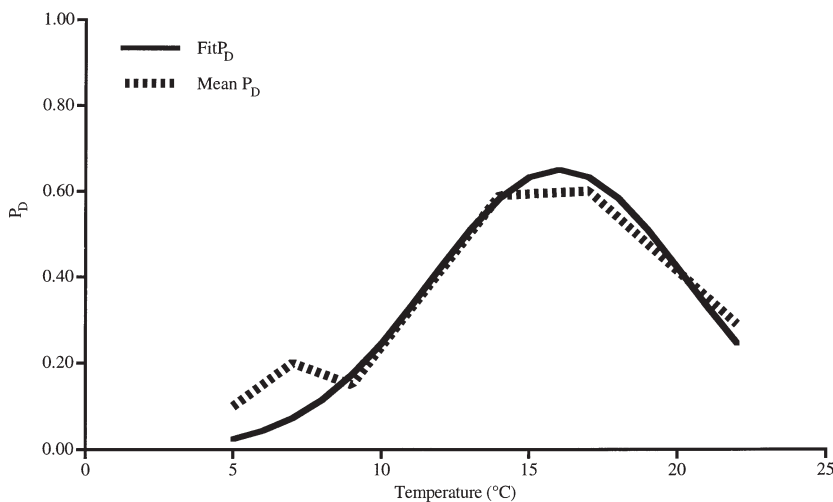

Fig. 3. Plot of FitP_D (see text, Eq. 4) and mean P_D (from Fig. 2) versus temperature

Thus, combining Eqs (4), (5) & (6) yields for total denitrification:

$$\text{Fit}P_D \times \text{SuboxMin} \times \gamma_{N_2}^{NO_3} \quad (8)$$

and combining Eqs (4), (5) & (7) yields for total DNRA:

$$(1 - \text{Fit}P_D) \times \text{SuboxMin} \times \gamma_{NH_4}^{NO_3} \quad (9)$$

Note that the standard formula for nitrate reduction used in the earlier version of this model (Kelly-Gerreyn et al. 1999) and in other diagenetic models (e.g. Boudreau 1995), is an equation similar to Eq. (8) but without FitP_D.

In Eqs (8) & (9) it must be assumed that the temperature-dependent components, FitP_D and Q_{10}fact, are mutually exclusive. In FitP_D, it is assumed that temperature is selecting different types of nitrate-reducing bacteria (King & Nedwell 1984, Ogilvie et al. 1997a). In other words, denitrifying bacteria and nitrate ammonifiers have optimally adapted to different temperature ranges. Consequently, the effect of temperature works at the adaptive (genetic) level of the organism. In contrast, Q_{10}fact works on the metabolic (enzymatic) level of the bacteria. Hence, these 2 temperature components, FitP_D and Q_{10}fact, can be considered as independent effects on nitrate reduction which justifies them being multiplied together in Eqs (8) & (9).

Derivation of k_{NO_3} was achieved by fitting modelled rates of D_w to the peak rates of measured D_w which occurred at 14°C at all sites. The value of k_{O_2} and k_{SO_4} (first order rate constants for oxygen respiration and sulphate reduction, respectively) at each site is taken as the mean value (8.7 and 10 yr^{-1}, respectively) from Sites 1 to 4 in the Gt. Ouse (Table 6, Kelly-Gerreyn et al. 1999). All remaining parameter values have not been changed from their settings in Kelly-Gerreyn et al. (1999). The advantage of this is a model with only 1 parameter (k_{NO_3}) to fit, yielding a low degree of freedom.

Finally, to distinguish D_w in the model and thus facilitate comparisons with the measurements, total modelled denitrification ($D_n + D_w$, Eq. 8) is multiplied by the ratio of the nitrate flux to the sediment to the sum of the nitrate flux plus the depth-integrated rate of nitrification thus:

$$D_w = \frac{NO_3^- \text{ flux}}{\left(NO_3^- \text{ flux} + \sum\limits_{z=z_{max}}^{z=z_0} \text{nitrification} \right)} \quad (10)$$
$$\times \text{Fit}P_D \times \text{SuboxMin} \times \gamma_{N_2}^{NO_3}$$

where the interval z_0 to z_{max} is the total depth (15 cm) considered in the model. Note that although nitrification has been assumed to have a negligible effect on the

calculation of P_D (because of the use of the acetylene blockage technique), this does not mean that nitrification is not occurring in the lower Gt. Ouse sediments. Hence, nitrification is included in the model.

MODEL RUNS

The model is run for each site and each temperature (i.e. for different months). Differences between model runs at each site are thus caused by temperature and additionally by variations in the water column boundary values for the three measured solutes O_2, NO_3^- and NH_4^+. Differences between sites are due to differences in TOC concentrations, porosity and top boundary values. Temperature does not vary between sites. Model and measurement-derived results (i.e. D_w and $DNRA_w$ rates) are displayed with respect to temperature. The contribution of DNRA to total ammonium production is also presented. Nutrient fluxes across the SWI are only mentioned (and not displayed) for completeness, as they are not the main topic of this paper.

RESULTS

Nitrate reduction

Measured and modelled rates of sedimentary D_w are plotted in Fig. 4 against sediment temperature at the 6 sites in the lower Gt. Ouse. The general pattern in the observations shows a bell-shaped curve with rates of denitrification peaking at 14°C (May 1994) at all sites. Modelled rates of D_w (which use Eq. 10) show the same relationship with temperature as the observations. From here on, this model run is referred to as $M+FitP_D$. The comparison between $M+FitP_D$ and the measurements is highly significant (p < 0.001). For comparison purposes, model output which does not account for temperature-based proportioning of nitrate reduction (i.e. Eq. 8 without $FitP_D$; henceforth this model run is called $M-FitP_D$) is also plotted in Fig. 4. The correlation between $M-FitP_D$ and the observations is not significant (p = 0.18). As with $M+FitP_D$, $M-FitP_D$ was derived by fitting the model to rates of D_w measured at 14°C. Fitted values for the first order rate constant k_{NO_3} derived by $M+FitP_D$ and $M-FitP_D$ are shown in Table 4. k_{NO_3} values are higher in $M+FitP_D$ by a mean factor of 2.36 compared to $M-FitP_D$.

Rates of D_w in $M-FitP_D$ overestimate the observations by a mean factor of 5.8 at temperatures <14°C compared to a factor of 1.4 for $M+FitP_D$. For temperatures >14°C, D_w rates in both $M-FitP_D$ and $M+FitP_D$ are a mean factor of ~2 higher than the observations. Concentrations of nitrate in the overlying water col-

umn are also plotted in Fig. 4. As expected, nitrate levels decrease with increasing temperature at all sites, reflecting weather induced seasonality (i.e. higher runoff in winter compared to summer). This in part accounts for the decrease in both model and measured D_w at temperatures >14°C (see 'Discussion').

D_w rates in $M+FitP_D$ are consistently higher than the observations (mean factor = 4) at 16°C. Site 4 is the exception to this. Note that values of $FitP_D$ are at a maximum (0.66) at this temperature.

Fig. 5 compares modelled and calculated rates of $DNRA_w$ at all sites in the lower Gt. Ouse. Calculated rates of $DNRA_w$ were derived as the difference between the measurements of the flux of nitrate into the sediment and the rates of D_w. Variability in the calculated rate was determined by adding the variances of both the nitrate fluxes and the D_w rates and then subtracting double the covariance of the 2 measurements:

$$Var(DNRA_w) = Var(NO_3^- \text{ flux}) + Var(D_w) - 2\,CoVar(NO_3^- \text{ flux}, D_w) \quad (11)$$

where Var is the variance and CoVar is the covariance. This assumes that the nitrate flux and the rate of D_w are not independent of one another.

In some cases (Site 4 March 1995, at 7°C; November 1994, 9°C; May 1994, 14°C; and September 1994, 15.5°C; see Fig. 5), the standard error is larger than the calculated rate of $DNRA_w$. This impossible spread in $DNRA_w$ is caused by the large variation in the nitrate flux (i.e. within the same sample of triplicate measurements both influxes and effluxes of nitrate were measured). However, overall, the modelled rates of $DNRA_w$ compare well with the calculated rates. Linear regression shows a significant correlation (p < 0.0001) between modelled and calculated $DNRA_w$. In some months (March 1995, 7°C; November 1994, 9°C at Site 7; March 1995, 7°C at Site 8) calculated rates (~1000 µmolN m^{-2} h^{-1}) of $DNRA_w$ are much greater than the modelled rates (~150 to 300 µmolN m^{-2} h^{-1}). Overall, the model underestimates the calculated rates of $DNRA_w$ (regression slope = 0.3).

Table 4. Values of the first order rate constant for nitrate reduction used in the model output with ($M+FitP_D$) and without ($M-FitP_D$) Eqs (8) & (9) (units, yr^{-1}; NB: k_{O_2} = 8.7 yr^{-1}; k_{SO_4} = 10 yr^{-1}; these latter 2 parameters are the mean values for the 4 sites in the Gt. Ouse, Kelly-Gerreyn et al. 1999)

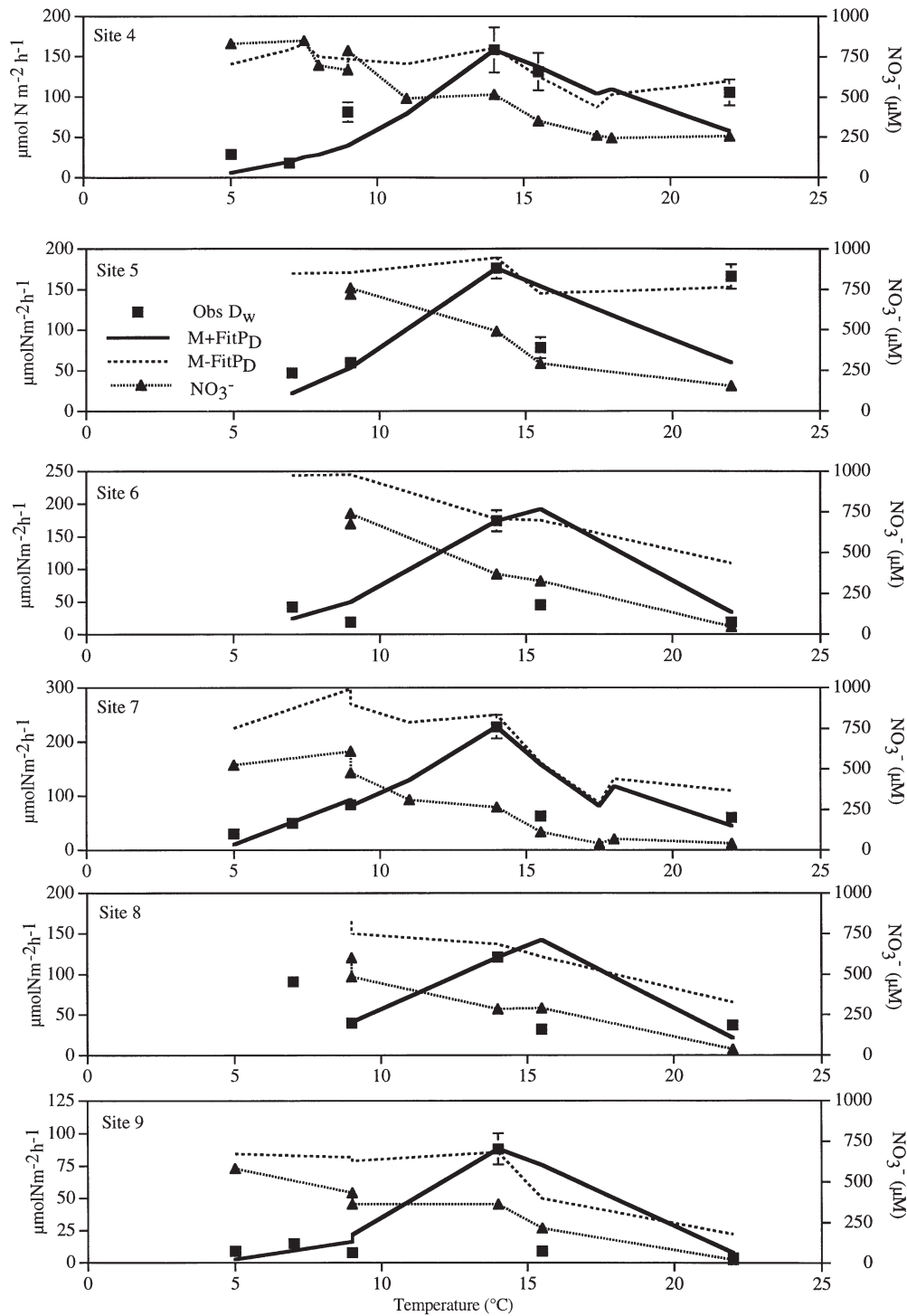| Site	$M+FitP_D$	$M-FitP_D$	Factor difference
4	11.57	4.68	2.47
5	0.79	0.34	2.29
6	4.83	1.90	2.54
7	1.18	0.52	2.25
8	1.45	0.61	2.36
9	0.83	0.37	2.25

Fig. 4. Modelled (M+FitP_D and M–FitP_D, see text for details) and observed rates of uncoupled denitrification (D_w) at 6 sites in the lower Gt. Ouse; error bars = ±SE; nitrate in the overlying water column is also plotted. Data from Trimmer et al. (1998)

Fig. 6 shows the percentage contribution of total DNRA to total ammonium production for each temperature at all sites. (DNRA ammonium production consists of ammonium derived from both the nitrate nitrogen and from the nitrogen bound in the organic matter (see Eq. 7). The remaining percentage is due to the respiration of TOC by oxygen reduction, denitrification and sulphate reduction. Site 4 has the highest percentage contribution of DNRA to the total production of ammonium (15 to 58%, mean = 36%), then, in descending order of
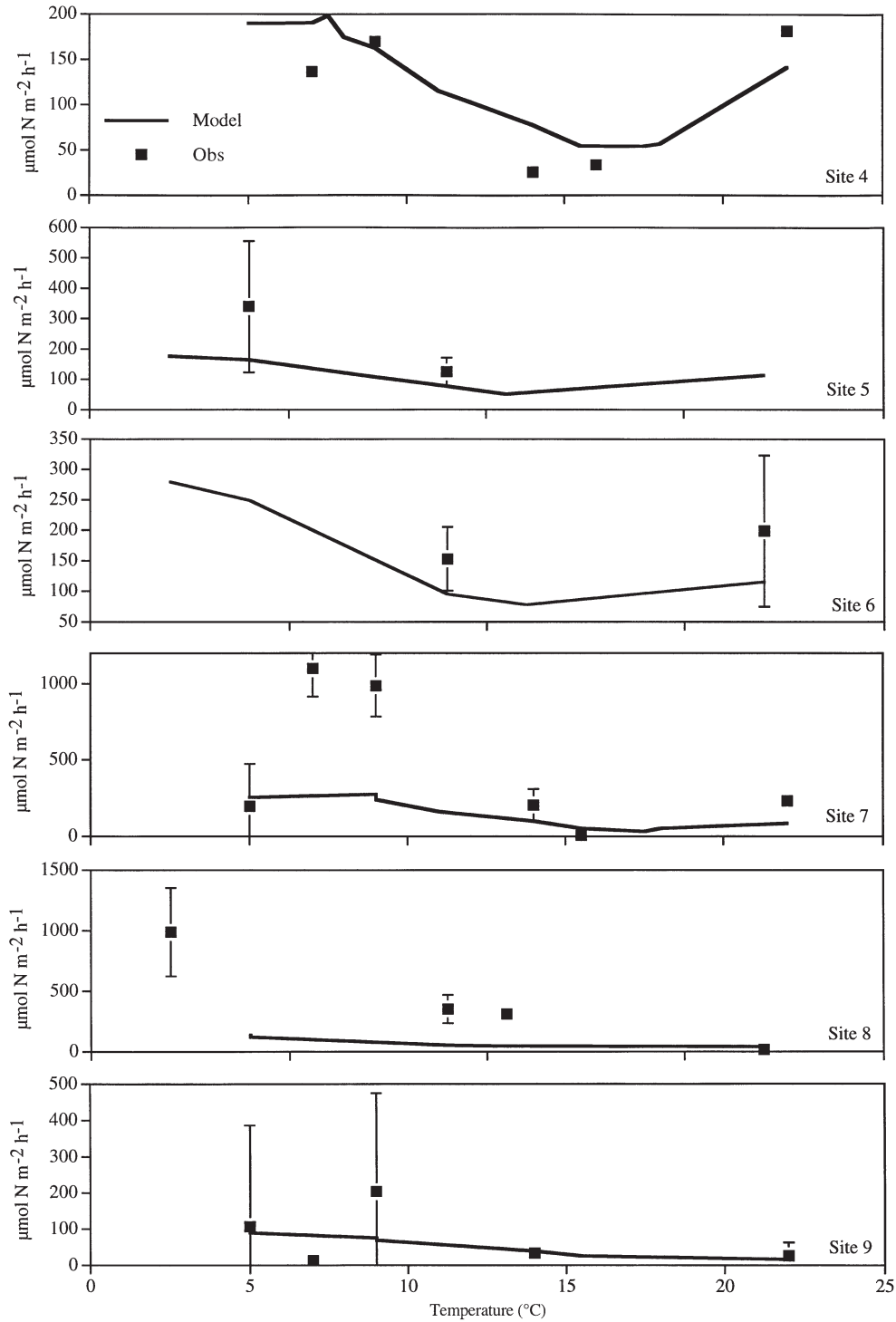
Fig. 5. Modelled and calculated rates of sedimentary $DNRA_w$ (see text for details) at 6 sites in the lower Gt. Ouse. Calculated rates = measured nitrate flux to sediment – measured rate of denitrification (D_w); error bars = ±SE. Data from Trimmer et al. 1998)

contribution, Site 6 (7 to 47 %, mean = 24 %), Site 8 (4 to 31 %, mean = 17 %), Site 7 (2 to 37 %, mean = 16 %), Site 5 (5 to 31 %, mean = 16 %) and Site 9 (1 to 16 %, mean = 7 %). Each site shows a similar pattern: decreasing percentage contributions to the ammonium pool from total

DNRA with increasing temperatures. Sites 5 and 7 show a slight increase (by 2 %) in the percentage contribution between 15.5 and 22°C and between 18 and 22°C, respectively. Site 4 percentage contributions increase by a greater amount, from 15 to 28 %, between 18 and 22°C.
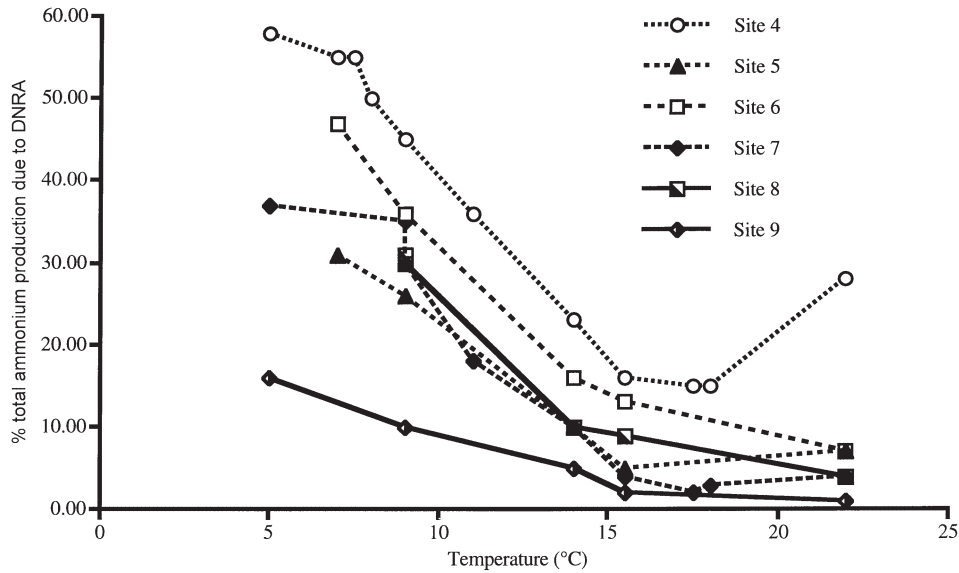
Fig. 6. Percentage contribution of DNRA to total ammonium production at each temperature at 6 sites in the lower Gt. Ouse. The remaining percentage is due to TOC mineralisation

For a complete report of the performance of the model, the nutrient (NO_3^- and NH_4^+) exchange output (not displayed) from the model is significantly (p < 0.05) correlated ($r^2 = 0.63$ and $r^2 = 0.71$, respectively) with the observed data. Similarly, modelled oxygen fluxes are significantly (p < 0.05) correlated ($r^2 = 0.66$) with the measurements. This aspect of the model is not discussed further.

DISCUSSION

The range of values of $FitP_D$ (0.07 to 0.66) suggests that NR_w (and by assumption, total nitrate reduction) in the lower Gt. Ouse sediments is always made up of contributions from both DNRA and denitrification. One

process never fully dominates the other, suggesting considerable overlap of denitrifying and nitrate ammonifying activity.

The P_D values also show that $DNRA_w$ (and by assumption, total DNRA) is the more significant process. This is in line with many coastal studies of nitrate reduction from different parts of the world (Table 1). For a number of east coast UK estuaries, Herbert & Nedwell (1990) showed that fermentative bacteria were numerically dominant and potentially the most active nitrate reducing bacteria in the sediments. Similar bacterial findings have been reported for a wide range of sediment types in the northwest European shelf region (Cole & Brown 1980).

According to the temperature relationship derived from this data ($FitP_D$, Eq. 4) both D_w and $DNRA_w$ occur to varying degrees, at all temperatures. However, both colder (<14°C) and warmer (>17°C) temperatures favour $DNRA_w$ over D_w while D_w is the favoured pathway in NR_w at moderate temperatures (14 to 17°C). Given the significant correlations (p < 0.05) between nitrate fluxes and ammonium effluxes in these sediments, it is likely that this temperature effect is also true for total nitrate reduction.

The relationship of P_D to temperature may be explained by observations which suggest that nitrate ammonifying bacteria and denitrifiers are adapted to different temperatures (King & Nedwell 1984, Ogilvie et al. 1997a). However, plotting the King & Nedwell (1984) results alongside $FitP_D$ (Fig. 7) shows differences in the relationship between the proportioning of nitrate reduction and temperature.
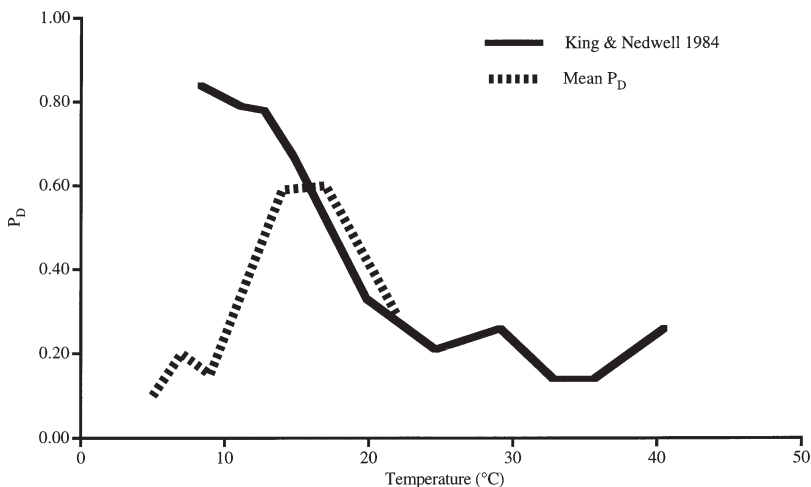

Fig. 7. Comparison of $FitP_D$ and data from King & Nedwell (1984) versus temperature. (King & Nedwell data calculated from their Fig. 4)

Using anoxic estuarine sediment slurries and chemostat experiments, King & Nedwell (1984) show that colder temperatures favour denitrification while warmer temperatures are preferred by nitrate-ammonifying bacteria, leading to the idea that denitrifiers are psychrophilic and that nitrate ammonifiers are mesophilic. Their results have subsequently been supported by fieldwork (Ogilvie et al. 1997b) from the same estuary (the Colne, UK east coast, a high-nitrate, temperate estuary). These 2 quoted studies suggest that $FitP_D$, derived from the lower Gt. Ouse data, does not reflect a causal relationship between sediment temperature and the pathway selected in nitrate reduction. The 'cold' response of NR_w favouring $DNRA_w$ may be an artefact of $FitP_D$. That is, the assumption that the nitrate flux to the sediment is equivalent to dissimilatory NR_w may not be true. This is difficult to check without measurements of DNRA and this assumption has been warned against in previous studies (Jørgensen 1989). However, this warning is concerned with sediment populated by either heterotrophic bacteria, which carry out assimilatory nitrate reduction to meet nutritional requirements, and/or benthic algae. Assimilatory nitrate reduction is known to be inhibited in the presence of ammonium (Cole & Brown 1980) and can therefore be ignored in this data. It has already been mentioned that the effects of benthic algae were removed by dark incubations. Although it has been shown that nutrient assimilation can continue after the onset of darkness (Rysgaard et al. 1993), seasonal measurements of both light and dark nutrient exchange and of chlorophyll a (consistently <3 µg g^{-1} dry sediment) showed that light had no significant effect on the nutrient flux (Trimmer et al. 1998). In contrast to the latter, where chlorophyll concentrations are much higher (e.g. >26 µg g^{-1} dry sediment; Dong et al. 2000), it has been shown that light makes a significant difference to nutrient fluxes compared to dark incubations.

The preferred selection for $DNRA_w$ at the colder temperature range indicated by $FitP_D$ is caused by the high winter nitrate fluxes relative to the low rates of D_w. The latter are likely to be caused by cold temperatures slowing down bacterial metabolic activity. A major cause of high solute fluxes can be the activity of macrofauna (Aller & Aller 1998). However, the lack of benthic animals (a consistent finding during a total of 4 yr of study in which hundreds of cores were sifted; Trimmer 1997) in the lower Gt. Ouse sediments excludes this factor. Diffusive enhancement by turbulence across the SWI may cause increased solute fluxes (Lohse et al. 1996) but the core incubations used to derive the data in Trimmer et al. (1998) removes this effect. It is concluded that the high nitrate fluxes observed in the colder months (e.g. Site 7, November 1994, March 1995, temperature = 9 and 7°C respec-

tively, Table 3) is due to high nitrate-ammonifying activity.

Alternative explanations for the dominance of $DNRA_w$ in summer may be due to the fact that (i) sediments become increasingly reduced environments (Jørgensen 1989) or that (ii) labile carbon to nitrate ratios (Herbert & Nedwell 1990) are high relative to those in winter. These factors cannot be excluded from this work and it is likely that the dominance of DNRA in summer is caused by a combination of temperature, labile carbon:nitrate ratios and pH. However, the temperature relationship with NR_w (Fig. 3) suggests an important controlling effect. This implies that in the lower Gt. Ouse sediments, nitrate-ammonifying bacteria are best adapted to both colder and warmer temperatures, while denitrifiers only outcompete them over a small intermediate temperature range. This runs counter to the findings from laboratory based work (King & Nedwell 1987, Herbert & Nedwell 1990) which show that high nitrate concentrations (as found in winter) favour denitrification. However, plotting $FitP_D$ against overlying nitrate concentrations in the lower Gt. Ouse (not shown) shows no relationship between high nitrate concentrations (shown to be proportional to the nitrate concentration in the top 1 cm of sediment in the Gt. Ouse sediments; Nedwell & Trimmer 1996) and $FitP_D$. Consequently, for the lower Gt. Ouse sediments, it is proposed that temperature is a dominant controlling factor in determining the end products (N-gases or ammonium) of total nitrate reduction.

It is possible that the temperature range favouring denitrification is wider than is suggested by the calculations of P_D. There is a 5°C gap between 9 and 14°C and between 17 and 22°C for which there is no data for P_D (Table 3). If true, seasonal denitrification may be of a longer duration compared with DNRA. However, this does not change the main conclusions of this work (see below) although the overall annual balance of the 2 nitrate competing processes may favour the production of N-gases over ammonium. Note that Trimmer et al. (1998) calculated that 46% of the nitrate flux into these sediments was converted to N-gases, the remainder ending up as ammonium.

Attempts to model D_w in the lower Gt. Ouse sediments without partitioning nitrate reduction (M−$FitP_D$) were not successful across the full range (5 to 22°C) of observed temperatures. Measured rates of D_w could not be reproduced by the model (M−$FitP_D$) at the lower temperatures (<14°C). In contrast, for temperatures ≥14°C the effect of decreasing nitrate concentrations in the overlying water column on D_w (M−$FitP_D$) was similar to that with the run of M+$FitP_D$. A test run was carried out to determine whether the decrease in D_w for temperatures ≥14°C is due to: (1) lowering

nitrate concentrations in the water column; (2) the effects of temperature selection favouring $DNRA_w$; or (3) both (1) and (2). The test run (not shown) used $M+FitP_D$ with a constant top boundary value for nitrate (the mean across all sites was used = 406 μM) for all temperatures at all sites. As before, the model was calibrated to rates of D_w at 14°C. Modelled D_w rates for temperatures >14°C were higher than the standard run (i.e. $M+FitP_D$ with observed boundary values) by a mean factor of 2.3. This suggests that lowering nitrate concentrations are needed to better represent the observed rates of D_w in summer. Hence, both temperature selection and changing nitrate concentrations are needed in the model.

It is possible that the variability in P_D may be caused by the variable efficiency of the acetylene blockage technique (Seitzinger et al. 1993). However, these latter authors added acetylene to only the overlying water to measure sediment denitrification. In the denitrification data collected by Trimmer et al. (1998), acetylene was injected into the sediments and in this way the method has been shown to give reliable estimates (Koike & Sørensen 1988, Knowles 1990, van Raaphorst et al. 1992) as argued by Ogilvie et al. (1997b). Furthermore, rates of D_w are well correlated (r = 0.83) with seasonal variations in overlying nitrate concentrations (Trimmer et al. 1998) which has been shown in other studies (Ogilvie et al. 1997b, Dong et al. 2000).

Nitrification is inhibited by the acetylene blockage technique and consequently has little effect on the calculation of P_D. This does not mean that nitrification is absent in these sediments. Only 10% of the nitrate fluxes are directed out of the sediment (Table 3) indicating, in these situations, that nitrification is greater than total nitrate reduction. However, the large majority (90%) of the measured nitrate fluxes are directed into the sediment (Table 3) and more importantly, they are significantly (p < 0.05) correlated to both rates of D_w and ammonium effluxes. This suggests that total nitrate reduction, not just NR_w, is correlated to the nitrate flux which supports the assumption that the relationship between P_D and temperature can be extended to total nitrate reduction in these sediments. Consequently, for these sediments, nitrification is (1) negligible and invariant with temperature or (2) in constant proportion to nitrate reduction.

The percentage contribution of total DNRA to total ammonium production in the lower Gt. Ouse sediments (Fig. 6) varies between 1 and 58% across all temperatures and sites. This is a large variation fuelled by the range (21 to 830 μM NO_3^-) in overlying nitrate concentrations since most (>70% for all sites) of the ammonium nitrogen produced by DNRA derives from the nitrate nitrogen rather than the nitrogen bound in the

organic matter. This is not surprising given the stoichiometry of Eq. (7) which yields 1 mol of ammonium for every mole of nitrate reduced and 0.15 (16/106) mol of ammonium for every mole of TOC mineralised via nitrate. Consequently, variations in concentrations of nitrate in the water column have a considerable effect on the production of ammonium from DNRA. This helps to explain the significant (p < 0.05) correlations found between the measured nitrate fluxes and the ammonium effluxes in the lower Gt. Ouse sediments (Trimmer et al. 1998). The increase in the percentage of ammonium production from DNRA at Sites 4, 5 and 7 (Fig. 6) is caused by increases in the nitrate concentration in the overlying water between 15.5 and 22°C. This effect also explains the increases in modelled $DNRA_w$ rates at the same sites and temperatures (Fig. 5).

The differences between the sites (Fig. 6) are related to differences in both the first order rate constant (k_{NO_3}) for nitrate reduction (Table 4) and the nitrate concentrations in the overlying water (Fig. 4). A comparison between the mean percentage contribution of DNRA to total ammonium production at each site with both the mean nitrate concentration in the water column and the k_{NO_3} value at each site is shown in Table 5. High k_{NO_3} values coincide with high percentage contributions of DNRA to total ammonium production (Sites 4, 6, 7 and 8). The order of the percentage contribution of DNRA to ammonium production in the last 2 sites in Table 5 does not match the order of the k_{NO_3} values. This is because the mean nitrate concentration is greater at Site 5 (484 μM NO_3^-) than at Site 9 (330 μM NO_3^-) even though the 2 sites have similar k_{NO_3} values (0.79 and 0.83 yr^{-1}, respectively). A similar argument explains why Sites 5 and 7 have the same percentage: the higher k_{NO_3} value by a factor of 1.49 at Site 7 compared to Site 5 compensates for the lower mean nitrate concentration at Site 7 compared to Site 5.

The range of fitted values of the first order rate constants, k_{NO_3}, for nitrate reduction (0.79 to 11.57 yr^{-1}, Table 4) falls within the published range of first order rate constants for TOC degradation (e.g. 0.1 to 4.8 yr^{-1},

Table 5. Comparison of the mean percentage contribution of DNRA to total ammonium production (% DNRA⇒NH_4^+) with both k_{NO_3} values and the mean nitrate concentration in the water column at 6 sites in the lower Gt. Ouse

Site	% DNRA⇒NH_4^+	k_{NO_3} (yr^{-1})	NO_3^- (μM)
4	36	11.57	540
5	16	0.79	484
6	24	4.83	432
7	16	1.18	271
8	17	1.45	340
9	7	0.83	330

McNichol et al. 1988; 0.005 to 53 yr^{-1}, Andersen 1996; 0.2–7 yr^{-1}, Middelburg et al. 1996). The larger values in model run $M+FitP_D$ compared to $M-FitP_D$ (Table 4) are caused by the presence of $FitP_D$. That is, only a fraction of the nitrate reduction in $M+FitP_D$ can follow the denitrification pathway, compared to 100% in $M-FitP_D$. Thus, higher k_{NO3} values are needed in $M+FitP_D$ to fit rates of denitrification to the observed rates at 14°C.

CONCLUSIONS

In the lower Gt. Ouse sediments, temperature selection in dissimilatory NR_w can be used to model both D_w and $DNRA_w$. It is assumed from the significant correlations (p < 0.05) between nitrate fluxes and both the rates of D_w and the ammonium effluxes that this temperature effect can be applied to the partitioning of total nitrate reduction.

Use of Eq. (4) in the diagenetic model has been shown to be an effective way to simulate observed rates of D_w. The same equation can be used to model rates of $DNRA_w$ which compare well to calculated rates. This represents a first attempt to simulate DNRA in a diagenetic model. Future models will need to rely on more mechanistic equations (which require more detailed work on the underlying microbiology and kinetics) to describe the proportioning of nitrate reduction into denitrification and DNRA. Until such detailed experimental work is done, the work presented here shows that a simple model can be used to interpret field observations. Furthermore, the simplicity of this modelling approach is highlighted in the fact that only 1 free parameter (k_{NO_3}) needs to be fitted.

It is concluded that over the measured temperature range (5 to 22°C) in the lower Gt. Ouse sediments, temperature is an important control in partitioning nitrate reduction into denitrification and DNRA. The narrowness of the temperature range suggests that there is an overlap in the 2 pathways which is indicated by the fact that P_D is never equal to 1 or 0. Thus, both pathways occur to varying degrees at all temperatures in the lower Gt. Ouse sediments.

Overall, the implication is that during an extended warm summer in temperate estuaries receiving high nitrate inputs, nitrate reduction may contribute to, rather than counteract, a eutrophication event. The conversion of nitrate to the more biologically preferred form of the nitrogen nutrient, ammonium, means that nitrate reduction has considerable fertilising potential. This implication acts as a caveat for studies which concentrate solely on 1 aspect of nitrate reduction (i.e. denitrification) with respect to nitrogen inputs. The search for similar relationships from other data sets must be continued before general conclusions about

the response of nitrate reduction to temperature (and other environmental factors) can be made.

Finally, it is concluded that diagenetic models of the nitrogen cycle can and should include DNRA.

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