

# Hypernutrified estuaries as sources of $N_2O$ emission to the atmosphere: the estuary of the River Colne, Essex, UK

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**ABSTRACT:** Measurements in the estuary of the River Colne, Essex, UK, showed strong gradients of nitrate and ammonium concentrations, increasing upriver due to inputs from the river and a large sewage treatment works. In the low salinity region (<10 to 12 psu) nitrate concentrations in the water column were sometimes >1 mM, but rapidly decreased within the top 1 cm of sediment. Concentrations of  $N_2O$  in the water column correlated with nitrate concentrations, due to denitrification and  $N_2O$  formation in the surface sediment. There was no formation of  $N_2O$  in the water column.  $N_2O$  in the estuary water was always supersaturated with respect to  $N_2O$  in air, and in the low salinity/high nitrate part of the estuary could be up to 50 times air equilibration. Water-air  $N_2O$  fluxes, calculated from a thin film model, also showed marked gradients up the estuary. The emission fluxes of  $N_2O$  from the surface of tidally exposed sediments decreased with time after exposure. This was the result of the fast turnover (<40 min) of the sedimentary nitrate pool, and its depletion when it was no longer recharged by transport of nitrate from the water column. The sediments were, therefore, extremely important processors of nitrate from the water column, but only when covered by the tide. Water-air emission fluxes in each sector of the estuary were calculated and showed that maximum  $N_2O$  emission at high tide was from the sector below that where peak unit area emission fluxes were detected, because of the greater area of water surface in the sector. Total  $N_2O$  emission from the estuary did not vary with tidal state because the high nitrate/high  $N_2O$  water remained within the estuary even at low tide. Integration of the emission fluxes with time suggested that about  $1.2 \times 10^5$  mol of  $N_2O$ -N were emitted to the atmosphere in a year, of which 83 % was from the water surface. This emission accounted for 0.5 % of the Total Oxidised Nitrogen load to the estuary, or 0.3 % of the Total Nitrogen load. Benthic  $N_2O$  production corresponded to <2 % of the nitrate denitrified in the bottom sediments, but could nonetheless give rise to significant export of  $N_2O$  to the atmosphere. If the  $N_2O$  fluxes in the Colne estuary were extrapolated globally, the total estuarine  $N_2O$  production would be equivalent to between 0.13 and 0.45 Tg  $N_2O$ -N yr<sup>-1</sup>. This is equivalent to the source strengths of adipic acid and nitric acid productions, but less than the hypothesised missing global source(s) of  $N_2O$ .

**KEY WORDS:** Eutrophication · Denitrification · Nitrous oxide · Greenhouse gas

## INTRODUCTION

Nitrous oxide ( $N_2O$ ) is the third most important greenhouse gas in terms of its overall effect

(Houghton et al. 1992), although it has 270 times the global warming potential of  $CO_2$  over a 20 yr period. Tropospheric  $N_2O$  is increasing at a rate of ~1 ppb yr<sup>-1</sup>, indicating that current global sources exceed sinks (Bouwman et al. 1995). According to Mathews (1994) known global sinks exceed known sources by 40 %, which implies either unknown sources or under-estimation of known sources. Prinn et al. (1990) deduced that fossil fuel combustion alone could not explain all of the observed rise in a 10 yr suite of measurements. Instead, growing sources from tropical

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land disturbance, and from a northern mid-latitude increase in fertiliser usage and fossil fuel combustion were proposed.

Current global budgets do not generally include estimates of sources of  $N_2O$  in estuaries and coastal seas, although the impact of these environments on the nitrogen flux from land to sea is well established. In particular, estuarine sediments may be important sites for denitrification, particularly where nitrate loads to an estuary are high (Nedwell 1975, Seitzinger et al. 1980, Ogilvie et al. 1997). McElroy et al. (1978) demonstrated the presence of elevated  $N_2O$  in the Potomac estuary, Maryland, USA, and estimated that 1 to 5% of the total N input to the estuary was converted to  $N_2O$ . Similar high  $N_2O$  concentrations and high fluxes to atmosphere have been described in other estuaries and coastal seas (Sørensen 1978, Jensen et al. 1984, Seitzinger et al. 1984, De Angelis & Gordon 1985, Kieseckamp et al. 1991, Law et al. 1992), although their significance as a proportion of the N load to an estuary has not usually been clear.

The present work was undertaken in the estuary of the River Colne, Essex, UK, in an integrated programme to measure the effect of denitrification within the estuary in attenuating the N load and the end-products of such denitrification. The significance of  $N_2O$  as a product of N loads to the estuary and the estuary as a source of  $N_2O$  was investigated.

## METHODS

**Study area and sampling sites.** The River Colne has a macrotidal, turbid estuary (tidal flushing time 0.9 d) with large expanses of mud flat due to its sheltered location, entering the North Sea at Brightlingsea (National Grid reference TM0801). The estuary is hypernutriented and exhibits strong gradients of nitrate and ammonium up the estuary (King & Nedwell 1984). This results from run-off from the 500 km<sup>2</sup> catchment area, much of which is rich arable land, and from the population of 107 000 around the estuary. Its N inputs are relatively well defined as the river is gauged just above its tidal limit by the Environment Agency, UK. The dominant forms of nitrogen inputs to the estuary are nitrate in the river water and ammonium in the sewage effluent. Total nitrogen (TN) inputs to the estuary from both the river and the sewage treatment works (STW) are relatively constant at about  $4$  to  $5 \times 10^7$  mol N yr<sup>-1</sup>. The major riverine input is about  $2 \times 10^7$  mol N yr<sup>-1</sup> of Total Oxidised

Nitrogen (TON), of which the largest part (<95%) is nitrate. During the summer river flow is low due to water abstraction, and N inputs are then dominated by those from a large STW at Colchester Hythe. Colchester STW accounts for >95% of the STW input to the estuary.

Four sites were selected, covering the range of the estuary (Fig. 1), for sediment concentration profiles and gas emission surveys: Brightlingsea (site A); Alresford (site B); Wivenhoe (site C) and The Hythe (site D).

**Axial profiles of dissolved  $N_2O$  concentrations along the estuary.** From February 1993 to March 1994, 12 axial surveys were completed, 6 each at high and low tide. Twenty sampling stations were selected at regular intervals along the estuary from Brightlingsea to The Hythe (Fig. 1) and were sampled  $\pm 1$  h either side of low or high tide. Single samples of water were collected at each station for the first 4 surveys, and triplicate samples from each station on subsequent surveys. Samples for dissolved  $N_2O$  determination were taken by injecting 20 ml of column water into 60 ml

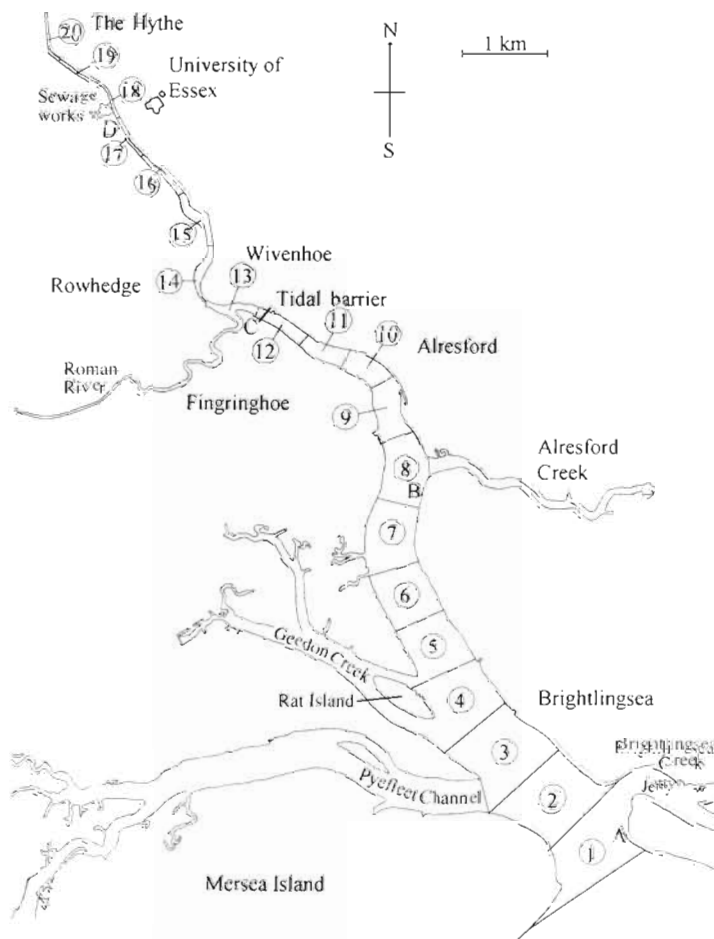


Fig. 1. Map of the Colne estuary, east coast UK, showing positions of sampling sites

glass bottles containing station air before immediately inserting butyl stoppers. Simultaneously, samples of water were also collected for nutrient and salinity determinations. All water samples were immediately frozen in dry ice and subsequently kept frozen ( $-20^{\circ}\text{C}$ ) until analysis. Air samples were also collected at each station using 25 ml glass tubes with butyl stoppers. Water and air temperatures were measured at each station with an electronic thermometer (RS 650 419, Radiospares Ltd, Corby, UK), and atmospheric pressure with a standard mercury barometer.

Prior to analysis, water samples were allowed to equilibrate to room temperature, and headspace samples were then taken for analysis (see below). The dissolved N<sub>2</sub>O concentrations expected from equilibration with the measured air or headspace N<sub>2</sub>O concentrations were calculated from solubility coefficients corrected for temperature and salinity (Weiss & Price 1980). This enabled the measured dissolved N<sub>2</sub>O concentrations to be expressed as a percentage of the dissolved concentration expected from air-equilibration.

**Calculation of water-air N<sub>2</sub>O flux.** A thin film flux model (Scranton 1983) was used to estimate N<sub>2</sub>O emission at each station using the dissolved and air concentrations of N<sub>2</sub>O:

$$F = D \cdot \frac{(C_w - C_a)}{(Z_w - Z_a)}$$

where  $F$  = water-air flux ( $\text{nmol N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ );  $D$  = temperature-corrected N<sub>2</sub>O diffusivity in water ( $\text{m}^2 \text{ h}^{-1}$ ) (Broecker & Peng 1974);  $C_w$  = N<sub>2</sub>O concentration in water ( $\text{nmol N}_2\text{O-N m}^{-3}$ );  $C_a$  = N<sub>2</sub>O concentration in water from air equilibration ( $\text{nmol N}_2\text{O-N m}^{-3}$ );  $Z_w$  = lower limit of thin film (m);  $Z_a$  = upper limit of thin film (m). Thin film thickness ( $Z_w - Z_a$ ) was estimated from a wind speed dependent relationship (Upstill-Goddard et al. 1990) using wind speed readings from an anemometer at the harbour master's office at Wivenhoe.

**Surveys of N<sub>2</sub>O concentrations in sediment pore water.** Five surveys were completed between March 1993 and February 1994 to investigate vertical distributions of N<sub>2</sub>O and nutrients in sediments. At each of the 4 sites, cores (8 cm diameter by approximately 20 cm deep) were taken with Perspex core tubes from exposed sediment at the low tide mark for N<sub>2</sub>O and nutrient analysis. Water samples for water column N<sub>2</sub>O and nutrient determinations and air samples for atmospheric N<sub>2</sub>O were also taken simultaneously. Air, water and exposed sediment temperatures were all measured.

**N<sub>2</sub>O extraction.** On return to the laboratory (within 1 h) cores were fitted with a metal collar to enable extraction with a cut-off plastic syringe of small horizontal cores (1 cm diameter by 4 cm deep) from 0 to 10 cm below the surface. The contents of each syringe

were expelled into a 25 ml glass tube containing 10 ml UHP water. For the first survey mercuric chloride was added as a preservative to a final concentration of  $\sim 40 \text{ mM}$ , but was omitted from further surveys after it was found to catalyse chemical denitrification of  $\text{NO}_2^-$  to N<sub>2</sub>O in the presence of iron sulphide (Kieskamp et al. 1988). Azide also did not stabilise N<sub>2</sub>O concentrations. Subsequently, formaldehyde (20 ml of 10% v/v solution, giving 80 mM final concentration) was used to preserve N<sub>2</sub>O in samples, and preliminary experiments showed no change in headspace N<sub>2</sub>O concentrations up to 3 d. A butyl stopper was immediately fitted to each glass tube and the sample was shaken to form a slurry prior to gas chromatography analysis. Analyses were carried out within 1 h of equilibration to minimise any losses of N<sub>2</sub>O.

**Sedimentary nutrient profiles.** Parallel cores for nutrient determinations were sectioned at 1 cm depth intervals and sediment centrifuged ( $1000 \times g$  for 20 min) to extract pore water. Pore water samples were filtered through glass fibre filters (GF/F, Whatman, Maidstone, UK) and stored at  $-20^{\circ}\text{C}$  until analysed.

**Direct measurements of emissions of N<sub>2</sub>O from sediment.** N<sub>2</sub>O emissions across the sediment-air interface were measured initially from cores of sediment held in the laboratory at *in situ* temperature and then by an *in situ* method.

Six large sediment cores [8 cm inner diameter (i.d.), 20 cm length] were taken with overlying water from each site for emission measurement. Six small cores (2.4 cm i.d., 10 cm length) were collected with overlying water for N<sub>2</sub>O analysis, and a further 12 small cores for nutrient exchange measurements.

On return to the laboratory, cores were placed in a water bath at *in situ* temperature. For water-air exchange measurement 500 ml of column water was removed from each of the 8 cm i.d. core tubes and air tight caps with gas sampling septa were then fitted. Air samples (200  $\mu\text{l}$ ) were taken from each core tube at  $T_0$  with a gas tight syringe and then at 30 min intervals for a period of 3 h. Air samples were immediately injected into the ECD-GC (electron capture detector-gas chromatograph). Samples of overlying water were also taken at  $T_0$  for measurements of dissolved N<sub>2</sub>O and for dissolved nutrient analyses.

Sediment-air N<sub>2</sub>O exchange rate measurements were effected by siphoning the remaining water from above the large cores and repeating the headspace analyses, as for water-air emission. At the start of the sediment-air exchange measurement the water overlying all the smaller nutrient cores was siphoned off and 6 were removed from the water bath. The top 1 cm sediment layer of each of these 6 cores was immediately removed and centrifuged to remove pore water for nutrient analyses which was then filtered and

stored at  $-20^{\circ}\text{C}$  to await analysis. A further 6 cores for determination of  $\text{N}_2\text{O}$  in the exposed sediment were also removed from the bath at  $T_0$ . The top 1 cm section of sediment was sliced from each core and transferred to a 70 ml glass jar, 20 ml formaldehyde solution (10% v/v) was added and a cap with a butyl seal was fitted. The jars were quickly placed on a shaker to permit rapid equilibration before a headspace sample was taken by syringe and immediately injected into the ECD-GC. At the end of the measurement period the remaining 6 cores were processed as for the cores at  $T_0$ .

In many measurements of sediment-air fluxes the efflux of  $\text{N}_2\text{O}$  declined after 1 to 2 h, suggesting run-down of the  $\text{NO}_3^-$  pool (see 'Results'). During April 1994, the 6 cores were divided and 3 continued as controls for  $\text{N}_2\text{O}$  emissions. To each of the other 3 cores 20 ml 500  $\mu\text{M}$   $\text{NO}_3^-$  was added after 6 h, and measurements of the efflux of  $\text{N}_2\text{O}$  were continued.

***In situ* measurements of  $\text{N}_2\text{O}$  exchange rates.** Three Perspex emission boxes, each covering 0.24  $\text{m}^2$  sediment and with an enclosed volume of 31 l, were placed on exposed sediment at the low tide mark. Air samples (60 ml) were extracted from the boxes with a plastic syringe via a septum. Each sample was stored by flushing the contents of the syringe through a 10 ml glass vial fitted with a butyl stopper. Samples were taken from each box at  $T_0$  and then at 20 min intervals until the rising tide covered the sediment. Six exposed sediment cores were also collected for nutrient analyses at  $T_0$  and frozen immediately with liquid  $\text{N}_2$  before storing in dry ice. A further 6 cores were collected before tidal inundation at the end of the measurement period. Triplicate water column samples for  $\text{N}_2\text{O}$  and nutrient analysis were collected at  $T_0$  just as the sediment became exposed to the air.

**Analysis of  $\text{N}_2\text{O}$ .** Samples for  $\text{N}_2\text{O}$  analysis were equilibrated to room temperature, and headspace samples (200  $\mu\text{l}$ ) were then extracted with a gas tight syringe and injected into a gas chromatograph (Shimadzu Model 14-A, Dyson Instruments Ltd, Houghton-le-Spring, UK) with an electron capture detector (injector  $50^{\circ}\text{C}$ , column  $25^{\circ}\text{C}$ , detector  $340^{\circ}\text{C}$ ).  $\text{N}_2\text{O}$  was separated using a stainless steel column (2 m long  $\times$  4 mm outer diameter) packed with Porapak QS (60/80 mesh size) and argon/methane (95%/5%) as the carrier gas (50  $\text{ml min}^{-1}$ ). Headspace concentrations of  $\text{N}_2\text{O}$  were calculated from peak areas using an electronic integrator (Shimadzu Model CR6A, Dyson Instruments Ltd). The detection limit was 10  $\text{pmol N}_2\text{O-N}$ .

**Measurements of water samples.** Nitrate and nitrite were measured colorimetrically (Strickland & Parsons 1972) with ammonium chloride buffer added to prevent reduction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$  (Collos et al. 1992). Ammonium was measured with a modification of the

indo-phenol blue method (Harwood & Kuhn 1970) with dichloroisocyanurate replacing bleach as the electron donor (Krom 1980). Salinity was measured using an optical refractometer (model 10419, Reichert-Jung, Cambridge Instruments, Buffalo, NY, USA).

## RESULTS

### Axial profiles of nutrients and $\text{N}_2\text{O}$

All surveys showed pronounced gradients of nutrients along the estuary, with maximum concentrations at high tide at The Hythe in Colchester (site D) where nitrate concentrations reached  $>1$  mM (Fig. 2). Nutrients concentrations were inversely related to salinity and often showed conservative mixing in the region of the estuary where salinity was  $>10$  psu. Generally, winter and spring dissolved  $\text{NO}_3^-$  concentrations were higher than in summer or autumn; this is associated with higher rainfall and riverine  $\text{NO}_3^-$  loads and low biological production in these seasons. At low tide the high nutrient estuarine water spread down the estuary to about site B (Alresford), so that the high  $\text{NO}_3^-$ , low salinity region of the estuary was above that point. Similar longitudinal gradients of  $\text{NO}_2^-$  were seen, but at concentrations 2 orders of magnitude lower than  $\text{NO}_3^-$  (maximum  $\text{NO}_2^-$  concentration 30  $\mu\text{M}$  at site D). Ammonium was intermediate to nitrate and nitrite, reaching  $>500$   $\mu\text{M}$  at The Hythe during summer when the STW effluent discharged from the Colchester STW was poorly nitrified.

There were pronounced  $\text{N}_2\text{O}$  gradients along the estuary, with concentrations increasing upstream (Fig. 3). At the seaward end  $\text{N}_2\text{O}$  ranged only between 5 and 79  $\text{nmol N}_2\text{O-N l}^{-1}$ . Ten of the 12 surveys showed a peak in  $\text{N}_2\text{O}$  concentration at an intermediate point in the estuary, usually just above or below Wivenhoe (site C). This also tended to be the region of the turbidity maximum within the estuary (data not shown). Dissolved  $\text{N}_2\text{O}$  concentrations at this maximum ranged from 158 to 1300  $\text{nmol N}_2\text{O-N l}^{-1}$  in January 1994 and September 1993, respectively. Plots of water column  $\text{N}_2\text{O}$  concentration against salinity (data not shown) indicated that the peak in concentration occurred at low salinities, between 0 and 12 psu, i.e. in the high nitrate part of the estuary. Water column  $\text{N}_2\text{O}$  concentrations were positively correlated with both nitrate and nitrite concentrations seaward of the  $\text{N}_2\text{O}$  maxima on all surveys (average  $r^2$  was 0.90). Where  $\text{N}_2\text{O}$  concentrations declined upstream of the  $\text{N}_2\text{O}$  maximum, a significant ( $p < 0.05$ ) negative correlation with nitrate concentration was evident in 8 out of 9 surveys.

Water column  $\text{N}_2\text{O}$  saturations exhibited a corresponding gradient (Fig. 4). The seaward Stns 1 to 6

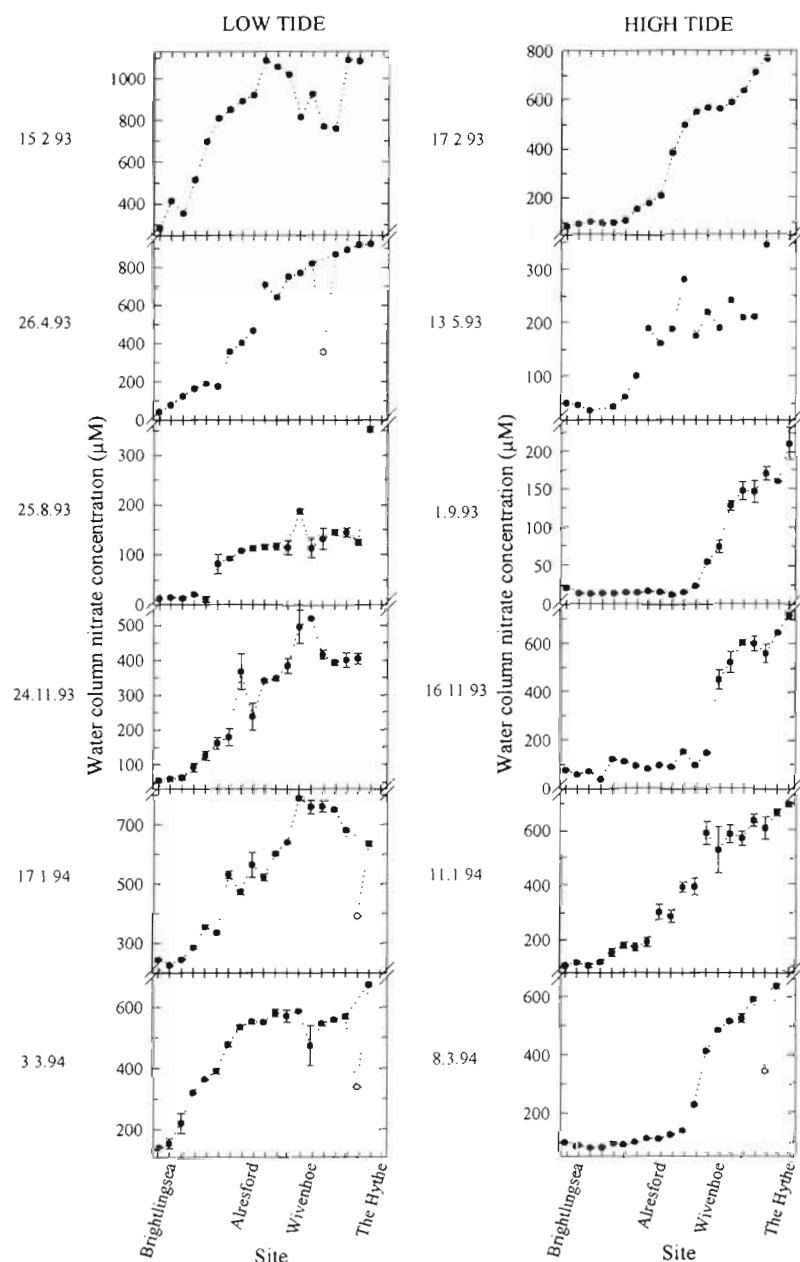


Fig. 2. Gradients of nitrate concentrations along the estuary. Dates are given as day.month.year

showed slight supersaturation (>100 %) at low tide, or undersaturation at high tide, when coastal seawater intruded into the estuary. The water column was supersaturated on all surveys upstream of Stn 6 on the axial surveys, indicating that this high nitrate, low salinity part of the estuary was a source of atmospheric N<sub>2</sub>O at all times. The highest water column saturation of 5190 % was recorded at Stn 19 in September 1993.

Water-air emission fluxes of N<sub>2</sub>O calculated from the thin film model (Fig. 5) increased up the estuary, reflecting the water column concentrations. Boundary

layer thicknesses tended to be greater in summer when windspeeds were low, but wind speed differences between surveys had a relatively minor effect on emission estimations compared to variations in water column N<sub>2</sub>O concentration. The highest emission fluxes of N<sub>2</sub>O occurred in the low salinity area of the estuary in August 1993 with 55.8 µmol N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> at Stn 14. In contrast, the water column undersaturations observed at the mouth of the estuary on some surveys gave negative N<sub>2</sub>O emission fluxes, suggesting that the coastal seawater might act as a weak sink for atmospheric N<sub>2</sub>O.

#### Estuarine water-air N<sub>2</sub>O flux in 1993–94

The area of the estuary was divided into 20 sections or cells, each centred around one of the 20 sampling stations for the axial surveys. The measured N<sub>2</sub>O fluxes per unit surface of water were multiplied by the corresponding area of water surface in the section for either the high or the low tide situation (Fig. 6). When the water surface area of each section of the estuary was taken into account, the sector of greatest total emission at high tide was in the middle reaches of the estuary, around Wivenhoe. The rates of N<sub>2</sub>O efflux per m<sup>2</sup> were smaller in this sector than at The Hythe, but this was countered by the greater surface area. It also meant that a small unit area sink for N<sub>2</sub>O in the sediments at the estuary mouth could become a large term when multiplied by the large sediment surface area in this sector.

Hourly whole estuary outputs of N<sub>2</sub>O from water to air are shown in Table 1. At low tide the high N<sub>2</sub>O/NO<sub>3</sub><sup>-</sup> water moved into the lower reaches of the estuary. The surface area of water in the estuary at low tide was only 44 % of that at high tide. However, the high N<sub>2</sub>O, low salinity water held upstream at high tide did not exit the estuary at low tide but increased its surface area as it smeared downstream at low tide, which compensated for the lower total surface area of water in the estuary at low tide. A *t*-test on the whole estuary emissions indicated no significant difference

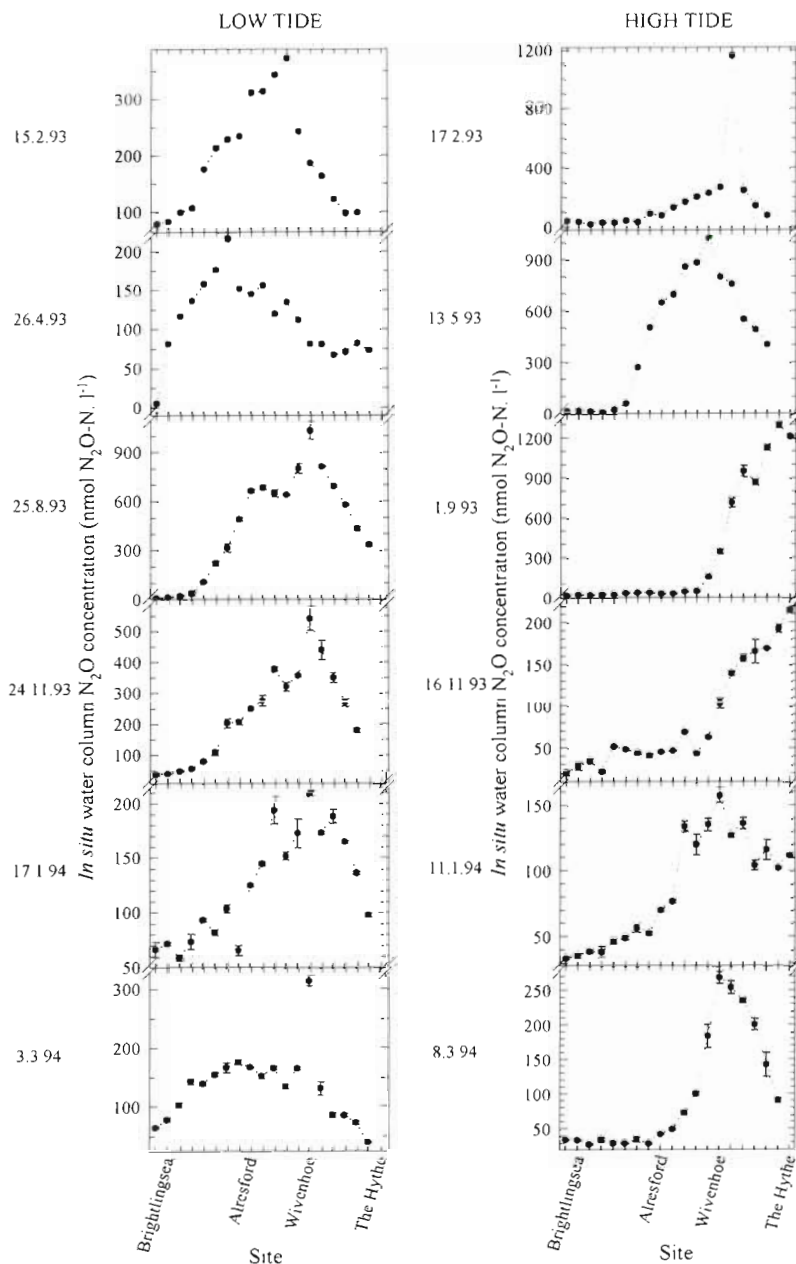


Fig. 3. Gradients of  $\text{N}_2\text{O}$  concentrations along the estuary

between the hourly estuarine  $\text{N}_2\text{O}$  emission rates between low tides and high tides. Therefore, estimation of daily rates of estuarine water-air  $\text{N}_2\text{O}$  emission from the estuarine water surface was simplified, as the daily rate of  $\text{N}_2\text{O}$  emission for the whole estuary could be derived by multiplying the average of the hourly low tide and high tide emission rates for the estuary by 24. Annual  $\text{N}_2\text{O}$  emission from the water surface within the estuary was then estimated by integrating with respect to time by linear interpolation between sampling dates. This gave a figure for annual water-air

$\text{N}_2\text{O}$  emission in the estuary during 1993–94 of  $1.16 \times 10^5 \text{ mol N}_2\text{O-N}$ .

#### $\text{N}_2\text{O}$ in the sediment

In the top 1 cm of exposed sediment  $\text{N}_2\text{O}$  was always present in concentrations well above air equilibrium, and the upper 1 to 2 cm of sediment generally had the highest  $\text{N}_2\text{O}$  concentrations. Typically, the surface layer of sediment had higher  $\text{N}_2\text{O}$  concentrations than in the adjacent tidal water (Table 2), confirming it as the site of  $\text{N}_2\text{O}$  production in the estuary. Nitrate was confined to the top 0 to 1 cm layer of sediment at sites C and D, being rapidly reduced and removed by denitrification (Ogilvie et al. 1997). Water column nitrate concentrations were typically between 10 and  $100\times$  higher than in the top 1 cm of sediment, indicating fluxes of  $\text{NO}_3^-$  into the sediment, which maintained the high benthic denitrification rate.

#### Direct measurements of $\text{N}_2\text{O}$ emissions to the air from the sediment

The laboratory-based measurements of sediment-air  $\text{N}_2\text{O}$  fluxes with sediment cores (data not shown) confirmed that at site A (Brightlingsea) exposed sediment acted as a small sink for atmospheric  $\text{N}_2\text{O}$ , with negative fluxes ranging from  $-20$  to  $-37 \text{ nmol N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ . The sediments at sites B to D were always sources of  $\text{N}_2\text{O}$  to the atmosphere. Site C (Wivenhoe) was the strongest source of  $\text{N}_2\text{O}$  with fluxes ranging from  $716$  to  $8266 \text{ nmol N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ . The sediment-air emission of  $\text{N}_2\text{O}$  at this site often became asymptotic after 1 to 2 h, indicating run-down of the sedimentary  $\text{NO}_3^-$  pool. Turnover of the  $\text{NO}_3^-$  pools in these sediments is rapid (typically  $<40 \text{ min}$ ; Ogilvie et al. 1997). Experimental addition of  $\text{NO}_3^-$  to replicates of site C sediment (Fig. 7) greatly stimulated emission of  $\text{N}_2\text{O}$  compared to unenriched controls. Table 3 summarises the sediment-air emission rates measured at low tide with the *in situ* method. Sites B to D were again confirmed as strong sources of  $\text{N}_2\text{O}$ , with site A having low fluxes.



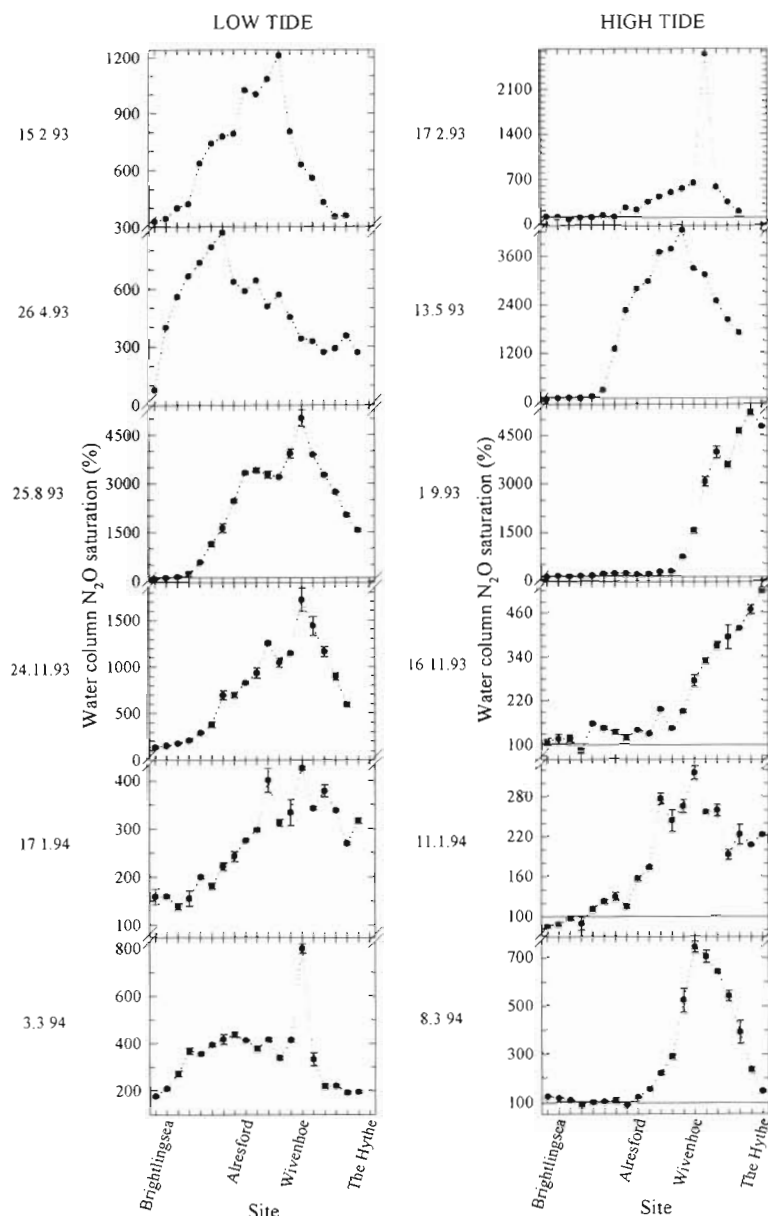


Fig. 4. N<sub>2</sub>O saturations along the estuary. Horizontal line shows 100% saturation

### N<sub>2</sub>O emissions during 1994–95

During 1994–95, water-air N<sub>2</sub>O emissions were estimated by taking low tide samples of water at each of the 4 sampling sites used for measurements of sediment-air N<sub>2</sub>O fluxes, by measuring the dissolved N<sub>2</sub>O and calculating the water-air flux rate with the thin film model. The water-air N<sub>2</sub>O fluxes on the 7 sampling occasions were averaged, and then multiplied by 8760 h yr<sup>-1</sup> and by the low tide water surface area of the sector to derive the annual N<sub>2</sub>O emission for that sector. The 4 sectors were then totalled to derive

the annual estuarine emission. By this simpler method an annual estuarine water-air N<sub>2</sub>O emission of  $0.85 \times 10^5$  mol N<sub>2</sub>O-N was obtained for 1994–95, which was similar to the value for 1993–94 ( $1.2 \times 10^5$  mol N<sub>2</sub>O-N). Furthermore, we had a corresponding estimate of the sediment-air flux in these 4 sectors of the estuary for the same period.

An equivalent calculation was made for sediment-air fluxes. There were obvious tidal effects on the emission of N<sub>2</sub>O to atmosphere from the intertidal area. At high tide there was virtually no exposed sediment, and in contrast there was a maximum exposed area at low tide. A sine wave model was used to integrate with time the gas fluxes from exposed sediment. The surface areas of water and exposed sediment at high and low tide in each of the 4 sectors were estimated from marine charts. Tidally related variations in the areas of water and sediment in each cell were modelled with a simple sine wave model for tidal exposure of sediment:

$$M_a \int_0^{24} \sin(ax+1)dx = M_a \left[ -1/a \cos(ax) + x \right]_0^{24}$$

where  $M_a$  = exposed sediment area at mid-tide (Brightlingsea: 537 536 m<sup>2</sup>; Alresford: 712 651 m<sup>2</sup>; Wivenhoe: 166 623 m<sup>2</sup>; Hythe: 57 947 m<sup>2</sup>);  $a$  = number of days per tidal cycle (1/1.92);  $x$  = hour of day. The measured hourly sediment-air area flux rates were then multiplied by the time-integrated exposed sediment area to derive the daily output rates for each sector. The daily rates were then averaged over all sampling occasions, and this value multiplied by 365 to give an estimate of annual sediment-air emissions from each sector (Table 4).

The sediment-air emissions showed similar trends to water-air emissions. Alresford was the most important sector for sediment-air emissions, 72% of the flux arising from the 48% of the estuarine sediment exposed in this sector. Wivenhoe contributed 12% of the flux from 11% of the exposed sediment area, and The Hythe gave 11% from only 4% of the exposed sediment. Finally, the Brightlingsea sector which represented 37% of the exposed sediment area gave only 5% of the total sediment-air flux. The total estuarine N<sub>2</sub>O emission from both water and exposed sediment was  $1.02 \times 10^5$  mol N<sub>2</sub>O-N yr<sup>-1</sup>, of which 17% ( $0.17 \times 10^5$  mol N<sub>2</sub>O-

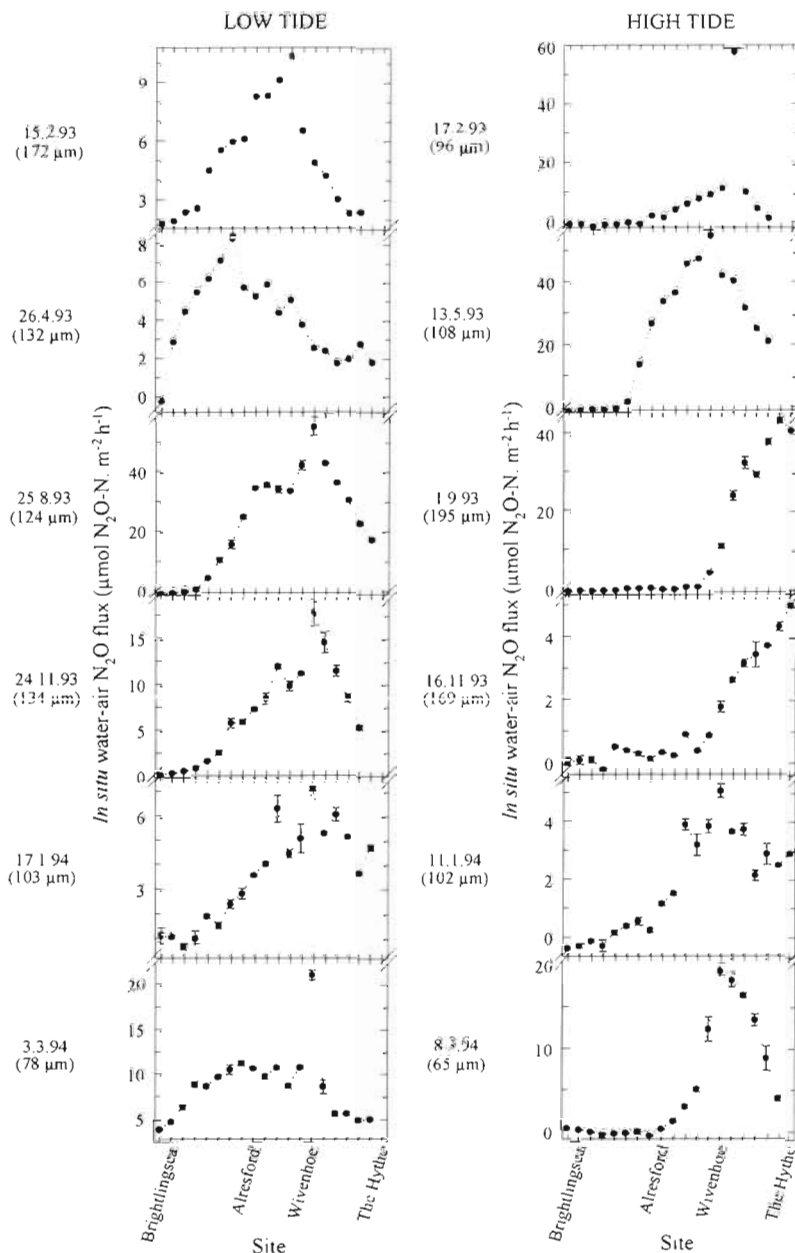


Fig. 5. Emission fluxes of  $N_2O$  along the estuary. Calculated from the thin film model (boundary layer thicknesses given in parentheses for each survey)

$N \text{ yr}^{-1}$ ) was emitted from the exposed sediment and 83% ( $0.85 \times 10^5 \text{ mol } N_2O-N \text{ yr}^{-1}$ ) from the water surface.

## DISCUSSION

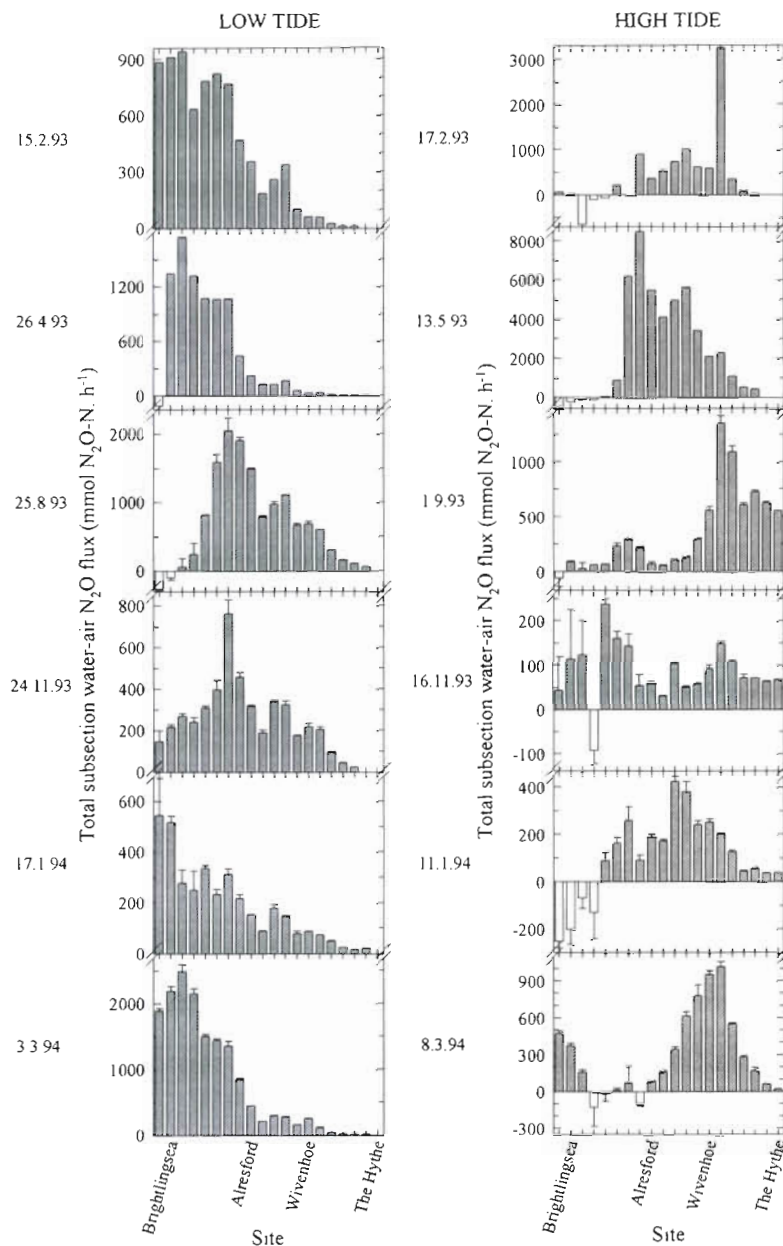
Our data showed very clearly that the turbid, hyper-nitrified, muddy estuary of the River Colne was a strong source of  $N_2O$  efflux to the atmosphere.  $N_2O$

can originate from both nitrification (Poth & Focht 1985, Anderson & Levine 1986) and denitrification. The absence of any significant production of  $N_2O$  in water column controls (Ogilvie et al. 1997) supported the contention that benthic denitrification, not nitrification, was the major source of  $N_2O$  in this high nitrate estuary. Measurements of denitrification in the Colne estuary as part of the same research programme (Ogilvie et al. 1997) confirmed that there were strong gradients of benthic denitrification up the estuary, correlated with the overlying nitrate load. The role of estuaries as sinks for nitrogen has been known for a considerable period (Nedwell 1975, Seitzinger et al. 1980, 1984), although the magnitude of the attenuation of N load has been subject to controversy and appears to vary considerably depending upon the flushing time and upon the nitrogen load of the estuary (Balls 1994, Nixon et al. 1996). The process giving rise to this nitrogen sink in estuaries is denitrification in the bottom sediments, both from direct denitrification of nitrate transported into the sediments from the overlying water ( $D_w$ ) and by coupled nitrification-denitrification in the sediments ( $D_n$ , as in Nielsen 1992). Rates of transport of nitrate into the sediment, and of benthic denitrification, increased with the nitrate concentration in the overlying water, at least up to a concentration of approximately 400 to 600  $\mu M$  nitrate (Ogilvie et al. 1997). Above that concentration the rate of nitrate uptake by the sediment becomes nitrate-saturated. As nitrate load increases, therefore, there is both an increase in the rate of benthic nitrate uptake and an increase in the proportion of the nitrate

which is denitrified within the sediment. Both of these factors contribute to the increased significance of benthic denitrification as a sink for nitrate as nitrate loads to an estuary increase.

At the 4 sites in the Colne estuary the concentrations of  $N_2O$  were greatest in the top 1 to 2 cm of sediment, lower in the water column, and smallest in air (Table 2). There were, therefore, emission fluxes of  $N_2O$  from water to air and from sediment to air when sediment was exposed. Estimates of the relative con-



Fig. 6. Total N<sub>2</sub>O production in each sector of the estuary

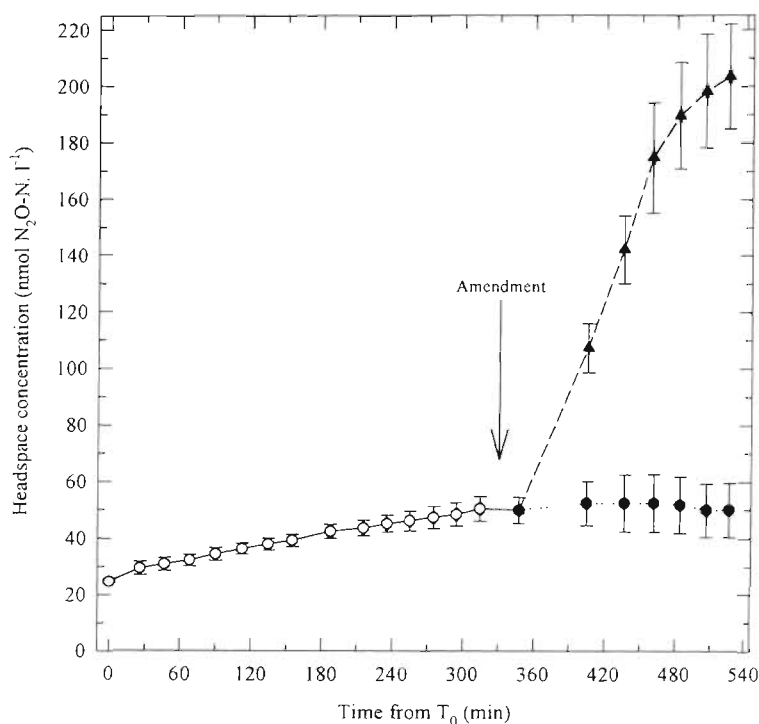
tributions of water-air and sediment-air N<sub>2</sub>O fluxes in the estuary suggested that emissions from the water surface were about 4-fold that from the surface of sediment exposed at low tide, despite the very high concentrations of N<sub>2</sub>O measured in the surface sediment and despite the large area of the sediment exposed at low tide. One factor in this was the greater surface area of water than sediment in the estuary, but it was also clear from *in situ* measurements that sediment-air fluxes of N<sub>2</sub>O rapidly became asymptotic, tapering off 1 to 2 h after tidal exposure. This resulted from the rapid depletion of the sediment nitrate pool which led to nitrate-limitation of benthic denitrification once the sedimentary pool was no longer being recharged by transport from the water column. Experimental addition of nitrate to exposed sediment reinstated rapid N<sub>2</sub>O sediment-air efflux (Fig. 7). Furthermore, if the sediment nitrate pool is depleted, N<sub>2</sub>O may be reused as an electron acceptor in benthic microbial respiration and reduced to N<sub>2</sub> or ammonium (Elkins et al. 1978, Kieskamp et al. 1991), which will further decrease the amount of N<sub>2</sub>O available for efflux from exposed sediment. In these very hypernutrified estuaries, therefore, the sediments act as processing sites for nitrate only when the sediments are covered by water and when there is rapid recharge of the sedimentary nitrate pool from the overlying water and N<sub>2</sub>O transfer to the water column from the sediment. This in itself will tend to ensure that the surface of the water, not the exposed sedi-

Table 1 Total estuary N<sub>2</sub>O output (hourly rate) from the water surface at low and high tides

Low tide		High tide	
Survey date	Total estuary emission (mol N <sub>2</sub> O-N h <sup>-1</sup> )	Survey date	Total estuary emission (mol N <sub>2</sub> O-N h <sup>-1</sup> )
15 Feb 1993	7.6	17 Feb 1993	8.1
26 Apr 1993	8.78	13 May 1993	44.7
25 Aug 1993	13.3	1 Sep 1993	7.1
24 Nov 1993	4.8	16 Nov 1993	1.7
17 Jan 1994	3.6	11 Jan 1994	2.1
3 Mar 1994	15.8	8 Mar 1994	5.9
Average	9.0	Average	11.6

Table 2. Air-equilibration, water column and surface sediment (0 to 1 cm)  $\text{N}_2\text{O}$  concentrations, and percent saturations of  $\text{N}_2\text{O}$  at 4 sites in the Colne estuary

Site	Survey date	$\text{N}_2\text{O}$ concentration ( $\text{nmol N}_2\text{O-N l}^{-1}$ )			$\text{N}_2\text{O}$ saturation (%)	
		Air-equilibration	Water column	Surface sediment	Water column	Surface sediment
Brightlingsea	May 1993	42	66	528	157	1257
	Oct 1993	24	68	677	283	2821
	Dec 1993	32	52	313	163	978
	Jan 1994	44	40	584	91	1327
	Mean	36	46	526	174	1596
Alresford	May 1993	47	462	1414	983	3009
	Oct 1993	30	399	376	1330	1253
	Dec 1993	38	113	45	297	118
	Jan 1994	37	102	568	276	1535
	Mean	38	269	601	722	1479
Wivenhoe	May 1993	46	510	562	1109	1222
	Oct 1993	26	354	285	1362	1096
	Dec 1993	38	95	182	250	479
	Jan 1994	43	119	429	277	998
	Mean	38	270	365	750	949
The Hythe	May 1993	46	199	403	433	876
	Oct 1993	29	232	379	800	1307
	Dec 1993	40	111	193	278	483
	Jan 1994	44	95	66	216	150
	Mean	40	159	260	432	704
Estuary average		38	189	438	519	1182

Fig. 7 Stimulation of  $\text{N}_2\text{O}$  emission by addition of nitrate to exposed sediment. (o) Before amendment; (●) unamended controls; (▲) amended sediment

ment surface, is the major site for  $\text{N}_2\text{O}$  emissions.

The various estimates of annual emissions of  $\text{N}_2\text{O}$  from the estuary were consistent. The annual water-air emission of  $\text{N}_2\text{O}$  was calculated as  $1.16 \times 10^5 \text{ mol N}_2\text{O-N yr}^{-1}$  during 1993–94 and  $0.85 \times 10^5 \text{ mol N}_2\text{O-N yr}^{-1}$  during 1994–95. During 1994–95 the whole estuary  $\text{N}_2\text{O}$  emission from both sediment and water was estimated as  $1.02 \times 10^5 \text{ mol N}_2\text{O-N yr}^{-1}$ , of which 83% was from the water surface.

How significant is the production of  $\text{N}_2\text{O}$  in the Colne estuary? Comparison of the benthic  $\text{N}_2\text{O}$  production with the total benthic denitrification measured simultaneously (Ogilvie 1996, Ogilvie et al. 1997) suggested that <2% of the denitrified nitrate was reduced to  $\text{N}_2\text{O}$ , the majority being transformed to  $\text{N}_2$ . In 1993 the TON load to the estuary (of which >95% was nitrate), from both the river and the STW, was  $1.84 \times 10^7 \text{ mol N yr}^{-1}$  (TN load  $4.1 \times 10^7 \text{ mol N yr}^{-1}$ ), and annual  $\text{N}_2\text{O}$  emissions represented 0.53% of the TON load, which was 0.26% of TN load. Estuarine emissions of  $\text{N}_2\text{O}$  have not so far been

Table 3. Range of sediment-air N<sub>2</sub>O fluxes measured at low tide at each site by the *in situ* method during the period September 1994 to March 1995. Mean values are shown  $\pm$  SE, n = 6. Dates are shown in parentheses

Site	N <sub>2</sub> O flux (nmol N <sub>2</sub> O-N m <sup>-2</sup> h <sup>-1</sup> )	
	Lowest values	Highest values
Site A: Brightlingsea	-70 $\pm$ 30 (10 Nov 1994)	454 $\pm$ 108 (8 Feb 1995)
Site B: Alresford	77 $\pm$ 59 (29 Sep 1994)	7284 $\pm$ 573 (25 Nov 1994)
Site C: Wivenhoe	627 $\pm$ 147 (27 Sep 1994)	2602 $\pm$ 151 (15 Nov 1994)
Site D: The Hythe	884 $\pm$ 372 (27 Jan 1995)	9113 $\pm$ 491 (10 Oct 1994)

included in the inventories of greenhouse gas emissions, but may be significant.

Assuming the Colne estuary to be representative of estuaries globally, it is possible to calculate their significance in global emissions. The average unit area emission from the Colne estuary, 1993–1995, was 0.32 g N<sub>2</sub>O-N m<sup>-2</sup> yr<sup>-1</sup>, and global estuarine area has been estimated as  $1.4 \times 10^{12}$  m<sup>2</sup> (Woodwell 1980). This gives an average source strength of N<sub>2</sub>O from estuaries of 0.45 Tg N<sub>2</sub>O-N. A second approach is to estimate the percentage of the land-sea N load which is converted to N<sub>2</sub>O in estuaries. The data from the Colne estuary suggested that 0.26 % of the TN load, or 0.53 % of the

TON load, was converted to N<sub>2</sub>O. The global input of N from land to sea through estuaries has been estimated as 25 Tg N yr<sup>-1</sup> (Devol 1991). Application of the percentage conversions to N<sub>2</sub>O N derived from the Colne estuary would yield values of 0.07 to 0.15 Tg N yr<sup>-1</sup>, respectively. As TON is the predominant form of nitrogen load entering into most estuaries, the higher value based on TON conversion is probably more appropriate.

The 2 methods of estimating global estuarine source strengths give values of 0.15 and 0.45 Tg N yr<sup>-1</sup>, close to the estimate of 0.44 Tg N yr<sup>-1</sup> by Law et al. (1992) based on data from the water column of the relatively unpolluted Tamar Estuary in Devon, UK. This suggests that the global estuarine N<sub>2</sub>O source strength is less than the estimated oceanic source of 1.4 Tg yr<sup>-1</sup> (Butler et al. 1989), but would be the second most significant source after the open ocean. Recently, Capone (1996) proposed a much higher, biologically constrained, estimate of oceanic N<sub>2</sub>O production as 11 Tg yr<sup>-1</sup>, in which case the calculated estuarine production would appear to be trivial. However, Capone's estimate is an upper

Table 4. Fluxes of N<sub>2</sub>O from tidally exposed sediment. Estimated area of sediment exposed in each sector at low tide is shown in parentheses

Site	Survey date	Area N <sub>2</sub> O flux (nmol N <sub>2</sub> O-N m <sup>-2</sup> h <sup>-1</sup> )	Daily N <sub>2</sub> O flux (mol N <sub>2</sub> O-N d <sup>-1</sup> )	Annual emission (mol N <sub>2</sub> O-N yr <sup>-1</sup> )
Brightlingsea (1 075 072 m <sup>2</sup> )	15 Sep 1994	388	5	822
	18 Oct 1994	-3	0	
	10 Nov 1994	-70	-1	
	9 Jan 1995	173	2	
	8 Feb 1995	583	8	
	24 Mar 1995	-64	-1	
Site average			2	
Alresford (1 425 302 m <sup>2</sup> )	29 Sep 1994	77	1	12372
	25 Nov 1994	7284	130	
	13 Dec 1994	559	10	
	25 Jan 1994	620	11	
	9 Mar 1995	984	18	
Site average			34	
Wivenhoe (333 246 m <sup>2</sup> )	27 Sep 1994	627	3	2072
	24 Oct 1994	815	3	
	15 Nov 1994	2602	11	
	12 Jan 1995	853	4	
	10 Feb 1995	1927	8	
Site average			6	
The Hythe (115 893 m <sup>2</sup> )	13 Sep 1994	4306	6	1912
	10 Oct 1994	9113	13	
	8 Nov 1994	4661	7	
	29 Nov 1994	2240	3	
	27 Jan 1995	884	1	
	28 Feb 1995	514	1	
Site average			5	
Estuary total				17177

limit on oceanic  $\text{N}_2\text{O}$  production rather than an actual value. Further work is required to refine these estimates. Furthermore, the calculation of the significance of the estuarine source strength for  $\text{N}_2\text{O}$  depends heavily on the percentage conversion of nitrate to  $\text{N}_2\text{O}$  during denitrification. While the % conversion of nitrate to  $\text{N}_2\text{O}$  appeared to be <2% in the Colne estuary (and in other reported estuaries), in other high nitrate estuaries we have measured % conversions of up to 30% of nitrate reduced; this would have very dramatic implications on the global significance of the estuarine  $\text{N}_2\text{O}$  source. The estuarine  $\text{N}_2\text{O}$  source is as important as other anthropogenic sources mentioned in current budgets. For example, power plant stacks release only  $0.05 \text{ Tg N yr}^{-1}$  (Khalil & Rasmussen 1992a, b), while adipic acid production accounts for  $0.2$  to  $0.4 \text{ Tg N yr}^{-1}$  (Bouwman et al. 1995). In contrast to control of concentrated industrial sources (Thiemen & Trogler 1991), the estuarine source of  $\text{N}_2\text{O}$  may be difficult to control, as loads to estuaries increase because of the diffuse nature of the inputs. While N loads in Europe and North America may have peaked, fertiliser application in East Asia (37% of the global total) still increases at about  $10\% \text{ yr}^{-1}$  (Mathews 1994).

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