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Spatial and seasonal fluxes of the greenhouse gases N_2O, CO_2 and CH_4 in a UK macrotidal estuary

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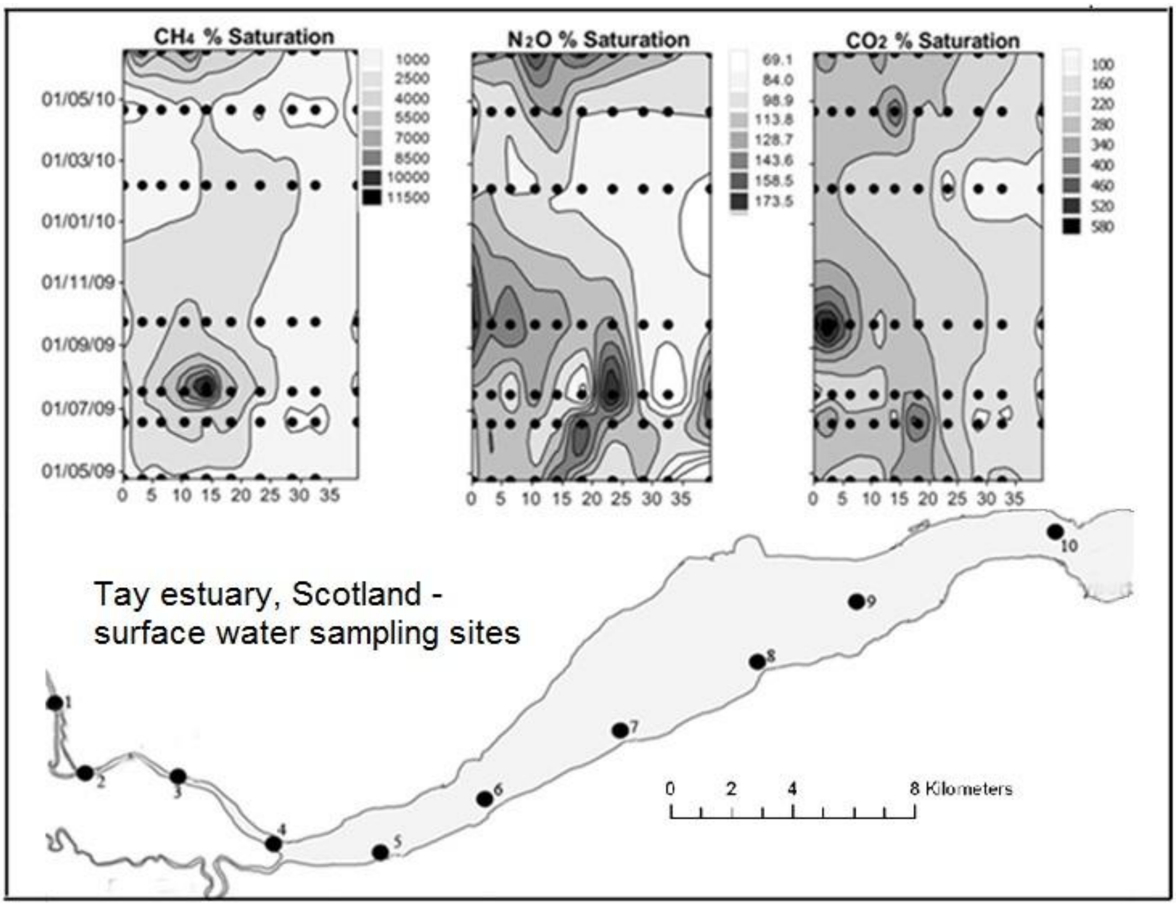
Abstract

The spatial and seasonal dynamics of surface water fluxes of the greenhouse gases (GHG) CO_2, CH_4, and N_2O were quantified in the Tay estuary, Scotland, on seven sampling occasions every 3 months during 2009/2010. This estuary is a relatively pristine river-dominated macrotidal estuary system of a type that is sparsely represented in global GHG flux studies. Significant spatial and temporal variability in GHG fluxes were measured, with similar spatial dynamics to that of other European estuaries. Greatest temporal and spatial variability in gas saturations were found for CH_4, which was higher in the summer, with peaks in saturation occurring in the freshwater upper estuary and sharply decreasing in the mid-estuary mixing zone. Concentrations of CO_2 and N_2O were also generally higher in the upper to middle estuary in summer, although seasonality was less pronounced. Estimated air-sea fluxes also displayed significant spatial and temporal variability. Total annual CO_2 emissions were greatest in the middle estuary zone (13.8 x 10^6 kg C yr^{-1}), and lowest in the upper estuary (1.52 x 10^6 kg C yr^{-1}). Seasonally, the highest CO_2 emissions integrated across the estuary were in spring and autumn, with the lowest in winter. Total annual CH_4 emissions were also highest in the middle estuary (0.05 x 10^6 kg C yr^{-1}) and lowest in the upper estuary (0.01 x 10^6 kg C yr^{-1}), whereas total N_2O emissions, whilst highest in the middle estuary (2344 kg N yr^{-1}), were lowest in the outer estuary (-435 kg N yr^{-1}). Emissions of CH_4 and N_2O were substantially higher in the summer than any other season and lowest emissions were found in winter. The estimated annual exchange of both CO_2 and N_2O is substantially lower than those reported in other European macrotidal estuaries.

Graphical Abstract



Highlights

- CO_2 dominated the total emissions budget of the Tay estuary (~96%), compared to CH_4 and N_2O as CO_2-eq.
- GHG emissions were spatially variable and highest in the middle and lower estuary.
- Emissions were seasonally variable: CO_2 peaked in spring and autumn, and CH_4 and N_2O in summer.
- CO_2, CH_4 and N_2O emissions were lower when estimated from individual results compared to means.

Keywords

Biogeochemistry, carbon dioxide, estuaries, nitrous oxide, methane;

United Kingdom, Scotland, Tay Estuary 56.40 - 56.46° N, -3.44 - -2.86° W

1. Introduction

Estuaries act as the link between land and ocean, receiving large amounts of dissolved and particulate carbon (C) and nitrogen (N) transported by rivers. In recent years, numerous studies have identified estuaries as significant sources of the greenhouse gases (GHG) carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) to the atmosphere driven by enhanced biogeochemical cycling (e.g., Barnes and Upstill-Goddard 2011; Borges and Abril, 2011). There is increasing evidence that the inherent environmental complexities between estuarine systems (macro vs. microtidal, well mixed vs. stratified, high vs. low anthropogenic influence) may lead to substantial variation in air-water fluxes, particularly of CO_2 and N_2O (Barnes and Upstill-Goddard 2011; Borges and Abril, 2011; Crosswell et al. 2012). Although microtidal estuaries may contribute as much as 55% of the total estuarine area worldwide, they are overall much smaller sources of CO_2 (Crosswell et al. 2012) and thus GHG emissions from macrotidal estuaries are used widely in global estimates (Laruelle et al. 2010). However, many previous studies were conducted at sites which have a strong anthropogenic influence and are therefore large emitters of both CO_2 and N_2O. A recent comprehensive study of several UK estuaries (Barnes and Upstill-Goddard, 2011) found large variations in N_2O emission, influenced by the degree of anthropogenic pollution, suggesting that reported N_2O emissions from European estuaries should be reduced. Moreover, a long term analysis of the carbon dynamics of the Elbe estuary (Amann et al. 2012) suggests that CO_2 emission has been reduced in-line with improvements in water quality over the past ~30 years. More data on CO_2, CH_4 and N_2O from relatively pristine estuaries would help reduce uncertainty in regional-to-global estuarine emissions estimates for these gases. Poor seasonal and spatial coverage also adds increased uncertainty within the emission dataset. For example, many of the emission rates listed in recent global estimates (Laruelle et al. 2010) for

CO_2 are comprised of only one or two sampling occasions or with limited spatial coverage (see Frankignoulle et al. 1998).

In this paper, we report the spatial and seasonal dynamics of dissolved CH_4, CO_2 and N_2O saturations in the Tay estuary (NE UK), a large macrotidal estuary with little anthropogenic impact. These are used to calculate air-water fluxes for individual compartments within the estuary and the total estuarine area which are compared with other estuaries in the UK and Europe. The implications for inventories of GHG fluxes at the European and global scale are discussed.

2. Material and Methods

2.1 Study site

The Tay estuary is situated between Perth and Dundee on the east coast of Scotland and drains into the North Sea (Fig. 1). The estuary has an area of 122 km^2 (OSPAR, 2006) with a tidal range of 3.5 m at Dundee and 2.5 m at Perth and Bridge of Earn (Nassehi and Williams, 1987), creating an intertidal area of 75 km^2 which is mainly on the northern shore of the lower estuary. Overall the estuary is shallow and classified as macrotidal (mean tidal range >2 m), with partial to well-mixed waters (OSPAR, 2006). The estuary receives a significant input of freshwater from the Rivers Earn and Tay, with the latter being the UK's largest river in terms of discharge with an annual mean flow of 167 m^3 s^{-1} at the tidal limit upstream of Perth (Williams and West, 1975), and with an estuarine water residence time between 2 and 14 days (Balls, 1992). For the purposes of this paper, the Tay estuary is defined as extending from the city of Perth in the west to the mouth which is bounded by Tayport to the south and Broughty Ferry to the north. It includes a section of predominantly freshwater intertidal river, downstream from Perth to Newburgh (between points 1 and 5 in Fig.1).

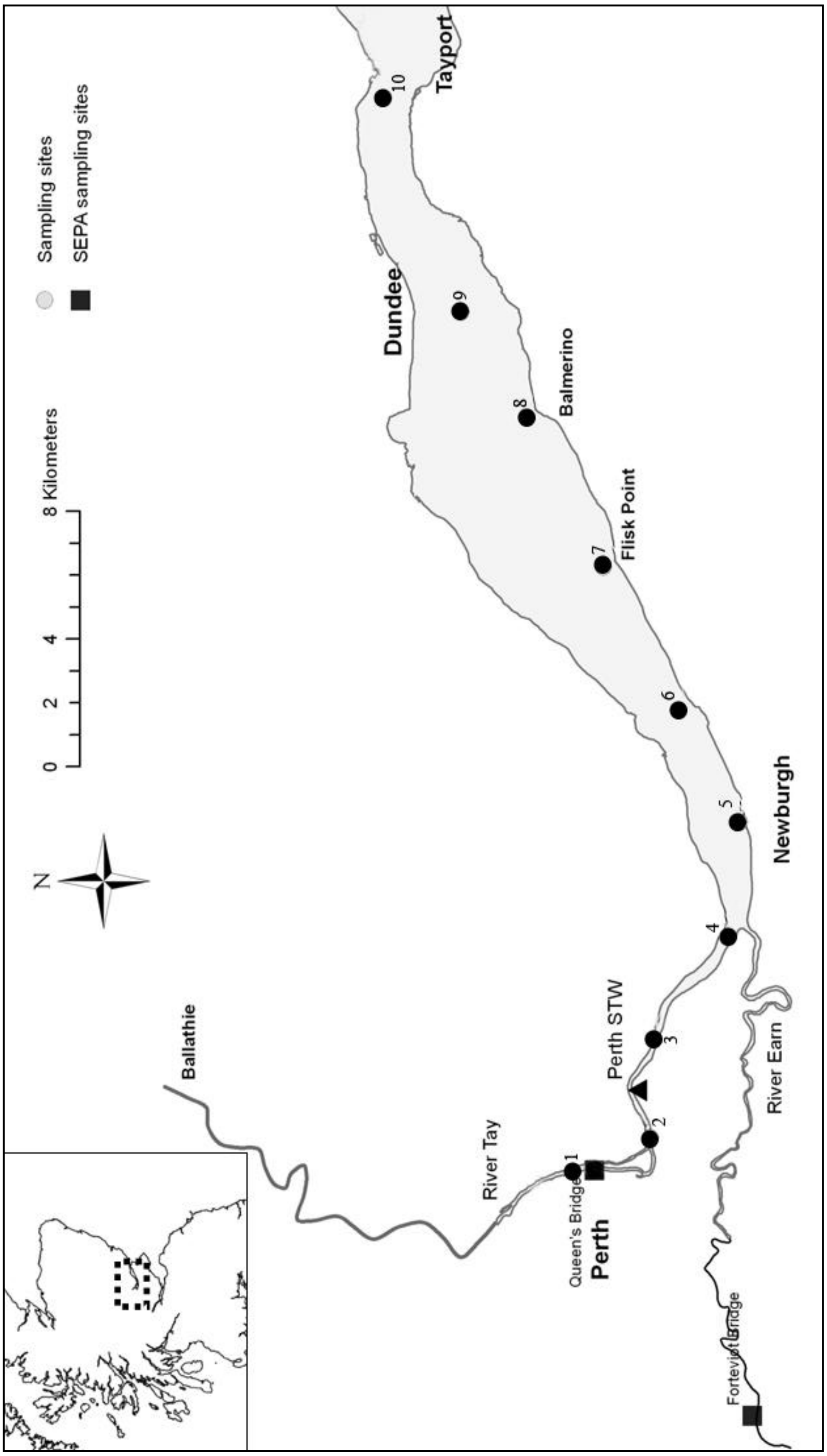


Figure 1: Map of estuary showing main sampling locations, and main features of estuary.

2.2 Water sampling and analysis

Estuary water was sampled for chemical analysis and determination of GHG concentrations from a rigid inflatable boat on a transect of 10 sites on seven occasions from April 2009 to June 2010. To minimise the effects of temporal variation associated with the tidal cycle at each location, sampling always started upstream in the morning at high tide and continued travelling downstream on the outgoing tide with all sampling complete within about 4 h (i.e. mid-tidal cycle at Tayport). On one other occasion (August 2010) sampling was conducted over an 8-h period, with samples take every 2 h, at one site (site 5) to assess the temporal variation over a half tidal cycle from high tide to low tide. Dissolved oxygen (DO), temperature (±0.15°C), pH (±0.2) and conductivity (a proxy for salinity) (±1%, temperature corrected to 25°C) were measured *in situ* at 10 cm below the water surface using a Hydrolab Quanta Probe (Hach) at each sample location, and replicate surface water samples were collected using three separate 10-l plastic buckets. From each bucket, a well-mixed, known volume of water (200-800 ml) was filtered through a pre-combusted (500°C for 10 h) and pre-weighed Whatman GF/F 0.7 µm filter paper using a Nalgene filtration unit and an electric vacuum pump, to obtain sub-samples for analysis of NO_3^- and NH_4^+. The filtered sub-samples were transferred to sample tubes (Sterilin 50 ml; high clarity polypropylene) and sealed and placed in an ice box for transportation to the laboratory freezer where they were stored until analysis. Samples were analysed colorimetrically using a SEAL AQ2 discrete analyzer by the sulphanilamide/NEDD (N-1-naphthylethyene diamine dihydrochloride) reaction for NO_3^- (detection limit 0.0025 mg N l^{-1}) and idophenol blue chemistry for NH_4^+ (detection limit 0.02 mg N l^{-1}). Immediately after filtration in the field all filter papers were placed in foil packets and stored in liquid nitrogen, then transferred to a freezer (-18ºC) on return to the laboratory for determination of total suspended solids (TSS) by oven-drying at 105°C for 4 h and re-weighing.

2.3 Measurement of dissolved CO_2, CH_4 and N_2O

Gas concentrations were determined using the headspace technique (for more details see: Billett and Moore 2008) in surface waters sampled in triplicate at 10 cm depth from each site. N_2O and CH_4 were analysed on a HP5890 Series II gas chromatograph (Hewlett Packard (Agilent Technologies) UK Ltd. Stockport, UK) with an electron capture detector (ECD) and flame ionisation detector (FID) with accuracy of 0.58 mg m^{-3} for N_2O and 0.49 mg m^{-3} for CH_4, respectively. CO_2 was measured simultaneously on another HP5890 Series II gas chromatograph with an accuracy of 20 mg m^{-3}. Concentrations were calculated from the peak areas of a set of four standard gas mixtures in N_2 ($N_2O/CH_4/CO_2$: 0.2/1.3/200; 0.3/1.8/350; 0.5, 5.1/675; 1.0/100/5000 mg m^{-3}). At least 3 sets of standards were included in each set of analysis. When many samples were analysed standards were included every 15-20 samples. The concentrations of dissolved (and expected saturation equilibrium in relation to atmospheric concentration) CO_2, CH_4 and N_2O were calculated from the concentrations measured from the headspace using the functions for the temperature and salinity dependent Bunsen solubility given by Wiesenburg and Guinasso (1979) for CH_4, and Weiss and Price (1980) for CO_2 and N_2O. Saturation values for the gases were calculated as the ratio of the concentration of the dissolved gas and the expected atmospheric equilibrium water concentration.

2.4 Estimating CH_4, CO_2 and N_2O air-water fluxes from the estuary

Gas fluxes (F) across the air-water interface were calculated using:

$$F = k_i (Gas_d - Gas_{eq}) \tag{1}$$

where k_i (m h^{-1}) is the gas transfer velocity, Gas_d (µmol m^{-3}) is the dissolved gas concentration and Gas_{eq} (µmol m^{-3}) is the dissolved concentration at equilibrium with the relevant atmospheric concentration. In estuaries, determination of k can be complex because turbulence is created through the combination of wind induced turbulence, tidal velocity, bottom friction and dynamic bed topography and, in macrotidal estuaries, tidal currents are also a significant influence (Zappa et al. 2007). Since k was not specifically measured in this study, gas fluxes were estimated using four parameterizations of k reported in the literature for relevant estuarine environments, derived using a range of methodologies (Eq. 2-5). Parameterizations used were chosen either because of their widespread usage in the literature (Clark et al. 1995; Raymond and Cole 2001 parameterizations) and/or their use in estuaries similar to the Tay, i.e. large, well-mixed, macrotidal and dominated by their tributary river.

C95: Clark et al. (1995) function: $k_{600} = 2.0 + 0.24(u_{10})$ (2)

RC01: Raymond and Cole (2001) function: $k_{600} = 1.91 \times \exp^{0.35 u_{10}}$ (3)

B04 Scheldt: Borges et al. (2004) function: $k_{600} = 4.045 + 2.580 \times u_{10}$ (4)

B04 Thames: Borges et al. (2004) function: $k_{600} = 9.6 + 3.64 \times u_{10}$ (5)

where k_{600} is the gas transfer velocity of CO_2 normalised to 20°C (cm h^{-1}) and u_{10} is the monthly mean wind speed in m s^{-1}, calculated from the mean daily wind speed measured at the nearest meteorological station at 10 m height (Leuchars, ~8 km south of the estuary, data accessed from the British Atmospheric Data Centre) of the 30-d period centred around the sampling date. Gas transfer velocity is influenced by temperature and salinity with the degree of influence differing between gases. Following the method set out by Ferrón et al. (2007), k_{600} values from each of the parameterizations were used to calculate k_i for each gas at the recorded temperature and salinity in the field using Eq. 6:

$k_i \div k_{600} = (Sc_i \div Sc_{600})^n$ or rearranged to $k_i = k_{600}(Sc_i \div 600)^{-0.5}$ (6)

The Schmidt number, Sc_i , is the ratio of the kinematic viscosity of water over the diffusivity of the gas and is calculated following Wanninkhof (1992) for salinity values of 0 and 35, assuming Sc_i varies linearly with salinity and k_i has a dependency proportional to $Sc^{-0.5}$ (Ferrón et al. 2007).

Using these calculated *k* values the gas flux density was calculated (Eq. 1) and upscaled to total estuarine area and different sections of the estuary using two methods. In Method A the mean flux density (n=69) was multiplied by the total estuary area. In Method B the estuary was divided into 10 compartments, with compartment boundaries equidistant between the sites. Each compartment area was multiplied by the median flux density (n=7), which was upscaled to give a total yearly emission value for each compartment, which were then summed to calculate the mean yearly emission for the whole estuary or sections of the estuary. The estuary was divided into the upper estuary (sites 1-4), the middle estuary (sites 5-7), and the lower estuary (sites 8-10). Fluxes were also expressed as CO_2 equivalents (CO_{2eq}) by multiplying emissions by their global warming potentials (GWP): 1 for CO_2, 23 for CH_4 and 298 for N_2O (100 yr time horizon) (IPCC, 2007).

2.5 Data analysis

Pearson's correlation coefficients were calculated to examine associations between the measured gas saturations and other determinants. A seasonality index was produced by splitting the data into two groups: winter/spring (February 2010, April 2009 & April 2010) and summer/autumn (July 2009, June 2009 & June 2010, September 2009). The summer/autumn means were divided by the winter/spring means to derive a seasonality index for the estuary and each sampling site, with a value close to 1 indicating little seasonal difference and values above 1 indicating higher gas saturations in summer/autumn than winter. Significant differences between winter/spring saturations and summer/autumn saturations at each site were tested with two sample t-tests.

Conservative mixing plots were also produced to further analyze spatial changes in CH_4-sat in the estuary using conductivity as a proxy for salinity.

All statistical analyses were conducted in Minitab v.16 with a significance level of $p<0.05$.

3. Results and Discussion

3.1 Spatial, seasonal and daily patterns in CO_2 saturation and controlling factors

The distribution of CO_2-sat in the Tay estuary displayed pronounced seasonal and spatial variability (Fig. 2) as well as temporal variability over a half tidal cycle (Fig. 3). Over the seven sampling dates the estuary was dominated by supersaturated CO_2 conditions with 66 out of the total 69 measurements supersaturated, ranging from 66 to 644 % saturation. The highest CO_2 saturations were in September 2009 (mean of 321 % of all stations) and the lowest in February 2010 (mean of 184 %) (Fig. 2), with saturations across the estuary always higher in the summer/autumn than winter/spring (Fig. 4). On all transects CO_2 saturation was higher in river water entering the estuary than at the estuary mouth, with maximum concentrations generally occurring in the middle estuary (Fig. 2). CO_2-sat, across all sampling transects, is higher in the upper freshwater estuary decreasing downstream with increasing salinity. Like many other estuaries, the Tay receives freshwater that is generally supersaturated in CO_2 due to organic carbon mineralization in soils, river waters and sediments (Neal et al. 1998; Cole and Caraco, 2001). The ventilation of riverine CO_2 has been found to be a significant source of CO_2 emission in other estuaries, particularly estuaries with short freshwater residence times (Abril et al. 2000), such as the Tay in which the residence time (2 -14 days) is relatively short compared to some other macrotidal estuaries in the UK (e.g. the Humber, 30-60 days; Barnes and Upstill-Goddard, 2011).

CO_2-sat was significantly correlated with physicochemical water parameters (Table 1) suggesting that there are other important controlling factors within the estuary. However, the correlations varied between sampling months (Table 1). For example, although there was no significant correlation between CO_2-sat and % dissolved oxygen (DO) for the whole dataset, a strong seasonal pattern was apparent. In transects conducted during colder conditions (April

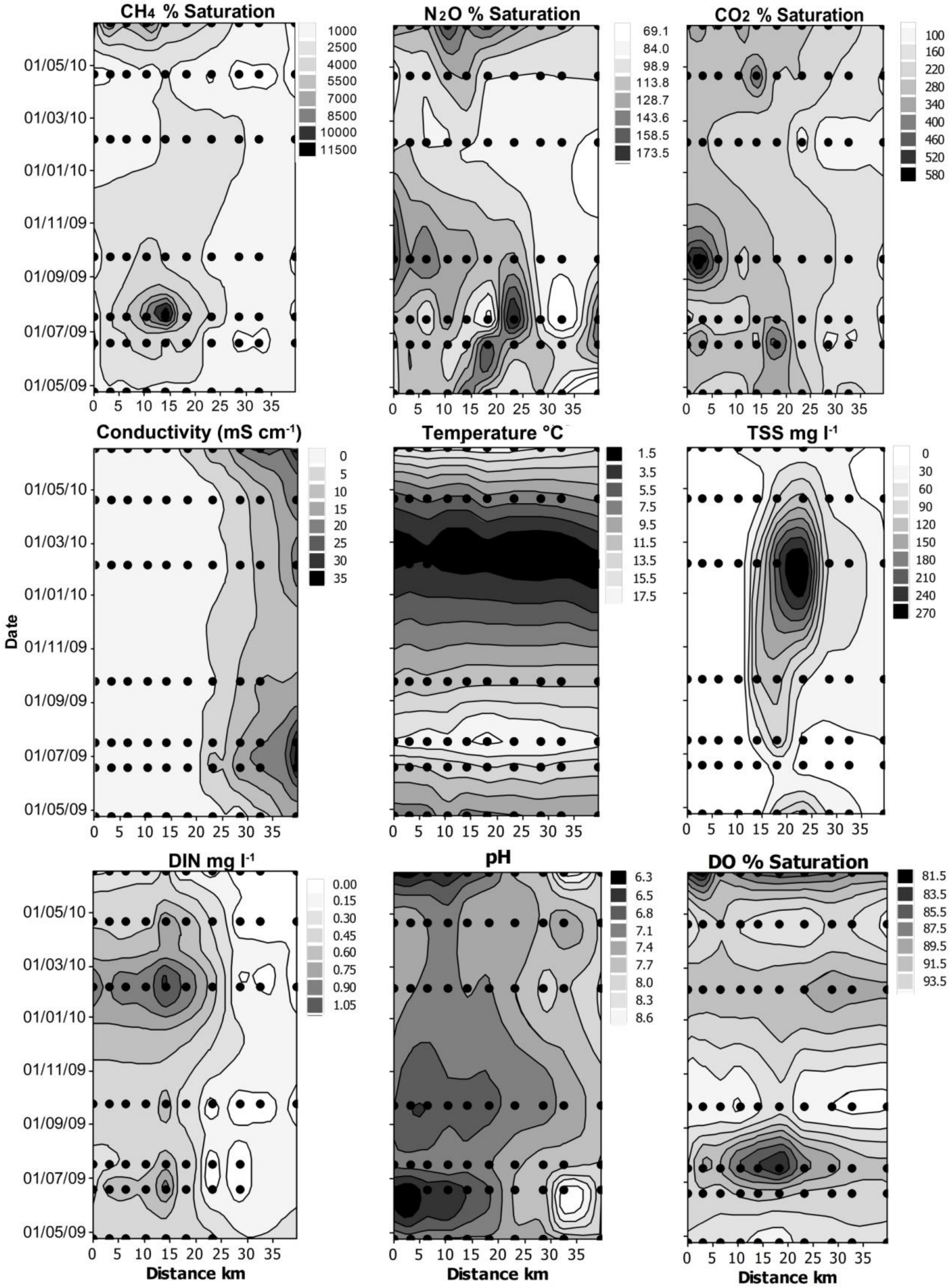


Figure 2. Surface contour plots showing CH_4, CO_2 and N_2O saturation and physicochemical water parameters measured at the 10 sites along the transects between April 2009 and June 2010. The x-axis represents the distance from tidal limit along the estuary and the y axis represents the sampling date which is highlighted by the black circles.

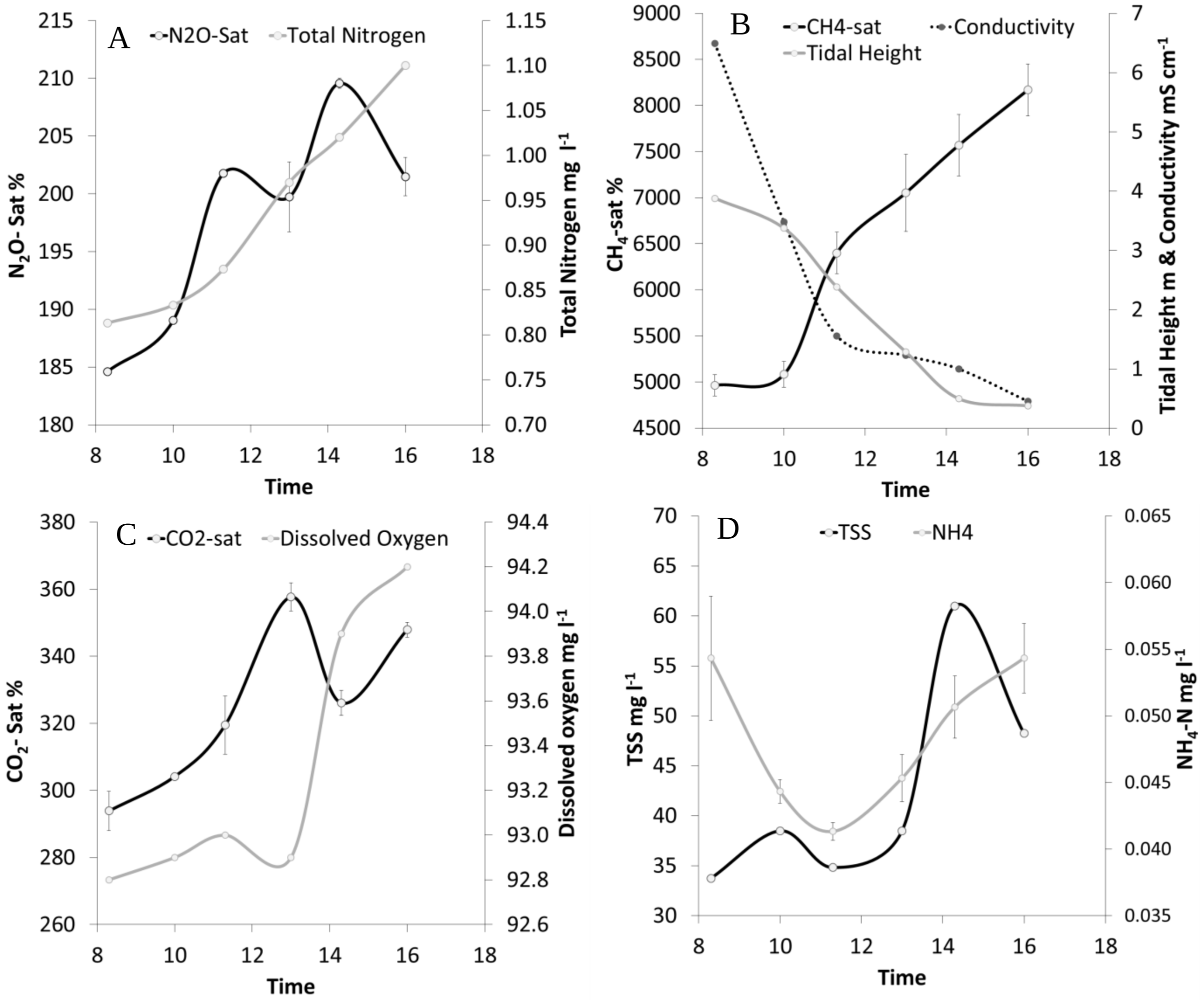


Figure 3. Mean gas saturations and water chemistry across a half tidal cycle at site 5, Newburgh (18.08.2010). Error bars equal the standard error of the mean (n=18).

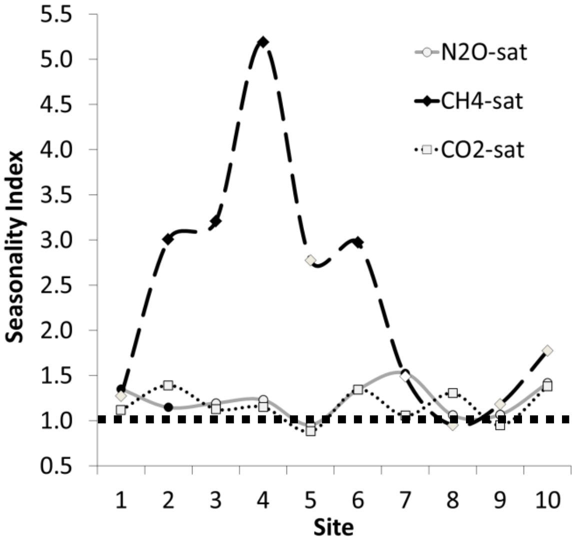


Figure 4. Seasonality Index (mean summer gas saturation divided by mean winter/spring saturations) along the estuary. Values above a seasonality index of 1 indicate higher summer saturations. Data points shaded black indicate significant differences between the seasonal index for each gas at each site ($p<0.05$, t-test).

2009 and February 2010), significant positive correlations were observed. Conversely, in the summer sampling surveys (June 2009, July 2009, June 2010) CO_2-sat and %DO were significantly negatively correlated. On these sampling occasions maximum CO_2-sat and TSS concentration were measured in the middle estuary, along with minimum DO. For example, the peak CO_2-sat in July 2009 (337%) corresponded to a DO-sat minimum of 84% and a peak TSS concentration of 106 mg l^{-1}. The summer time correlations between CO_2-sat, DO and TSS appeared to be mostly influenced by the location of the turbidity maximum zone (TMZ) within the estuary. The TMZ is typically an area of intense heterotrophy due to the decomposition of the labile POC from freshwater phytoplankton inputs which quickly die off in the brackish estuarine waters (Kerner, 2000). The bacterial respiration associated with this decomposition results in a DO minimum, known as the oxygen minimum zone (OMZ), and the production of CO_2 (Amann et al. 2012). It is also an area where autotrophy is severely light-limited, with the maxima of TSS causing steep light extinction inhibiting algal photosynthesis and promoting respiration by heterotrophic bacteria attached to the suspended particles (Crump et al. 1998; Goosen et al. 1999).

Outside the TMZ, pelagic phytoplankton blooms are a common occurrence in both the fresh and saltwater zones of estuaries corresponding to maximum light availability in the summer months (Borges and Abril, 2011). Gross Primary Production (GPP) in the summer months can therefore create a sink of CO_2 and a source of O_2 which could mask CO_2 sources such as respiration. However, there was little evidence of pelagic phytoplankton blooms in the Tay estuary during the study, with concurrent measurements of chlorophyll a (Dudley et al. unpublished) always < 30 µg l^{-1} and no significant concentrations in the upper estuary. Peak chlorophyll concentrations consistently coincided with the TMZ and are attributed to either the resuspension of benthic algae or a mechanism by which phytoplankton cells are trapped within the TMZ, allowing chlorophyll to accumulate (Cloern et al. 1983). The presence of a significant benthic algae population could however perform a similar function to that of pelagic phytoplankton blooms and explain the variability observed in CO_2-sat and % DO in the upper estuary. Variability in CO_2-sat, especially in the upper estuary between sites 1-4, could also arise from lateral transport of gas-rich waters from tidal flats and marshes as reported by Cai et al. (1999). Intertidal marshes are generally a net sink of atmospheric CO_2

Table 1. Pearson's correlation coefficients for pooled data (n=69) and by sampling occasion (n=10)

	N_2O-Sat.	**CH_4-Sat.**	**CO_2-Sat.**	**Temp °C**	**NO_3 mg N l^{-1}**	**NH_4 mg N l^{-1}**	**pH**	**DO mg l^{-1}**	**DO sat.**	**Cond. mS cm**	**TSS mg l^{-1}**
All data†											
N_2O-sat	1.00	0.55	0.69^{*}	0.85^{**}	-0.83^{**}	-0.51	-0.91^{***}	-0.80^{**}	-0.25	0.59	-0.69
CH_4-sat	0.55	1.00	-0.17	0.78^{**}	-0.45	-0.23	-0.29	-0.88^{***}	-0.77^{*}	0.67^{*}	-0.34
CO_2-sat	0.69^{*}	-0.17	1.00	0.38	-0.71^{*}	-0.61	-0.76^{**}	-0.23	0.39	0.08	-0.60
Jun-10											
N_2O-sat	1.00	0.74^{**}	0.80^{***}	0.71^{**}	-0.10	-0.34	-0.60^{*}	-0.78^{***}	-0.20	-0.71^{**}	0.18
CH_4-sat	0.74^{**}	1.00	0.78^{***}	0.63^{**}	-0.10	0.07	-0.63^{*}	-0.77^{***}	-0.22	-0.69^{**}	0.00
CO_2-sat	0.80^{***}	0.78^{***}	1.00	0.65^{**}	-0.41	-0.24	-0.72^{**}	-0.98^{***}	-0.65^{**}	-0.79^{***}	-0.17
Apr-10											
N_2O-sat	1.00	0.83^{***}	0.74^{**}	-0.41	0.40	0.54^{*}	-0.32	-0.02	-0.23	-0.28	-0.32
CH_4-sat	0.83^{***}	1.00	0.91^{***}	-0.53^{*}	0.69^{*}	0.55^{*}	-0.38	-0.10	-0.26	-0.58^{*}	-0.20
CO_2-sat	0.74^{**}	0.91^{***}	1.00	-0.80^{***}	0.43	0.35	-0.59^{*}	-0.19	-0.41	-0.79^{***}	-0.27
Feb-10											
N_2O-sat	1.00	-0.18	0.87^{***}	0.61^{*}	0.09	-0.52	-0.68^{**}	-0.42	0.61^{*}	-0.71^{**}	-0.43
CH_4-sat	-0.18	1.00	-0.31	-0.55^{*}	-0.09	0.44	-0.10	0.63^{**}	-0.20	-0.41	0.77^{***}
CO_2-sat	0.87^{***}	-0.31	1.00	0.83^{***}	0.33	-0.34	-0.75^{**}	-0.61^{*}	0.78^{***}	-0.63^{**}	-0.34
Sep-09											
N_2O-sat	1.00	0.49	0.76^{**}	-0.82^{***}	0.26	-0.76^{***}	-0.71^{**}	0.75^{**}	-0.29	-0.85^{***}	-0.36
CH_4-sat	0.49	1.00	0.32	-0.31	0.21	-0.69^{**}	-0.73^{**}	0.61^{*}	-0.28	-0.70^{**}	-0.01
CO_2-sat	0.76^{**}	0.32	1.00	-0.70^{**}	0.20	-0.65^{**}	-0.76^{***}	0.79^{***}	-0.16	-0.60^{*}	-0.43
Jul-09											
N_2O-sat	1.00	-0.02	-0.25	-0.20	-0.40	-0.06	0.06	0.13	0.13	0.09	-0.30
CH_4-sat	-0.02	1.00	0.66^{**}	0.32	0.86^{**}	-0.22	-0.54^{*}	-0.75^{**}	-0.80^{***}	-0.61^{*}	0.28
CO_2-sat	-0.25	0.66^{**}	1.00	0.64^{**}	0.75^{*}	-0.24	-0.56^{*}	-0.76^{**}	-0.80^{***}	-0.64^{**}	0.63^{**}
Jun-09											
N_2O-sat	1.00	0.33	0.51	0.33	-0.24	0.13	0.04	-0.28	-	0.21	0.66^{**}
CH_4-sat	0.33	1.00	0.62^{*}	-0.11	0.67	0.28	-0.65^{**}	-0.62^{**}	-	-0.57^{*}	-0.12
CO_2-sat	0.51	0.62^{*}	1.00	-0.03	-0.53	-0.12	-0.60^{*}	-0.50^{*}	-	-0.65^{**}	0.14
Apr-09											
N_2O-sat	1.00	0.58^{*}	0.20	-0.23	-0.01	0.41	-0.56^{*}	0.60^{*}	0.50	-0.58^{*}	-
CH_4-sat	0.58^{*}	1.00	-0.04	-0.15	-0.20	-0.40	-0.83^{***}	0.24	0.09	-0.60^{*}	-
CO_2-sat	0.20	-0.04	1.00	-0.48	0.64	0.90^{***}	-0.07	0.71^{*}	0.79^{**}	-0.25	-

*$p < 0.1$ ** $p < 0.05$ *** $p < 0.01$ significance † = Means of monthly data used

(Megonigal and Neubauer, 2009) due to high GPP, but they can also be a source of large amounts of CO_2 emitted when organic matter buried in the sediment is submerged. They are also thought to be a net source of carbon (both dissolved and particulate) to estuaries and that this could match riverine input (Cai et al., 2011; Regnier et al., 2013), however this is uncertain due to a scarcity of data for CO_2 emissions and carbon export from intertidal estuarine wetlands (Bauer et al., 2013). Verification of the influence of intertidal marshes on CO_2 fluxes in the upper Tay estuary is not possible since production and emission rates were not measured in intertidal areas

3.2 Spatial, seasonal and daily patterns in CH_4 saturation and controlling factors

The mean (2600%) and range (100–13100%) of CH_4- sat measured in the Tay estuary are within the range of values reported from other estuaries in the UK (Table 3). As in other studies there was considerable variability, up to three orders of magnitude, in dissolved CH_4 saturations within the Tay. CH_4-sat peaks occurred in the upper estuary, particularly in summer (Fig. 2) at site 4 which had the highest seasonality index score (Fig. 4). These data suggest that there are significant sources of CH_4 within this zone which are most active in summer. Similar CH_4 distributions have been reported in other European estuaries in which the dominance of CH_4 production over oxidation and degassing was associated with low salinity regions (Middelburg et al. 2002). The seasonal dynamics in CH_4-sat in the upper estuary can be explained by changes in temperature and DO affecting microbial methanogenesis activity in the bed sediments since CH_4-sat was significantly positively correlated with temperature (0.78, $p<0.05$) and negatively correlated with DO (-0.88, $p<0.01$ (Table 1). Water residence time could also be important. Seasonally lower flows in summer leading to an extension of the water residence time in the upper estuary could result in higher organic matter sedimentation rates, fuelled by seasonal increases in GPP that could enhance microbial production of CH_4 in bed sediments.

The temporal data across half a tidal cycle from site 5 (Fig. 3b) highlights CH_4 concentrations nearly doubling over the 8 h sampling period alongside a drop in tidal height and conductivity. It is unclear whether this points to lateral pumping of inter tidal areas (Bouillon et al. 2008; Grunwald et al. 2009) or is related to the mixing of river water from upstream as the tide ebbs. However, similar findings have been found in a number of other studies, clearly showing temporal peaks in CH_4 concentrations at low tide, even in systems with no freshwater inputs (Bouillon et al. 2008; Grunwald et al. 2009), which suggests it is more likely to be due to a physical process rather than due to salinity changes.

A sharp decrease in CH_4-sat was observed on most transects between sites 4 and 8 in the mid-estuary mixing zone which is characterised by increases in TSS and conductivity as freshwater meets seawater (Fig. 2). A number of factors may control the decrease CH_4-sat from the upper to the lower estuary. As for CO_2, one of the main sinks of CH_4 within estuaries is evasion to the atmosphere, which is likely to be most pronounced in the mid-estuary mixing zone. Microbial aerobic oxidation of CH_4 to CO_2 by methanotrophs in aerobic conditions, using CH_4 as a carbon source (Hanson and Hanson, 1996), has also been shown to be an important sink in a number of estuaries (e.g., Sansone et al. 1999; Abril et al. 2007). Salinity is an important control on CH_4 oxidation rates, with additions of salt inhibiting oxidation in freshwaters (De Angelis and Scranton 1993). The decrease in CH_4 was analysed further in relation to conductivity (representing salinity changes) and the gas transfer rate (scaled to area of the compartment around each sample site) in conservative mixing plots (Fig. 5). In July 09, April 2010 and June 2010 CH_4 dissolved concentration was considerably below the conservative mixing line in the lower estuary indicating substantial sinks in CH_4 that cannot be accounted for by a simple dilution mechanism. These may be largely attributed to gas evasion as the region of CH_4 loss corresponds closely to the TMZ (Fig. 2) where the estuarine compartment area increases substantially. The exception to this in our study was a significant positive relationship with TSS, observed in Feb 2010. At this time, mixing appeared to be conservative and there was no apparent major change in gas transfer rate.

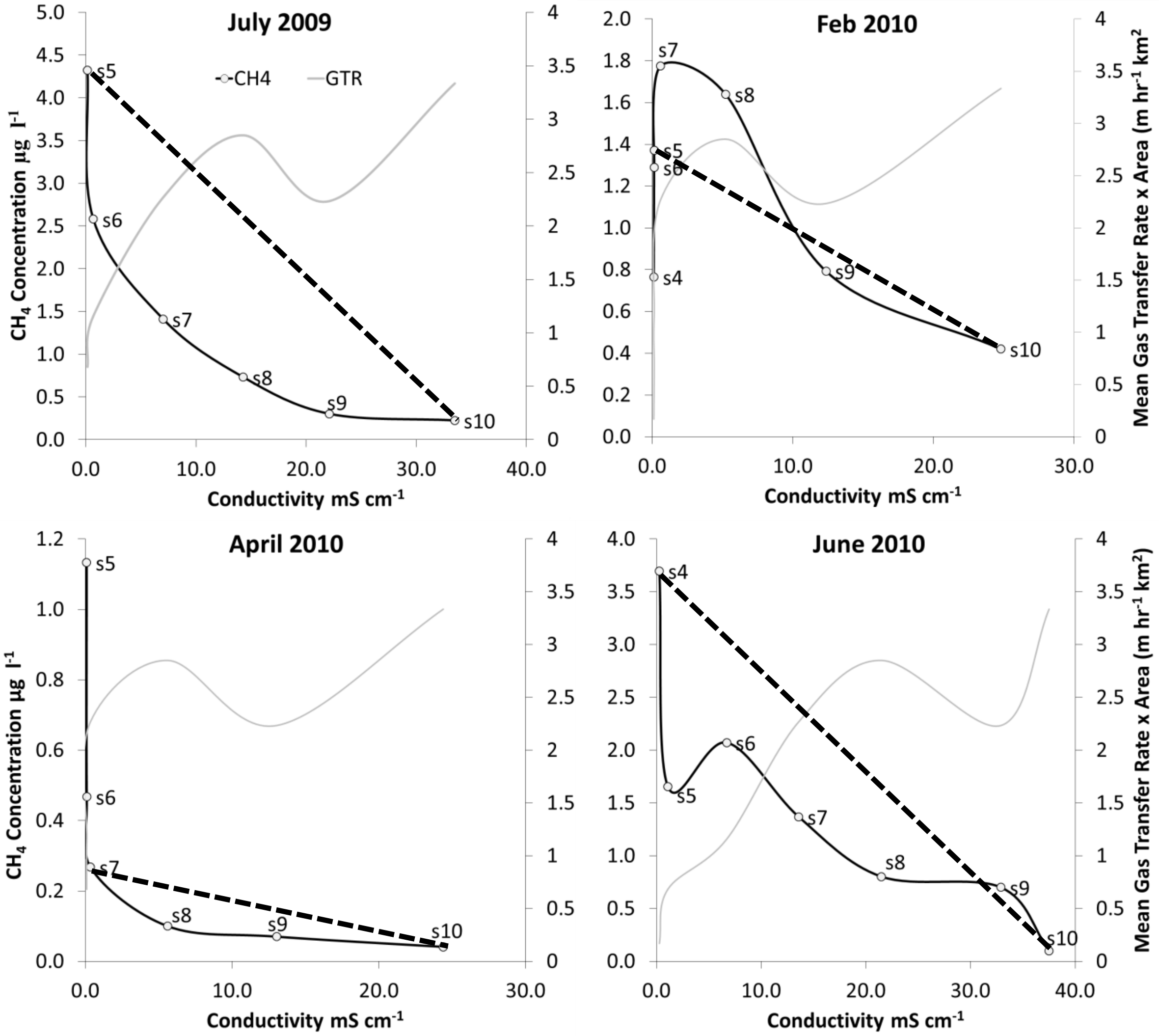


Figure 5. Conservative mixing diagrams for CH_4-sat plotted against conductivity (representing salinity) alongside the mean (of the four parameterizations) gas transfer rate (GTR) as a function of estuary compartment surface area for selected sampling occasions. The dotted straight line indicates the path that CH_4-sat should follow under conservative mixing. s1 to s10 represent the 10 sampling sites.

3.3 Spatial, temporal and seasonal patterns in N_2O saturation and controlling factors

Possible explanations are that CH_4 oxidation in the TMZ is strongly temperature dependent and thus was insignificant at the low water temperatures in the February transect. So sources of CH_4, such as release during active particle resuspension in the TMZ, may become more apparent. This process was suggested by Upstill-Goddard et al. (2000) as the reason for the positive relationship between TSS and CH_4-sat that they observed in the Tyne estuary TMZ. Dissolved N_2O concentrations ranged from 0.18 to 0.56 N_2O-N μg l^{-1} corresponding to saturations of 69% to 188% (Table 1, Fig. 2). Saturations of N_2O in the Tay estuary were similar to measurements made from the Tay estuary in April 2001 by Barnes and Upstill-Goddard (2011). Our saturations along the 10 transect points ranged from 92-130% (April 2009), 80-161% (April 2010) and had higher maxima than the Barnes and Upstill-Goddard (2011) measurements in April 2001 (99-104 % in 2001). Our data are also similar to those measured in other low nutrient estuaries in the UK such as the Tweed, Tyne, Conwy, and Stour and substantially lower than reported from enriched estuaries such as the Humber, Thames, Colne and Deben (Table 3). Spatial variability of N_2O in the Tay estuary followed a similar pattern to that reported in other studies (e.g. Barnes and Upstill-Goddard, 2011 and Dong et al., 2006) in that the concentrations and saturations usually peaked in the upper estuary suggesting a N_2O source upstream or within this area.

Sources of N_2O within estuaries include external inputs from diffuse or point sources in the catchment and internal inputs from in-situ microbial processing of benthic and suspended sediments. Two main microbial processes dominate N_2O formation in estuaries which include denitrification (i.e reduction of NO_3^- to N_2), and nitrification (i.e. oxidation of NH_4^+, to NO_3^-), indicating that dissolved N concentrations and N_2O-sat should be positively correlated. However, unlike Dong et al. (2004) who reported significant positive correlations between N_2O saturation and NO_3^- and between N_2O and NH_4^+ across a number of UK estuaries, N_2O-sat within the Tay estuary was significantly negatively correlated with NO_3^- and NH_4^+ in the pooled data, with no significant correlations in individual transects. Barnes and Upstill-Goddard (2011) also reported that N_2O was not well correlated with river-borne NO_3^- in six

UK estuaries (including the Tay) and concluded on the basis of this and other evidence that the dominant source of water column N_2O was nitrification. The overall negative correlation in our study may, however, be an artefact due to the differing seasonal patterns of temperature and DIN in the Tay estuary. Whilst maximum N_2O-sat and temperature occur in summer, maximum NO_3^- concentrations were measured in winter. The most likely explanation is that in winter NO_3^- loads from the catchment are highest due to flushing from catchment soils but there is little uptake of NO_3^- by algae and low rates of microbial denitrification due to the low temperatures. In summer the opposite conditions occur and within the estuary there are likely to be temperature induced increases in the rates of both denitrification and nitrification corresponding to the peak in N_2O-sat.

Peaks in N_2O-sat were found to correspond to the TMZ which is thought to be an area of intense microbial activity (as highlighted in this study by the peaks in CO_2 saturation, and DO minimum) and has been found to be an important source of N_2O. For example, Barnes and Upstill-Goddard (2011) found peaks in N_2O saturation in the TMZ which they linked to enhanced nitrification fuelled by the amonification of particulate organic nitrogen, as well as long particle residence times and high bacterial numbers. However, although we found peaks of N_2O-sat in this region, there was no significant correlation between N_2O-sat and TSS for the pooled data and the individual transects (Table 1), apart from Jun-09. However, N_2O-sat and DO concentrations were significantly negatively correlated for the pooled data and for some of the summer transects (Table 1) suggesting that N_2O-sat is linked to microbial processing. Furthermore, a significant positive correlation between CO_2-sat and N_2O-sat was observed in the pooled data and in 4 of the 7 transects (Table 1). This either results from the production of CO_2 from the process of denitrification and/or shared environmental controls, for example microbial respiration leads to a reduction in dissolved oxygen, which in turn can promote denitrification in the presence of NO_3^-.

On close inspection of N_2O spatial patterns, on several occasions (for example June 2009, July 2009) N_2O saturation was driven below atmospheric equilibrium at varying points within the estuary separated only by peaks of N_2O in the TMZ. However, N_2O saturations below atmospheric equilibrium have not been reported in European macrotidal estuaries, and likely means N_2O is being consumed (i.e. as an electron acceptor during denitrification) at a faster rate than it is being produced at spatially explicit zones within the Tay estuary. Recently, Daniel et al. (2013) reported similar spatially explicit under-saturations of N_2O (as low as 67%) in the relatively unimpacted Tubul-Raqui estuary (Chile) which were attributed to this process. We suggest that there could be other contributing factors such as spatial/temporal lows in DIN concentrations reducing denitrification or nitrification and/or reductions in external N_2O input (groundwaters, soil waters or tidal flushing) which would otherwise mask under-saturations. Estuaries with high nutrient loading are unlikely to exhibit similar under-saturations of N_2O as high levels of NO_3^- or NH_4^+ would drive the in-situ production of N_2O. Spatially explicit peaks in N_2O-sat were also observed in June and July 2009 at site 10, corresponding to peaks in NH_4^+ concentrations, possibly linked to pollution from the nearby city of Dundee driving increased rates of nitrification.

The variability of N_2O-sat found in the Tay estuary indicate that the N_2O sources and sinks (and the associated microbial processes) are both spatially and temporally dynamic.

3.4 Air-water gas fluxes

The gas transfer rates computed by each parameterization varied substantially, with the mean k_{600} values for each parameterization ranging from 5.55 cm h^{-1} to 20.8 cm h^{-1} (Table 2), highlighting the uncertainty in using k-wind speed parameterizations. However, by reporting a mean bracketed value that includes a minimum (C95; the widely used Clark et al. 1995 parameterization) and maximum value (BO4 T; Borges et al. 2004 parameterization for the macrotidal Thames Estuary) this uncertainty is outlined. Emissions from the Tay estuary were compared to those estimated in other studies in which only one parameterization was used (e.g., Barnes & Upstill-Goddard, 2011 who computed emission rates of N_2O from several UK estuaries using the C95 parameterization) (Table 3). Our annual N_2O flux estimate (4 x 10^6 g N_2O yr^{-1}), based on 7 measurement dates between April 2009 and June 2010 and the average of four k_{600} values, is in a similar range to that estimated by Barnes and Upstill-Goddard, 2011 of 3.4 x10^6 g N_2O yr^{-1} from a single survey of the Tay estuary in April 2001.

Total estuary emission was also calculated using two methods (Table 2). The first (Method A) was a simple multiplication of the mean flux density by total estuary area, whilst the second (Method B) was the sum of total emissions calculated for individual compartments within the estuary (with one compartment for each of the 10 sampling sites). The total emissions for Method B were substantially lower than those calculated from Method A for each of the three gases. For example, total estuary emissions of CO_2 using Method A, ranged between 20.2 – 74.1 x10^6 kg C yr^{-1}, whereas Method B resulted in a range between 12.7 – 47 x10^6 kg C yr^{-1}, highlighting the importance of resolving spatial changes in flux rates.

Water-air emissions of CO_2 displayed substantial spatial and seasonal variability. Emission rates were greatest in the middle and lower estuary (Table 2) with a maximum of 13.8 x10^6 kg C yr^{-1} in the middle estuary which is heavily influenced by the TMZ and oxygen minimum zone. Seasonally the highest emission rates were in spring and autumn in the middle estuary, driven by seasonally high monthly wind speeds (and therefore large *k* values) and high CO_2 saturations corresponding with the main changes in the growing season and annual temperature cycle.

Table 2. a) Estimated gas flux densities, annual emission and annual emission as CO_2 equivalents using the four gas transfer rate parameterizations: for the whole estuary using methods A and B (see text for explanation); for sub-compartments upper, middle and lower; b) and for season.

a)	**Mean Gas Transfer Rate (*k*)**		**CO_2**			**CH_4**			**N_2O**		
	C95	BO4 T	Flux Density g C m^{-2} yr^{-1}	Total Annual Emission x10^6 kg C yr^{-1}	Total Emission x10^6 CO_2eq kg yr^{-1}	Flux Density g C m^{-2} yr^1	Total Annual Emission x10^6 kg C yr^{-1}	Annual Emission x10^6 CO_2eq kg yr^{-1}	Flux Density g N m^{-2} yr^{-1}	Total Annual Emission x10^3 kg N yr^{-1}	Annual Emission x10^6 CO_2eq kg yr^{-1}
Whole estuary (Method A)*	-	-	362.2	41.6 (20.2-74.1)	152	1.02	0.12 (0.06-0.21)	3.90	0.059	6.79 (3.34-12.1)	3.18
Whole estuary (Method B)**	6.8	25.8	362.2	26.6 (12.7-47.8)	97.3	1.02	0.07(0.03-0.12)	2.58	0.059	2.16(1.01-3.94)	1.01
Upper **	-	-	455.8	1.52 (0.72-2.74)	5.56	1.25	0.01 (0.003-0.01)	0.18	0.085	0.25 (0.12-0.46)	0.12
Middle**	-	-	439.0	13.8 (6.32-25.4)	50.6	1.34	0.05(0.03-0.09)	1.57	0.074	2.34(1.07-4.32)	1.10
Lower**	-	-	150.6	11.2 (5.63-19.7)	41.0	0.35	0.04(0.02-0.06)	1.08	0.010	-0.44(-0.18-0.84)	-0.20
b)				Total Seasonal Emission x10^6 kg C	Total Seasonal Emission x10^6 CO_2eq kg	Flux Density g C m^{-2} yr^1	Total Seasonal Emission x10^6 kg C	Seasonal Emission x10^6 CO_2eq kg	Flux Density g N m^{-2} yr^1	Total Seasonal Emission x10^3 kg N	Seasonal Emission x10^6 CO_2eq kg
Spring***	6.7	25.9	105.5	8.92 (4.19-16.2)	32.7	0.10	0.01(0.00-0.01)	0.24	0.007	0.22 (0.10-0.40)	0.10
Summer***	6.0	24.6	79.92	6.11 (2.76-11.3)	22.4	0.36	0.03(0.02-0.06)	1.01	0.020	2.11.9(0.95-3.90)	0.99
Autumn***	11.3	32.4	158.5	9.63 (5.39-15.5)	35.3	0.31	0.00(0.00-0.01)	0.09	0.031	0.80 (0.45-1.28)	0.37
Winter***	5.0	22.6	34.74	0.44 (0.18-0.83)	1.60	0.15	0.00(0.00-0.01	0.08	-0.002	-0.85(-0.36-1.63)	-0.40

Spring = April 09 & April 2010; Summer = June 2009 & 2010, July 2009; Autumn = September 2009; Winter = February 2010

* Calculated by Method A, multiplying mean flux density by total estuary area. ** Calculated by Method B, multiplying median site/compartment flux density by site/compartment area, and summing to get total emission. Upper estuary is sites 1- 4; Middle estuary is sites 5 – 7; and Lower estuary sites 8-10. *** Calculated by summing total emission in the individual seasonal cruises and upscaled to represent the season i.e. total seasonal emission = x 10^6 kg C per 91 days.

The lowest emission rates occurred in the winter (mean flux density 34.7 g C m^{-2} yr^{-1}), corresponding to the lowest mean temperatures (2.9°C), lowest average monthly wind speed and lowest mean CO_2 saturations (184% saturation). Heterotrophy in the Tay is likely to be seasonally low during winter when temperatures are lowest and freshwater river input peaks (leading to decreased water residence time), resulting in lower CO_2 production and saturation and therefore lower emissions rates. However, after springtime increases in temperature, heterotrophic production of CO_2 is likely to increase, corresponding to the higher CO_2 saturations observed in spring and peaks in CO_2 emission. Autotrophy gradually becomes more important as the day length increases and conditions become more favourable for GPP during summer. The highest emissions of CH_4 occurred in the middle estuary (flux density 1.34 g C m^{-2} y^{-1}) and seasonally in summer (whole estuary flux density 0.36 g C m^{-2} y^{-1}). The lowest emissions of CH_4 were observed in the upper estuary zone and seasonally in winter (whole estuary flux density 0.16 g C m^{-2} y^{-1}). The fluxes and emission of N_2O also followed the seasonal cycle of temperature. The highest fluxes and emissions occurred in the summer and autumn and the lowest recorded spring, whilst in the winter the estuary acted as a sink for atmospheric N_2O. Estuary emission was also calculated in CO_2 equivalents using the 100 year global warming potentials (IPCC 2007). In the Tay estuary, CO_2 dominated the total emissions budget (~96.4%), compared to CH_4 (~2.6%) and N_2O (~1%) as CO_2-eq.

The values described here for GHG emissions are within the range reported in other studies (Table 3), although there are few published data from individual estuaries similar to the Tay to compare with the measured CH_4 emissions. A recent review of CH_4 emissions in unmanaged aquatic systems contained no emission rates from macrotidal estuaries and of the estuaries that were included, only a few were classed as temperate (Ortiz-Llorente and Alvarez-Cobelas 2012).

Table 3. Concentrations, range and mean of saturations and annual CH_4, CO_2 & N_2O emissions in temperate estuaries, including the Tay.

Estuary Site[1]	Area (km^2)	DIN (µM) Mean (max)	Concentrations (nmol l^{-1}) Range (mean)	Gas saturation (%) Range (mean)	Flux Density (g m^{-2} yr^{-1})	Annual Emission (g yr^{-1})	References
			N_2O		N_2O-N	N_2O-N	
Tweed	-	-	-	96-110 (100.4)	0.032	-	Barnes and Owens (1998)
Thames	47.5	-	11.2-93	93-681 (321)	0.706	-	De Bie et al. (2002)
Colne	4.81	~ 330	(197.3)	(992.9)	3.449	-	Dong et al. (2004)
Stour	24.4	~ 101	(24.9)	(119.9)	0.210	-	Dong et al. (2004)
Deben	9.27	~ 156	(32.6)	(186.9)	0.382	-	Dong et al. (2004)
Conwy	4.97	~ 31.3	(18.6)	(113.6)	0.089	-	Dong et al. (2004)
Humber	303.5	(~700)	-	157-6506 (395.7)	0.783	2.5 x 10^8	Barnes and Upstill-Goddard (2011)
Forth	84.0	(~150)	-	98-313 (152.3)	0.159	0.8 x 10^7	Barnes and Upstill-Goddard (2011)
Tamar	39.6	(~600)	-	99-210 (145)	0.083	3.7 x 10^6	Barnes and Upstill-Goddard (2011)
Tyne	7.9	(~250)	-	98-280 (123.5)	0.076	3.7 x 10^5	Barnes and Upstill-Goddard (2011)
Tees	13.5	(~2000)	-	106-2118 (383)	0.706	0.7 x 10^7	Barnes and Upstill-Goddard (2011)
Tay	121.3	(~100)	-	100-118 (107)	0.025	2.5 x 10^6	Barnes and Upstill-Goddard (2011)
Scheldt (NL)	269	-	-	710	0.681	8.9 x 10^7	BIOGEST see Barnes and Upstill-Goddard (2011)
Elbe (DE)	224	-	-	139-374(202	0.343	3.8 x 10^7	BIOGEST see Barnes and Upstill-Goddard (2011)
Ems (DE)	162	-	-	181-1794(418)	0.789	6.4 x 10^7	BIOGEST see Barnes and Upstill-Goddard (2011)
Gironde (FR)	442	-	-	120-463(218)	0.261	5.7 x 10^7	BIOGEST see Barnes and Upstill-Goddard (2011)
Loire (FR)	41	-	-	84-271(168)	0.146	3.1 x 10^6	BIOGEST see Barnes and Upstill-Goddard (2011)
Tay	**121.3**	**(~100)**	**-**	**69-188 (118.6)**	**0.059**	**2.2 x 10^6**	**This study (method)**
			CH_4		CH_4-C	CH_4-C	
Thames	47.5	-	1.7- 269	150 - 6700	-	-	Middelburg et al. (2002)
Tyne	7.9	-	13.5 -654	4500 - 20000	-	-	Upstill-Goddard et al. (2000)
Humber	303.5	-	13 – 667	370 - 21000	-	-	Upstill-Goddard et al. (2000)
Tay	**121.3**	**(~100)**	**4.5 - 361**	**100 - 13134**	**1.02**	**6. 9 x 10^7**	**This study (method b)**
			pCO_2 (µatm)		CO_2-C	CO_2-C	
Douro (PT)	2	-	1330-2200	-	1052	6.0 x 10^6	Frankignoulle et al. (1998)
Elbe (DE)	224	-	580-1100	-	789	2.1x 10^{11}	Frankignoulle et al. (1998)
Ems (DE)	162	-	560-3755	-	833	1.1 x 10^{11}	Frankignoulle et al. (1998)
Gironde (FR)	442	-	440-2860	-	377	1.6 x 10^{11}	Frankignoulle et al. (1998)
Loire (FR)	41	-	-	-	2830	-	Abril et al. (2003)
Loire (FR)	41	-	~293-2600	-	338	3.8 x 10^{10}	Bozec et al. (2012)
Rhine (NL)	71	-	545-1990	-	453	3.1 x 10^{10}	Frankignoulle et al. (1998)
Scheldt (NL)	269	-	125-9425	-	1745	1.7 x 10^{11}	Frankignoulle et al. (1998)
Tamar	39.6	-	380-2200	-	460	4.9 x 10^9	Frankignoulle et al. (1998)
Thames	47.5	-	465-5200	-	1096	2.3 x 10^{11}	Frankignoulle et al. (1998)
York River (USA)	-	-	-	-	270	-	Raymond et al. (2000)
Parker River (USA)	-	-			50		Raymond and Hopkinson (2003)
Tay	**121.3**	**(~100)**	**214 -2186**	**66 - 644**	**362**	**2.7 x 10^{10}**	**This study (method b)**

[1] country names are only provided for estuaries outside the UK

However, the median emission rate (0.116 mg CH_4 m^{-2} h^{-1}) from the 18 estuarine systems within the review is similar to that of the Tay (0.155 mg CH_4 m^{-2} h^{-1}). A comprehensive study of CH_4 was conducted in nine European estuaries (Middelburg et al. 2002) but the emission rates from individual estuaries were not published. Unlike CH_4, N_2O emission rates from estuaries have been studied in greater detail. It is clear from Table 3 that N_2O emissions are considerably higher in estuaries that are more impacted in terms of nutrient loading. Unsurprisingly, the Tay estuary which contains relatively low concentrations of DIN emits substantially less N_2O than other large estuaries in the UK and Europe with higher nutrient loads. Surprisingly, the Tay estuary at times acts as sink for N_2O, highlighting the potential importance of pristine estuaries to global aquatic fluxes of N_2O.

CO_2 emissions per unit area from the Tay estuary are substantially less than from other large European estuaries(see Laruelle et al., 2013 for a comprehensive compilation of estuarine CO2 fluxes). For example, 0.23 (0.11 – 0.42) kg C m^{-2} yr^{-1} (area weighted total emission) is emitted from the Tay, compared to 1.69 kg C m^{-2} yr^{-1} from the Scheldt, 1.1 kg C m^{-2} yr^{-1} from the Thames, and 0.83 kg C m^{-2} yr^{-1} $_f$ from the Ems (Table 3; Frankignoulle et al. 1998). Many workers have recently called in question whether recent global estimates of estuarine CO_2 emission accurately reflect the diverse range of estuary types and nutrient loads (see Crosswell et al., 2012). Furthermore, these emission estimates (such as from Laruelle et al. 2010) are dominated by flux estimates from a few studies. For example, in one of the first studies of its type, high CO_2 emissions were reported from nine eutrophic macrotidal estuaries in Northwestern Europe (Frankignoulle et al. 1998) which have dominated both European and global emission estimates (Laruelle et al., 2010). However, only two of the nine estuaries from Frankignoulle et al. (1998) were sampled on a seasonal basis, and the remaining estuaries were sampled on only one or two sampling occasions with often limited spatial coverage. In a recent study, Laruelle et al., (2013) provided a comprehensive compilation of CO_2 estuarine fluxes and revaluated the global CO_2 estuarine flux through a segmentation approach and reported a lower estimate of CO_2 emission (13 mol C m^{-2} yr^{-1}) than in previous work (21±18 mol C m^{-2} yr^{-1}) (Laruelle et al., 2010). The regional and global estimates from Laruelle et al., (2013) would benefit substantially from an increase in the availability of data that covers all estuary types over a range of nutrient loads that includes temporal and spatial coverage. The variation in flux density reported in this study highlights the importance of removing spatial and temporal bias in sample coverage. For example, estimates of early autumn and spring emissions of CO_2 were ~20 times higher than estimates for winter, and would have resulted in significant over estimations without the seasonal coverage. Moreover, the short-term temporal study at site 5 highlighted that GHG saturations also vary over tidal cycles, with CH_4-sat increasing by 65%, CO_2-sat by 18% and N_2O-sat by 9% of initial values over 8 h as the tide dropped. Spatial coverage is also important for estimating estuarine fluxes. Flux densities were highest in the upper estuary and total estuarine mean concentrations would be substantially lower without this spatial coverage. The upper freshwater Elbe estuary, despite comprising only a third of the total estuary area may contribute >50% of the estuary CO_2 air-sea flux (Amann et al. 2012). Similarly, in the Tay estuary, the permanently freshwater zone (around sites 1-6) comprises ~17% of the total area, but contributes ~33% of the total emission of CO_2, with half of this originating from the TMZ.

This result highlights important difficulties in up-scaling using mean saturation values to calculate total estuarine emission, especially when the highest flux densities are located in the upper estuary with the smallest total area or when there are large spatially explicit peaks (such as in the TMZ) or minima. The two emission calculation methods used in this study yielded different results, with the estimations from method A (using the estuary mean flux density and total area) being substantially higher than those from the more spatially-resolved method B (the sum of total emissions for each individual compartment (sites 1-10) (Table 2). To illustrate the importance of this point, annual emission of N_2O for the Tay estuary was estimated in another study (Barnes and Upstill-Goddard, 2011; using the C95 parameterization for *k* and mean flux density from one transect in April) to be 4.0 x 10^6 g N_2O yr^{-1}, similar to our own emission estimate using method A of 5.2 x 10^6 g N_2O yr^{-1} (C95 parameterization). However, both of these estimates are substantially higher than the emission estimate derived from method B, 1.6 x 10^6 g N_2O yr^{-1} (C95 parameterization), despite the fact that we report a higher mean flux density (C95: 0.059 g N_2O-N m^{-2} yr^{-1}) due to the increased seasonal coverage in our study. Thus to yield more accurate estimates of GHG fluxes from estuaries, spatial changes in water surface area within estuaries and temporal variability in emissions must be accounted for, rather than relying upon a mean flux density or saturation, especially if higher fluxes occur in upper estuary zones, or there are substantial areas acting as a sink of CO_2.

4. Conclusions

The estimations of seasonal and annual CH_4, CO_2 and N_2O emissions reported here are important for future global GHG budgeting. Estuarine emissions of GHGs are still highly uncertain (Ivens et al. 2011, Laurelle et al. 2013) with recent work suggesting that the contribution of European estuaries to global CO_2 and N_2O emissions may be substantially overestimated (Barnes and Upstill-Goddard, 2011). This over estimation may be in part because of a bias towards nutrient impacted estuaries in global extrapolations of carbon (Laruelle et al. 2013) and nitrogen budgets (Barnes and Upstill-Goddard, 2011) or the continuing uncertainty in what drives GHG production in aquatic environments and how this changes from system to system (Bauer et al. 2013; Regnier et al. 2013). Recent work has suggested that carbon cycling in estuaries changes with changes in water quality (Amann et al. 2012). However, although nutrient priming (leading to enhanced decomposition of autochthonous organic material) along the land-ocean continuum is thought to alter CO_2 fluxes and net heterotrophy, it is yet to be quantified (Regnier et al. 2013)suggesting that it is important to account for temporal and spatial changes in water quality in global extrapolations of GHGs. To date, there has been considerable bias towards studying nutrient impacted estuary systems (see Frankignoulle et al. 1998). However, to improve global and regional extrapolations of GHG emissions, more studies are required to constrain GHG emission rates from all types of estuaries, with all degrees of anthropogenic disturbance and across wide spatial and temporal ranges. An increase in the availability of data from a wide range of estuarine environments would also help constrain and improve current and future modelling efforts that are a complementary tool for understanding temporal dynamics within estuarine systems (Vanderborght et al., 2002) and extrapolating between systems (Regnier et al., 2013). This study of the Tay estuary provides much needed spatial and temporal estimates from a relatively pristine estuary, to redress the reported bias in studies towards nutrient impacted estuaries, and help reduce the uncertainty associated with global and regional GHG budgets.

The estimated annual exchange of both CO_2 and N_2O is substantially lower than reported in other European macrotidal estuaries, providing further evidence that suggests European CO_2 and N_2O emissions are substantially overestimated, leading to incorrect global budget estimates.

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