Marine Pollution Bulletin 174 (2022) 113240

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Review

Anthropogenic-estuarine interactions cause disproportionate greenhouse gas production: A review of the evidence base

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ARTICLE INFO

Keywords:
Greenhouse gas
Nitrous oxide
Methane
Estuary
Salt-wedge
Fully-mixed
Nutrients
Urban wastewater
Ammonium
Nitrate
Nitrite
Phosphate
Tidal range
River flow

ABSTRACT

Biologically productive regions such as estuaries and coastal areas, even though they only cover a small percentage of the world's oceans, contribute significantly to methane and nitrous oxide emissions. This paper synthesises greenhouse gas data measured in UK estuary studies, highlighting that urban wastewater loading is significantly correlated with both methane ($P < 0.001$) and nitrous oxide ($P < 0.005$) concentrations. It demonstrates that specific estuary typologies render them more sensitive to anthropogenic influences on greenhouse gas production, particularly estuaries that experience low oxygen levels due to reduced mixing and stratification or high sediment oxygen demand. Significantly, we find that estuaries with high urban wastewater loading may be hidden sources of greenhouse gases globally. Synthesising available information, a conceptual model for greenhouse gas concentrations in estuaries with different morphologies and mixing regimes is presented. Applications of this model should help identification of estuaries susceptible to anthropogenic impacts and potential hotspots for greenhouse gas emissions.

1. Introduction

The climate is considered unequivocally to have warmed significantly since the 1950s with increasing levels of greenhouse gases (GHGs), with the largest contribution derived from carbon dioxide (CO_2) followed by methane (CH_4) and nitrous oxide (N_2O) (IPCC, 2013). Shelf seas including estuaries and coastal areas, cover approximately 9% of the world's oceans (Harris et al., 2014) and are highly biologically productive, driving between 10 and 30% of marine primary production (Sharples et al., 2019) and contributing about 75% of the oceanic methane emissions (Bange et al., 1994). Shelf seas are a major nitrous oxide source, with European shelf sea (9.4% of total shelf) contributing 26% of global oceanic nitrous oxide (Bange, 2006), largely through denitrification-nitrification cycling from terrestrial runoff. Additionally, the outflows from urban wastewater (UWW) contribute to enhanced nitrous oxide production (McElroy et al., 1978; de Angelis and Gordon, 1985; Seitzinger, 1988; Law et al., 1992).

A review of the literature on estuarine methane emissions from different locations globally (Bange et al., 1994; Bernard, 1978; Oremland et al., 1983; Franklin et al., 1988; Munson et al., 1997; Torres-Alvarado et al., 2013; Bange et al., 1998; Lyu et al., 2018), suggests that estuaries can drive particularly high methane production, despite their varying physical conditions, where they have the following conditions; high levels of organic matter, active sedimentation processes moving both river and estuarine sediments to trap organic matter and low oxygen levels. Similarly, a range of studies (Wrage et al., 2001; Pfenning, 1996; Revsbech et al., 2005; Reay et al., 2003; Pattinson et al., 1998; Beaulieu et al., 2011; Yu et al., 2013; Rosamond et al., 2012) suggests there are several major controls on nitrous oxide production within estuaries in both nitrification and denitrification rates, including ammonium (NH_4^+) and nitrate (NO_3^-) concentrations, dissolved oxygen, organic matter availability and temperature. Greenhouse gas fluxes generated within the estuarine environment are often highly variable, as reflected in the considerable range observed in UK, European and global estimates (Upstill-Goddard and Barnes, 2016; Borges et al., 2016; Bange, 2006). European estimates range in the order of 0.007 to 1.6 Mt. N_2O yr^{-1} and 0.03–0.7 Mt. CH_4 yr^{-1}, with UK estimates accounting for more than 20% of these values. However, there is both a paucity of data for

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https://doi.org/10.1016/j.marpolbul.2021.113240
Received 30 July 2021; Received in revised form 3 December 2021; Accepted 4 December 2021
Available online 14 January 2022

estuaries globally and concerning the drivers of these emissions. There is a clear need for an improved understanding of anthropogenic impacts, largely in the form of urban pollution, as well as the interactive effects associated with tidal, flushing and river regimes, climate, temperature and land-use. In order to increase the confidence in the magnitude of these estuarine GHGs as part of the general IPCC process (IPCC et al., 2006) and the UK government's carbon emission strategy (Institute for Government, 2020), further elucidation of the mechanisms that generate GHG emissions from estuaries is required. Such understanding could inform policies to help reduce emissions in anthropogenically impacted estuaries.

Estuaries have long been considered an effective location for the disposal of urban and industrial waste; resulting in considerable legacy pollution (including metals). Nitrogen and phosphorus compounds are not typically removed from most wastewater discharges to estuaries, although this is dependent on legislation. In the EU and UK removal requirements are related to plant size, the quantity of nutrients and eutrophication risk (EEC, 1991). Where nitrogen compounds are not removed from wastewater, nitrous oxide production may occur when the treated wastewater is discharged to rivers and estuaries. Ammonia is rapidly oxidised, a process that consumes oxygen and other available electron receptors, which may promote methanogenesis and the presence of ammonium may further inhibit methane oxidation (Dunfield and Knowles, 1995; Bosse et al., 1993) (Fig. 1). Additionally, nitrification processes may deplete oxygen, preventing methane oxidation, and where oxygen concentrations are low or highly variable, as typical in the estuary environment, denitrification may be triggered (Marchant et al., 2017), even with oxygen present, thereby increasing nitrous oxide concentrations. Estuaries with high suspended sediment loads may also support nitrogen processing in the water column (Barnes and Upstill-Goddard, 2011). The effects of temperature, salinity, ammonium concentration and pH can further affect the nitrification rate (Isnansetyo et al., 2014) with a salinity optimum between 12 and 20 ppt, suggesting more nitrogen cycling would occur in an estuary than in either the freshwater or coastal environments. The estuary, therefore, is perhaps the least suitable environment of the land-ocean continuum for the discharge of UWW effluent when considering resultant GHG emissions.

2. Objectives

Investigations of GHG emissions from estuaries and coastal waters have typically been conducted with the purpose of improving the estimate of GHG emissions from estuaries on a UK, European or global scale. There has been less emphasis on determining the interplay of processes that result in these high GHG emissions and our understanding therefore remains incomplete. As estuaries vary significantly in their physical characteristics and degree of anthropogenic influence, it can be difficult to determine exact causation mechanisms for this globally important source. Existing data to our knowledge, have not been used to distinguish between natural or anthropogenic emissions, nor have opportunities to prevent or reduce these emissions been identified. This paper synthesises published GHG data from UK estuaries in conjunction with other public domain data to address the following objectives. To determine the: 1) causes of estuarine GHGs, 2) mechanisms that promote high estuarine GHG concentrations and 3) optimum approach for quantifying estuarine GHGs. It employs a series of case studies of UK estuaries examining possible causes of high GHGs and their interaction with different estuary typologies (Fig. 2). This results in a conceptual model of GHG concentrations for different estuary typologies and is followed by an overarching synthesis section. This synthesis section also considers how estuary GHG concentrations and estuary typology impact GHG emissions to the atmosphere and whether estuaries are an overall net carbon sink or source.

3. Methods

A literature search containing the following terms was used to select the papers to be considered in this review: ‘greenhouse gas’ OR ‘nitrous oxide’ OR ‘methane’ AND ‘estuary’. Only data from measurements made in the UK were applied in the analysis section to limit the variability in terms of geographic, climatic, nutrient and tidal regimes. Some estuarine GHG data from other geographic areas are contrasted in the discussion section. Methane and nitrous oxide concentration values from five studies conducted between 2005 and 2021 (Table 1), have been extracted as average values for specific surveys or estuaries (Table 2). These data were compared with other physical parameters from publicly available data associated with each estuary, including: estuary area and catchment, tidal range, river flow, oxygen concentration, land cover and the level of urban wastewater entering these estuaries (Table 3 and supplementary data Tables A1 and A2), together with data on nutrients and legacy pollution typically using linear regression methods. The thirteen estuary systems mainly considered in this analysis (Clyde, Clywd, Colne, Conwy, Dart, Deben, Forth, Orwell, Stour, Tamar, Tay, Tees and Tyne), see Fig. 3 for estuary catchment locations, represent

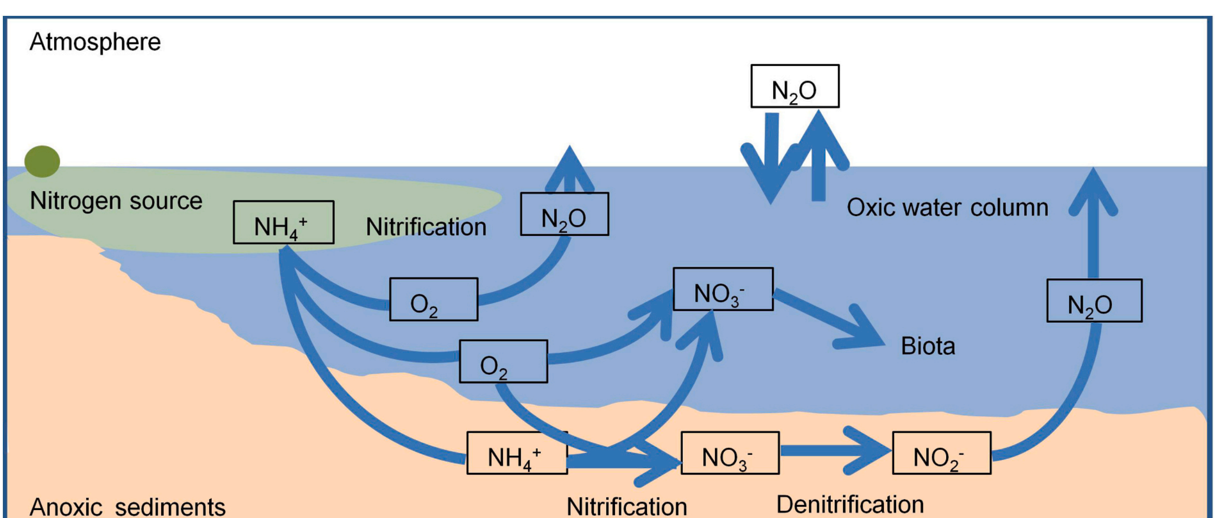

Fig. 1. Simplified nitrification-denitrification pathways in estuaries. Nitrification is shown in the aerobic water-column with oxygen from the water column also used in nitrification in the sediment layer. When insufficient oxygen is present de-nitrification can occur in the anoxic sediment layer. De-nitrification can also occur in the water column linked to sediments, when oxygen levels are low, such as below a pycnocline.

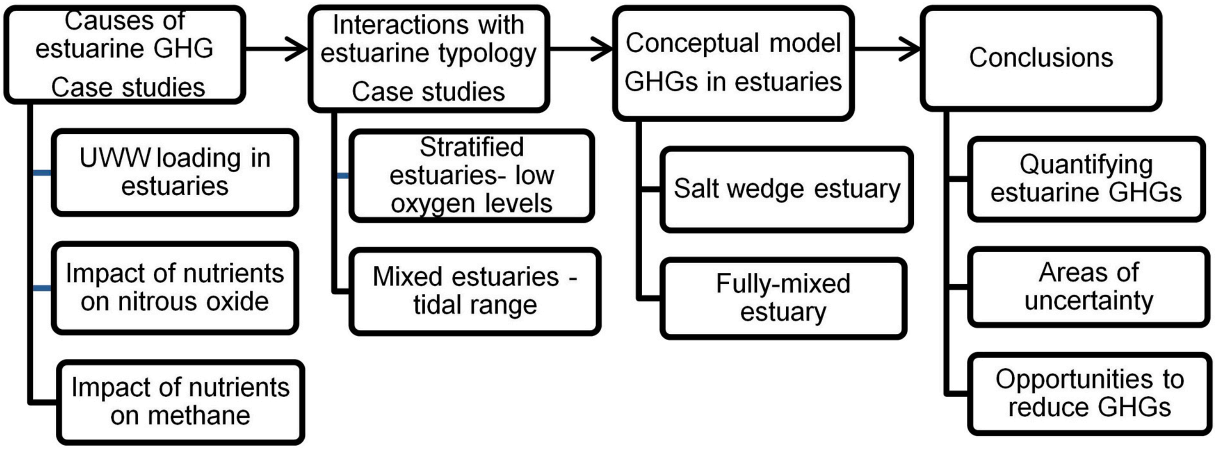

Fig. 2. Outline of approach in this paper.

Table 1
Summary of published data applied in this review.

	Study scope	GHGs sampled	Sample depth	Sampling durations	Sampling approach	Sampling resolution	Study reference
1	Tay, Forth, Clyde, Tamar, Dart, Conwy & Clywd	CO_2, N_2O & CH_4	Surface	Quarterly, usually Jul 2017, Oct 2017, Jan 2018, Apr 2018	Ebb tide starting at high water, sampling downstream	6 sites across a salinity gradient	(Pickard et al., 2022)
2	Tay	CO_2, N_2O & CH_4	Surface	Eight occasions from Apr 2009 - June 2010	Ebb tide starting at high water, sampling downstream	10 sites at fixed locations	(Harley et al., 2015), (Pickard et al., 2021)
3	Humber, Forth, Tamar, Tyne, Tees, and Tay	N_2O	1 m depth	Variable between Feb 2000 - Oct 2002 from 1 and 8 surveys	Flood tide starting after low water, sampling upstream	7–20 sites, due to estuary & local conditions	(Barnes and Upstill-Goddard, 2011)
4	Humber, Forth, Tamar, Tyne, Tees, and Tay	CH_4	1 m depth	Variable between Feb 2000 - Oct 2002 from 1 and 8 surveys	Flood tide starting after low water, sampling upstream	7–20 sites, due to estuary & local conditions	(Upstill-Goddard and Barnes, 2016).
5	Colne, Stour, Orwell, Deben, Humber,Conwy	N_2O	Surface	Quarterly, Aug 01, Nov 01, Feb 02, May 02. Conwy - 2002-3	Ebb tide starting at high water, sampling downstream	10–16 sites dependent on estuary	(Dong et al., 2005)

Notes for studies 1–5:
1. No data were available for the Clywd in January, and the Dart and Tamar in October. Target salinities were typically 0.2, 2, 5, 10, 15, 25 psu. Surveys covered different physical extent due to the salinity criteria applied. No CO_2 data was available for the Tamar and Dart.
2. Survey dates were Apr-09, Jun-09, Jul-09, Sep-09, Feb-10, Apr-10, Jun-10 and Aug-10 (final survey not included in publication.)
3. The number of surveys undertaken for N_2O were Tay: 1, Humber: 3, Tees: 3, Forth: 4, Tamar: 4 and Tyne: 8.
4. The number of surveys undertaken for CH_4 were; Tay: 1, Humber: 2, Tamar: 2 Tees: 3, Forth: 4 and Tyne: 6. (Methane surveys are a subset of those for nitrous oxide (3) with one additional survey for the Tyne).
5. The specific dates of the measurements are not provided. The rivers Mawddach and Dovey were measured but data were not provided for the estuaries, so this has not been included.
6. Abbreviations: - Greenhouse Gas (GHG), Methane (CH4), Nitrous Oxide (N2O), Carbon Dioxide (CO2)

12% of UK estuary systems and 9% and 15% of the UK estuary and catchment areas respectively (Nedwell et al., 2002). While a single survey was available for the Thames (Middelburg et al., 2002) and three for the Humber (see Table 1), these estuaries have not been included because of their size and complexity. Different studies use different surveying approaches; comparison between studies is possible but imperfect. The major differences between studies are in the depth of measurements, either surface or at 1 m and the phase of the tide on which the studies were conducted, either the ebb or the flood (detailed in Table 1). Both of these factors should be less significant for a fully mixed estuary compared to a salt wedge estuary. Seasonality is also not fully covered in all studies. Consideration of these results and the variances calculated for each estuary suggest that estuarine variability is more significant than the small differences in survey approach.

4. Case studies considering the effect of urban waste and nutrients on GHG production

The relationships between UWW and nutrients on both methane and nitrous oxide concentrations in the estuary environment are considered in the following three case studies: (i) effects of UWW loading on average GHG concentrations, (ii) causes of high estuarine nitrous oxide concentrations and (iii) effects of different nutrients on methane concentrations. Relationships between GHG concentrations and estuary, catchment and land-cover area are reviewed in supplementary data Table A2 and Fig. A1.

4.1. Wastewater loading is a primary driver of both methane and nitrous oxide emissions

The average methane and nitrous oxide concentrations for nine and thirteen estuaries respectively appear highly correlated with urban wastewater loading per mean river flow (Fig. 4).

River-estuary systems that have higher levels of UWW per unit river flow have both higher methane and nitrous oxide production on average (Fig. 4). The correlation coefficients for both methane $R^2 = 0.80$ (excluding the Clyde) and nitrous oxide $R^2 = 0.78$ (all data) are statistically significant despite the large number of factors that could influence methane and nitrous concentrations including: natural estuarine variability, anthropogenic affects and survey protocols. Natural

Table 2
Summary of average methane and nitrous oxide concentrations measured.

Estuary	Year	Reference[a]	No. of surveys	Average CH_4 (nM/l)	Average N_2O (nM/l)	Average CH_4 (% sat)	Average N_2O (% sat)	CH_4/N_2O ratio
Conwy	2017–18	1	4	103.2	13.0	2964	130	7.9
Clywd	2017–18	1	3	178.6	13.8	5571	140	12.9
Tamar	2017–18	1	4	214.6	17.5	7820	164	12.3
Dart	2017–18	1	3	187.1	16.0	6415	165	11.7
Tay	2017–18	1	4	53.3	12.0	1475	107	4.4
Forth	2017–18	1	4	158.3	34.4	4138	262	4.6
Clyde	2017–18	1	4	1120.6	32.4	31,285	251	34.6
Tay	2009–10	2	8	48.2	13.9	2698	118	3.5
Humber	2000–02	3 &4	2–3	55.1	71.4[b]	1546	396	0.8
Forth	2000–02	3 &4	4	178.4	20.1[b]	5067	152	8.9
Tamar	2000–02	3 &4	2–4	132.9	18.5[b]	3047	145	7.2
Tay	2000–02	3 &4	1	24.8	9.9[b]	584	104	2.5
Tees	2000–02	3 &4	3	500.1	68.8[b]	16,559	383	7.3
Tyne	2000–02	3 &4	6–8	910.0	14.0[b]	26,348	124	65.0
Colne	2001–02	5	4	*na*	197.3	*na*	993	*na*
Stour	2001–02	5	4	*na*	24.9	*na*	143	*na*
Orwell	2001–02	5	4	*na*	46.3	*na*	282	*na*
Deben	2001–02	5	4	*na*	32.6	*na*	187	*na*
Humber (Trent falls - Humber Br)	2001–02	5	4	*na*	32.1	*na*	187	*na*
Humber (Humber Br - spurn head)	2001–02	5	4	*na*	24.7	*na*	149	*na*
Conwy	2002–03	5	4	*na*	18.6	*na*	114	*na*

Abbreviations: - Methane (CH_4), Nitrous Oxide (N_2O)
[a] References see Table 1
[b] Estimated from concentration data provided in reference 3

estuarine variability would include: stratification, tidal range, tidal asymmetry, fresh water flushing time, average particle residence time, river flow, the shape and area of the estuary, area of tidal flats and sedimentation processes. Other significant anthropogenic affects might include the percentage cover and type of agriculture in the catchments, industrial waste, water extraction and legacy pollution. The main variation associated with the survey protocols include the number, seasonal balance and range of methods used. While on average all estuaries fit the relationship between GHG concentrations and UWW loading, the methane to nitrous oxide ratio is higher for the Clyde and Tyne compared to, for example, the Tay, Forth and Humber estuaries (Table 2). Here, estuary morphology may be an influencing factor. The large and exposed Tay, Forth and Humber systems may allow for more effective oxygenation of the surface waters resulting in more methane oxidation, in comparison to the physically restricted, narrow estuaries of the Clyde and Tyne. Morphological variation aside, these data underline the potential importance of UWW output on both methane and nitrous oxide concentrations in estuarine environments and undermine the assumption that discharge into estuaries is flushed away without environmental repercussions.

To further investigate the relationship between urban influences and estuarine GHGs, catchment land cover was considered (Morton et al., 2020), (see supplementary data Fig. A1). These relationships strongly support the inference that high urban populations increase both estuary methane and nitrous oxide but agriculture primarily impacts nitrous oxide concentration. The limited data for carbon dioxide (only available for five estuary systems) has a positive correlation with UWW loading. Bioavailability of anthropogenic derived organic matter may promote microbial production and degradation, rather than carbon sequestration (García-martín et al., 2018).

4.2. *Nitrous oxide concentrations significantly increased by activation of denitrification*

Nitrous oxide emissions from rivers and estuaries have been linked to the dissolved inorganic nitrogen (DIN) concentration for which agriculture and sewage treatments are considered the main sources (Dong et al., 2005; Barnes and Upstill-Goddard, 2011). Fig. 5 shows the average nitrous oxide percentage saturation against concentrations of nitrate, nitrite and ammonium respectively from (Dong et al., 2005; Pickard et al., 2022). While these plots confirm the strong correlations between nitrous oxide and particularly nitrite and ammonium, as previously reported (Dong et al., 2005) and are generally consistent for all authors, there are exceptions, specifically for the Colne, Forth and Clyde (see ringed points in Fig. 5 a, b, c) which demonstrate higher nitrous oxide concentrations compared to DIN loading. The relationship between DIN and nitrous oxide percentage saturation for six estuaries also shows higher nitrous oxide concentrations for the Forth (Barnes and Upstill-Goddard, 2011, Fig. 6). The river data (Dong et al., 2005), show no exceptions, even for the Colne. Additionally the relationship between nitrous oxide and ammonium (but not nitrate or nitrite) is different between the rivers and estuaries. Nitrification, which converts ammonium to nitrous oxide, requires oxygen, and rivers are typically more oxygenated than estuaries.

The Colne estuary is muddy and hyper-nutrified (Ogilvie et al., 1997) with strong gradients (increasing up river) of nitrate and ammonium due to inputs from the river and sewage treatment. Sediments located near the tidal limit were found to be major sites of denitrification and correlated with high nitrite concentrations (Robinson et al., 1998; Dolfing et al., 2002). Dissolved oxygen data for the Forth showed a strong negative correlation with nitrous oxide (Barnes and Upstill-Goddard, 2011), and both the Clyde and Forth are known to experience low oxygen conditions under some tidal and river flow regimes (Scottish Environment Protection Agency, 2020). These are all consistent with a denitrification mechanism for the higher nitrous oxide in the Colne, Forth and Clyde (Fig. 5). Uncoupled bacterial denitrification supported by nitrate diffusing into the sediment from the overlaying water column and by the sediment organic carbon content, can exhibit faster rates of nitrate reduction (Dong et al., 2000) with organic carbon content determining the potential capacity of denitrification when the nitrate concentration is not limiting with bacterial communities adapting to high nitrate concentrations. Hence when high levels of oxidised nitrogen and ammonium are delivered to an estuary this mechanism is likely to result in high nitrous oxide production. Nitrous oxide concentrations are more significantly impacted by the presence of ammonium compared to nitrate (Fig. 5), suggesting nitrification with exceptions for

Table 3
Physical characteristics of the estuarine systems.

	Estuary	Estuary catchment Area[a] (km^2)	Estuary area[a] (km^2)	Mean freshwater input[b] (m^3/s)	Tidal range HAT-LAT[c] (m)	UWWT Capacity Estuary[d] (pp equ)	UWWT Capacity River[d] (pp equ)	UWWT Capacity Total (pp equ)	UWWT Capacity/ Mean freshwater input (per 1000)	Mixing regime
1	Conwy	345	14.9	19.1	9.01	88,731	4072	92,803	4.86	Macrotidal, well mixed, can stratify on flood and mix on the ebb[e]
2	Clywd	598	1.2	11.2	9.70	88,248	27,037	115,285	10.28	Macrotidal, well mixed
3	Tamar	1338	39.6	22.7	5.91	358,096	46,641	404,737	17.83	Macrotidal, well mixed, low salinity TMZ, stratification occurs on ebb[f]
4	Dart	475	8.6	11.3	5.91*	36,084	22,134	58,218	5.16	Macrotidal, stratified neap & low freshwater runoff[g]
5	Tay	5669	121.3	201.1	6.31*	98,000	99,975	197,975	0.98	Macrotidal, partially mixed, stratified on ebb, longitudinal fronts[h]
6	Forth	1938	84.0	46.4	6.31	267,700	111,250	378,950	8.17	Macrotidal, well mixed, low salinity TMZ, double high/low waters[i]
7	Clyde	3854	54.9	57.1	3.90	1,159,202	886,846	2,046,048	35.84	Mesotidal, stratified at neap, channel straightened and deepened[j]
8	Humber	19,427	303.5	212.3	7.83				–	Macrotidal, well mixed, low salinity TMZ[k]
9	Tees	1930	13.3	22.4	5.99	932,367	10,892	943,259	42.13	Macrotidal, partially mixed, stratified at neaps and on ebb tide[l]
10	Tyne	2935	7.9	47.5	5.73	1,003,785	104,748	1,108,533	23.27	Macrotidal, partially mixed, low salinity TMZ[m]
12	Colne	255	23.4	1.1	4.71	144,152	28,675	172,827	161.52	Macrotidal, with extensive mud flat and tidal creaks[n]
13	Stour	578	23.3	3.1	4.71	48,355	55,932	104,287	33.68	Macrotidal with extensive mud flat and tidal creaks[n]
14	Orwell	–	–	1.4	4.71	178,075	11,731	189,806	140.7	Macrotidal with extensive mud flat and tidal creaks[n]
15	Deben	–	–	0.8	4.71	28,630	6000	34,630	43.78	Macrotidal,[n]

Abbreviations: Highest / Lowest Astronomical Tide (H/ LAT), Urban Wastewater Treatment (UWWT)
[a] (Nedwell et al., 2002)
[b] All flow data were derived from CEH (UK Centre for Ecology and Hydrology (UKCEH), 2020) and focus on the main rivers entering at the head of the estuary. The mean flow data represent the specific river mentioned unless stated below: Clywd is the sum of the Clywd and Elwy, Tay is the sum of the Tay and Earn, Clyde is the sum of the Clyde and the Kelvin, Humber is the sum of the Aire, Trent, Ouse, Don, Wharfe and Derwent, the Tees is the sum of the Tees and the Leven and the Tyne is the sum of the Tyne and the Derwent.
[c] (BODC, 2020), (*)Due to the location of standard ports the Forth estuary tidal range is applied to the Tay and the Tamar estuary tidal range is applied to the Dart
[d] (European Commission (Directorate General Environment), 2016)
[e] (Robins et al., 2014);
[f] (Uncles and Stephens, 1993)
[g] (Thain et al., 2004)
[h] (Wewetzera et al., 1999); (McManus, 2005)
[i] (Lindsay et al., 1996)
[j] (Scottish Environment Protection Agency, 2020)
[k] (Mitchell et al., 1999), (Mitchell et al., 1998)
[l] (Environmental Agency, 1999)
[m] (Upstill-Goddard et al., 2000)
[n] (Dong et al., 2005)

Colne, Forth and Clyde. The dynamic often low oxygen environment within these estuaries may trigger denitrification even with oxygen present (Marchant et al., 2017) and mid-salinity waters and ammonium concentration can further optimise nitrification rates (Isnansetyo et al., 2014). These two observations suggest that more nitrogen cycling can occur in an estuary than in either fresh or coastal waters. This data underlines the importance of preventing both excessive inputs of nitrate and ammonium and the occurrence of low oxygen condition within estuaries.

4.3. *Methane dynamics driven by ammonium concentrations*

Average methane concentration data from seven estuaries (Pickard et al., 2022) appear highly correlated with nutrients, particularly nitrite, ammonium, phosphate and (Fig. 6 b, c, d respectively). While causal factors are not clear, the higher correlations with nitrite, ammonium and phosphate ($P < 0.001$) point towards UWW as a contributor to methane production in the estuary. Conversely the poor, not statistically significant, correlation with nitrate concentrations, would not suggest agricultural run-off is significantly affecting estuary methane production. This is consistent with the land-cover data in supplementary data Table A2 and Fig. A1. Furthermore inputs from agriculture typically

Fig. 3. Map showing estuary catchments of the thirteen estuary systems mainly considered in this analysis.

occur higher in the catchment compared to UWW giving more time for processing to occur prior to water arriving in the estuary.

Methane concentrations can be influenced by DIN indirectly. Nitrification of ammonium requires oxygen and this process may consume sufficient oxygen to reduce methane oxidation through the water column. Additionally inhibition of methane oxidation by ammonium can occur in the surface layer of a sediment, allowing more methane evasion (Bosse et al., 1993; Dunfield and Knowles, 1995). Conversely if denitrification is the prevalent mechanism of nitrous oxide production, the low oxygen environment that promotes nitrous oxide production would also reduce methane oxidation, resulting in a secondary correlation. These potential mechanisms linked to oxygen levels are also consistent with the poor correlation with nitrate, which does not require oxygen for further processing. These relationships only hold for each estuary survey as a whole, not for each specific measurement point, suggesting that process timescales are important (Fig. 6).

4.4. Urban waste and nutrients summary

Estuary systems that have higher levels of nutrients from UWW per unit river flow have higher methane and nitrous oxide concentrations and both methane and nitrous oxide concentrations are more strongly correlated to nitrite and ammonium concentrations than nitrate. Analysis on the influence of land-cover (supplementary data Table A2 and Fig. A1) strongly support the inference that high urban populations increase both estuary methane and nitrous oxide but agriculture primarily impacts nitrous oxide concentration. Significantly higher levels of nitrous oxide and methane occur in estuaries that experience high urban loading and low oxygen conditions, likely via denitrification and inhibited oxidation pathways respectively. The natural but highly variable conditions in estuaries related to changing oxygen levels and mid-salinity values may act to increase nitrogen cycling rates in estuaries compared to either fresh or coastal waters and suggest that UWW discharge into estuaries has environmental repercussions related to GHGs.

5. Estuarine processes as drivers of GHG production

To elucidate the impact and interactions of estuarine processes on GHG production it is useful to consider different types of estuaries,

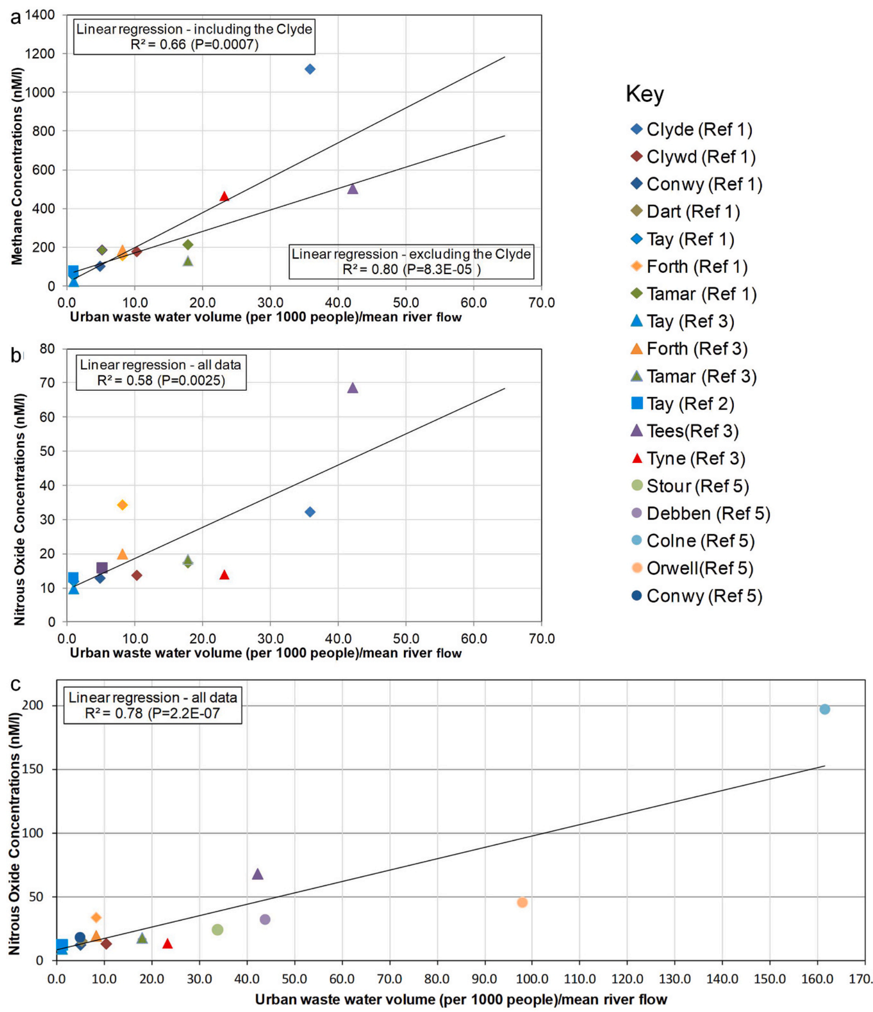

Fig. 4. UWW loading (urban wastewater volume (per 1000 people/mean river flow)) is compared with (a) Average methane concentration (Pickard et al., 2021, 2022 and Barnes and Upstill-Goddard, 2011); (b) Average nitrous oxide concentration data (Pickard et al., 2021, 2022; Upstill-Goddard and Barnes, 2016); (c) Average nitrous oxide concentrations as for (b) but including estuaries from SE England (Dong et al., 2005).

where there is sufficient data for interpretation, as morphology strongly influences estuarine processes. As such two different estuaries with high urban loading: (i) the Clyde (Pickard et al., 2022), which can be stratified and (ii) the Tyne, (Barnes and Upstill-Goddard, 2011; Upstill-Goddard and Barnes, 2016), which is well mixed with a distinct turbidity maximum, are considered and contrasted with more pristine systems. Note that estuary area was found to have no significant correlation with GHG concentrations.

5.1. *Estuary stratification leading to near bed anoxia driving GHG production*

Very high methane and nitrous oxide concentrations have been observed in the Clyde estuary (Pickard et al., 2022). This may in part be attributed to the frequent occurrence of near-bed anoxia, as evident in continuously monitored surface and near-bed oxygen data in the upper estuary by Inner Clyde Estuary (ICE) monitoring buoy (Scottish Environment Protection Agency, 2020). Anoxic events are most common when neap tides and low river flows align. The inner Clyde estuary, which is long and narrow, has been anthropogenically constrained with near vertical walls along much of its length and obstacles such as sandbanks removed by dredging. These factors together with the lower tidal range (Table 3) reduce turbulence and consequently mixing, in contrast with most UK inner estuaries. When low river flows coincide with neap tides the reduced energy conditions result in a strong pycnocline and low oxygen concentrations particularly associated with the lower portion of the water column. These low oxygen concentrations enhance conditions for GHG production.

Four surveys covering different river flows and tidal ranges, average methane and nitrous oxide concentrations within the Clyde estuary showed considerable temporal variability (Pickard et al., 2022; Table 4). Potential key drivers of this variability include tidal range, river flow, surface and bed salinity, temperature and oxygen levels. While there is insufficient data in four surveys for the mechanisms impacting GHG concentrations to be fully understood, the rank orders for methane and nitrous oxide concentrations are similar suggesting that the estuarine conditions influence both methane and nitrous oxide concentrations. This would suggest reduced methane oxidation and denitrification processing of DIN possibly occurring concurrently under low oxygen conditions. The lowest methane and nitrous oxide concentrations were associated with high river flow and spring tide conditions (January 2018) and associated with a mixed, highly oxygenated estuary and diluted nutrients. The higher methane and nitrous oxide concentrations were recorded when sampling took place during a neap tide that coincided with relatively low river flows, which had resulted in a highly stratified estuary and low oxygen conditions near the bed.

The Clyde has a high urban loading with UWW treatment plants adding significant volumes of wastewater discharging both directly into the estuary and at 3.5 km and 13.3 km upstream of the estuary's upper saline extent, without prior nitrate or phosphate removal at the time of

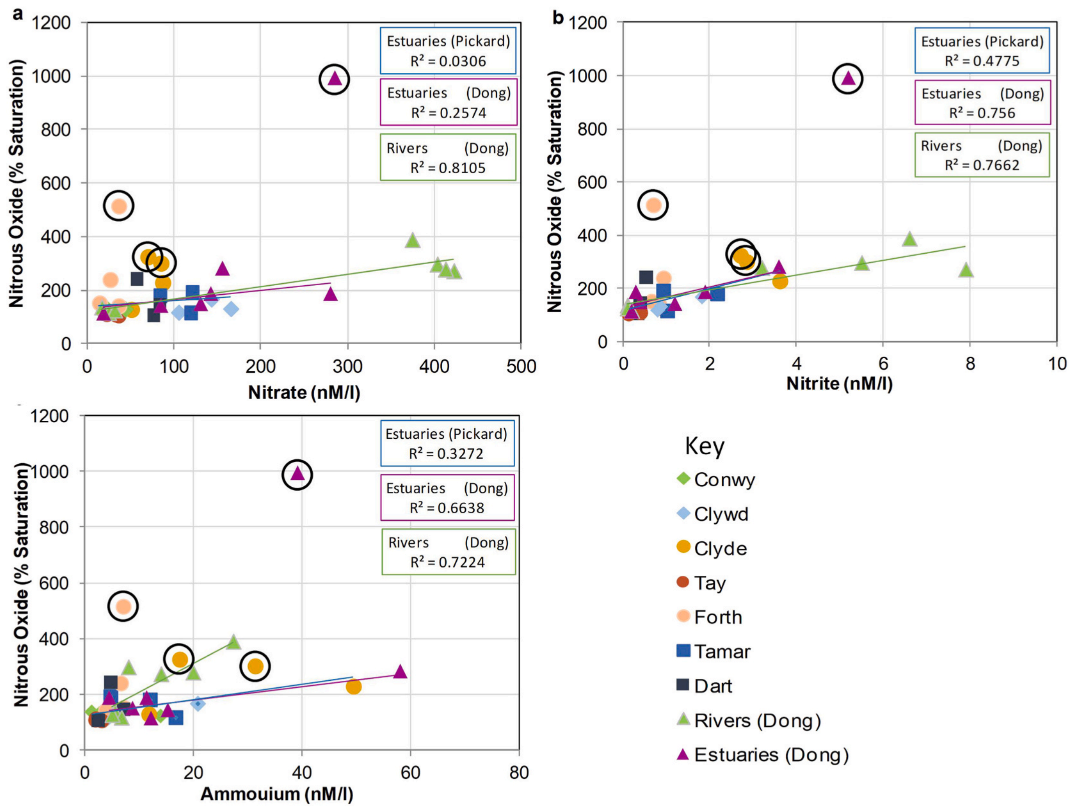

Fig. 5. Relative relationships between various DIN concentrations and average nitrous oxide percentage saturation, specifically (a) nitrate, (b) nitrite, (c) ammonium with data from (Dong et al., 2005; Pickard et al., 2022). Note ringed points related to the Colne, Forth and Clyde are not included in the regression lines.

this survey (European Commission (Directorate General Environment), 2016). The highest methane and nitrous oxide concentrations correspond to the proximity of the largest estuarine UWW discharge, amplified by its addition to an area often stratified with a pronounced anoxic layer.

The data from the upper Clyde as measured by ICE monitoring buoy also shows that in recent years (2016 to 2019) the May to July period had higher salinity intrusion and lower dissolved oxygen data (Scottish Environment Protection Agency, 2020). This appears linked to sustained low river flows during this period (UK Centre for Ecology and Hydrology (UKCEH), 2020), which would act to increase the saline intrusion and reduce estuary flushing, resulting in longer particle residence times. This together with the physically restricted estuary morphology would further limit the re-oxygenation of incoming saline water between tides. While these low oxygen levels during prolonged low river flow events would also be expected to result in higher GHG concentrations, the low river flow would result in an upward shift in salinity for all locations, effectively shifting the location of the estuarine water upstream impacting the effective estuary area and would need to be accounted for.

Association of near bed anoxia with weak tidal mixing and low river flow can be observed in other estuaries. Flow and stratification data across the Dart estuary showed that two layer flow occurs at neap tides during low water flow (Thain et al., 2004). Methane and nitrous oxide concentration data from the same estuary were collected across a range of river flows. Methane concentrations were an order of magnitude higher when sampling occurred at low river flow (34% of the mean flow), although all measurements occurred during neap tides (Pickard et al., 2022); Table 5).

While fully equivalent oxygen and nutrient data for the estuaries are not available, the urban loading of the Dart is one eighth of the Clyde (Table 3). The best estimate of surface oxygen levels for the Dart (Environment Agency, 2020) and the Clyde (Scottish Environment Protection Agency, 2020) shows that the Clyde has an average surface oxygen level of 82%, and the Dart 97% (Table A1). This ranking of both oxygen levels and UWW loading is aligned with the methane and nitrous oxide data available. The extent and frequency of stratification and near bed anoxia is not known for the Dart.

Stratified estuaries experiencing low river flows in summer, when oxygen levels may already be low are even more susceptible to high methane concentrations. Higher methane concentrations were observed in four estuaries measured in July (Pickard et al., 2022) the Clwyd, Tamar, Dart and Conwy, which had river flows between 21% and 40% of the mean flow on the measurement dates (NRFA, 2010) although no oxygen data were available. Overall this suggests that both tide and river flow interact with urban loading to influence methane concentrations in particular, and that surface oxygen levels may provide an initial indication of likely methane concentrations.

5.2. Tidal range impacting sediment oxygen demand driving methane production

The Tyne (together with the Humber, Forth and Tamar) is noted to have flood tide asymmetry, (Barnes and Upstill-Goddard, 2011), which forces marine sediments upstream, when river discharge is slow, resulting in a well-defined Estuary Turbidity Maximum (ETM). High suspended sediments associated with low oxygen levels have been measured on the tidal rivers Trent and Ouse (Mitchell et al., 1999) and attributed to the high sediment oxygen demand (SOD) of the suspended sediment particles. Organic material and metals (for example from industrial legacy waste) can adsorb onto the surface of sediments and lead to increased biochemical oxygen demand (BOD) (Mitchell et al., 1998). Sediments that are re-suspended from anoxic or anaerobic layers in the bed and moved to aerobic locations by river flow or tidal flow can use more oxygen than expected because they are newly exposed to aerobic organisms and contain chemicals or metal ions in a reduced state.

Across six surveys covering different river flows and tidal ranges in

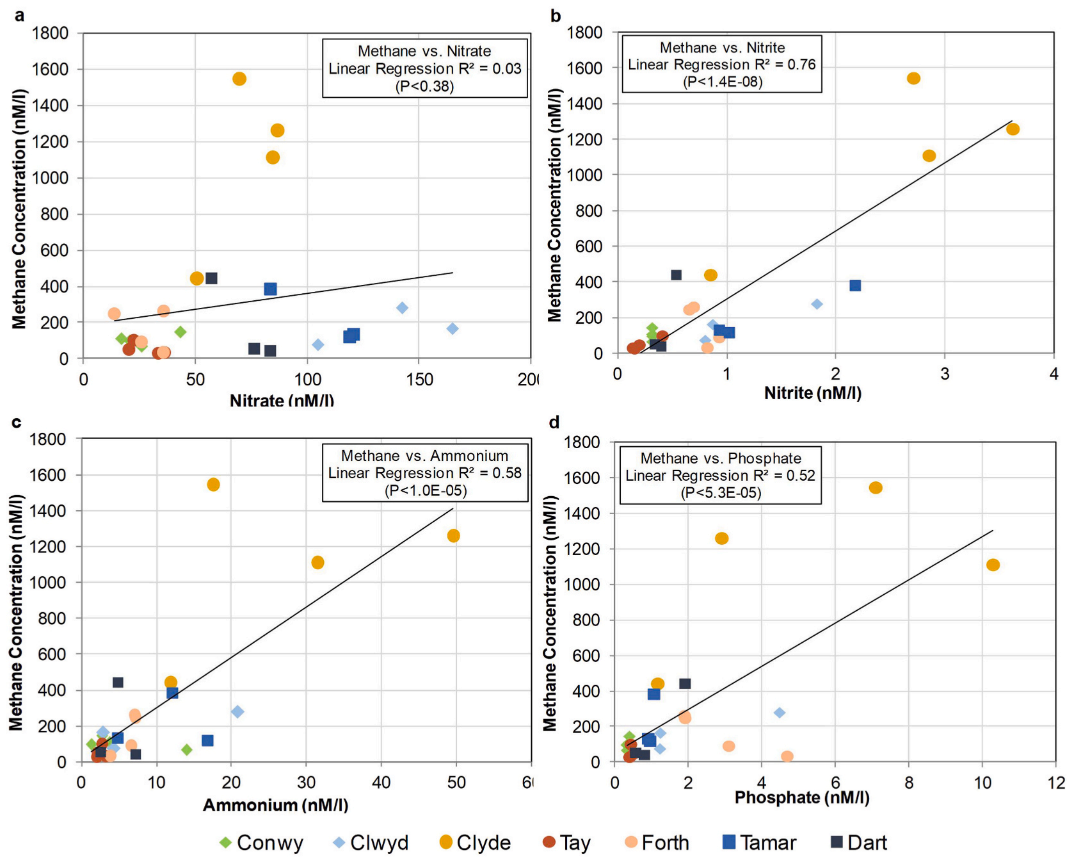

Fig. 6. Relationships between average methane concentration for each estuary and (a) nitrate, (b) nitrite, (c) ammonium and (d) phosphate concentrations with data from (Pickard et al., 2022).

Table 4
Clyde Estuary GHG concentrations associated with tidal, river, salinity and oxygen conditions.

	River flow Daldowie[b] (m^3/s)	Percent of mean flow (%)	Tidal range[c] (m)	Water Temperature Deg C[d]	Surface / Bed Salinity[a] (PSU)	Surface / Bed Oxygen[a] (mg/l)	Survey average[d] N_2O (nM)	Survey average[d] CH_4 (nM)
July-17	22.6	47	2.53	15.3	2.0 / 15.0	8 / 1	31	1114
Nov-17	53.1	110	2.14	12.1	0.5 / 20.0	11 / 6	51	1460
Jan-18	139.0	287	3.49	5.4	0.1 / 0.1	12 / 12	14	445
Apr-18	20.7	43	3.33	11.8	2.0 / 6.0	8 / 5	30	1263

[a] (Scottish Environment Protection Agency, 2020).
[b] (NRFA, 2010).
[c] (BODC, 2020).
[d] (Pickard et al., 2022).

the Tyne estuary, average methane concentrations showed considerable temporal variability (Upstill-Goddard and Barnes, 2016). Whilst similar methane concentrations occur across a range of river flows from 35% to 235% of the mean flow (NRFA, 2010), there is a strong correlation ($R^2 = 82\%$, $P < 0.02$) between methane concentrations and tidal range (using data from the standard port at Whitby at the mouth of the Tyne) (BODC, 2020), see Fig. 7. The higher tidal ranges have the potential to increase mixing and re-suspension of sediment, which could reduce oxygen concentrations. However, when high river flow occurs simultaneously with high tidal range, the extent of the tidal intrusion will be reduced, likely causing reduced methane production within the estuary area.

Other fully-mixed estuaries also show an increase in methane associated with high tidal range, but the limited number of survey occasions and confounding between potential driving variables means that methane is also correlated with low river flow and high temperature, both of which would reduce oxygen levels. These three possible causes are too strongly correlated to enable firm conclusions and all may contribute to elevated methane concentrations to some degree.

5.3. Estuarine processes summary

The Clyde and Dart estuaries provide examples of stratified systems with weak tidal mixing, frequently experiencing near bed anoxia, which is associated with high methane and nitrous oxide concentrations, particularly during neap tides and low river flows. Conversely, the Tyne estuary which is typically fully-mixed shows a strong correlation between methane concentrations and tidal range, which we consider to be linked to suspended sediments removing oxygen from the water column. The Tyne has considerable legacy pollution (Hall et al., 1996; Lewis, 1990) and hence high sediment oxygen demand may be associated with this condition. These interpretations, while interesting, are based on limited samples from what are highly variable systems and are unlikely

Table 5
Tide and River Condition associated with measurements occasions - Dart estuary.

	River flow Austins Bridge[a] (m^3/s)	Percent of mean flow (%)	Tidal range[b] (m)	Survey average N_2O[c] (nM)	Survey average CH_4[c] (nM)
July-17	3.87	34	3.45	21	442
Oct-17	14.37	127	3.46	–	–
Jan-18	53.64	475	3.54	11	54
Apr-18	25.85	229	3.71	15	41

[a] (NRFA, 2010).
[b] (BODC, 2020).
[c] (Pickard et al., 2022).

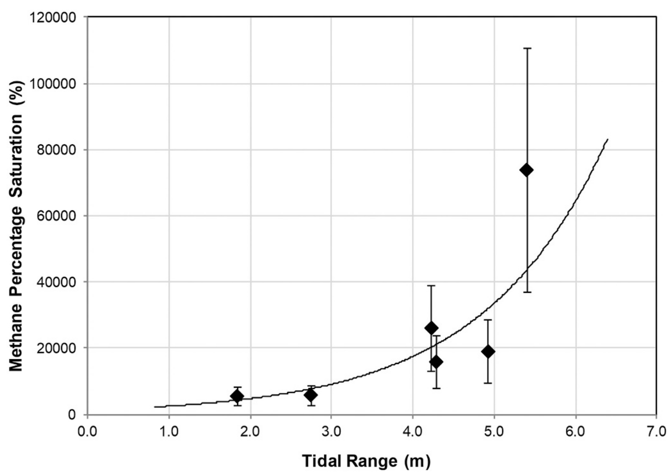

Fig. 7. Tyne Estuary average relationships between methane concentration and tidal range. Methane data from Upstill-Goddard and Barnes (2016) and tidal data from BODC (2020).

to fully characterise the GHG variability and associated mechanisms and should be treated with caution. Additionally there is insufficient data overall to determine the impact of temperature on nitrous oxide and methane concentrations, which would be expected to be significant. These relationships once established may vary between environments and further improve predictive power.

6. Conceptual model for methane and nitrous oxide within the estuary environment

Whilst spatial-temporal variability in estuarine systems is high, evidence collated here indicates the potential for robust conceptual understanding of GHG production pathways in estuaries. Summarising the key processes that have been presented in UK estuary case studies, a conceptual model for methane and nitrous oxide concentrations within the estuarine environment has been developed. This model aims to capture, as far as possible, the high variability between and within estuarine environments, influenced by the catchment, estuarine shape and dimensions, tidal regime and river flow, together with anthropogenic perturbations. To illustrate this model, four diagrammatic examples are provided relating to the two extremes of estuarine mixing; a salt-wedge estuary with significant stratification (Fig. 8) and a fully-mixed estuary (Fig. 9), both shown at high tide. The model also incorporates a prediction of how a low nutrient estuary (panel A) is influenced by the introduction of UWW (panel B) and how this change will interact with estuarine processes to increase both the methane and nitrous oxide emissions. Anthropogenic susceptibility can vary in different estuaries or due to different conditions within a particular estuary; for example, variation from spring to neap tides, changes in river flow and changes in temperature, can cause an estuary to change its level of stratification, oxygenation or the amount of suspended sediment. Additionally, flood or ebb tide dominance varies between estuaries with some systems becoming stratified only on the ebb and others only on the flood tide. These physical differences, which occur over varying temporal scales, will impact the interactions with UWW and can, in part, be inferred from our simplified model.

A high level of legacy pollution assimilated into the estuary sediments could further remove oxygen from the lower layer if sediments are disturbed, increasing anoxia and reducing methane oxidation. Conversely high river levels may more rapidly replenish oxygen to the upper layer, reducing the impact of UWW. As a result higher methane concentrations would be expected to increase as oxygen becomes depleted towards high tide and reach a maximum at the extent of the saline intrusion. Methane concentrations would be expected to reduce on the ebb tide as surface waters are replaced by oxygenated riverine waters and nutrient are no longer trapped in the estuary. The longitudinal profile of methane may peak where there is lowest oxygen levels while that of nitrous oxide may peak associated with mid salinity, DIN concentration and low oxygen. The location of these peaks will also be influenced by the river flow and associated with urban inflows which are then diluted seawards on the ebb. Any artificial barrages or weirs (more often found in stratified estuaries as they can remove tidal energy) may be associated with sediment or debris deposition which may act as a carbon source and hence be related to higher GHG production. Periods of drought will likely increase the extent of the saline intrusion and the estuary flushing times, which would change the location of the maximum GHGs and increase nitrous oxide concentrations. The lower estuary turbulence and the typically reduced concentration of GHGs at the surface may act to reduce emissions to atmosphere, although when mixing or overturning of the bottom layer occurs this could cause a dynamic release.

Where there are high levels of legacy pollution, sediment resuspension in the turbidity maximum leads to high sediments oxygen demand, reducing oxygen levels and increasing methane concentrations and evasion significantly. Higher tides would be expected to suspend more sediment, further reducing oxygen and increasing methane production. Changes in river flows may serve only to move the location of the methane and nitrous oxide production, which on high rivers flow would cause an overall reduction GHG production in the estuary area as water is pushed seaward. In a mixed estuary (with no stratification on the ebb) methane and nitrous oxide production are expected to be similar on the flood and ebb tide. Where stratification does occur on the ebb the lower portion of the estuary stagnates, depleting oxygen and thereby producing more methane when compared to the flood tide. If sediment suspension occurs at low tide, this could cause a rapid drop in oxygen and be associated with increased nitrous oxide concentrations due to high DIN concentrations and denitrification. The longitudinal profiles of methane and nitrous oxide may exhibit peaks associated with the low salinity turbidity maximum, areas where sediment is routinely deposited and UWW inflows. Nitrous oxide concentrations may be higher in the mid salinity range of the estuary diluting seawards. The higher estuary turbulence and continual mixing of GHGs to the surface will act to increase emissions to atmosphere.

7. Discussion and conclusions

There is convincing evidence from UK estuaries that excesses of nutrients from UWW result in both higher methane and nitrous oxide concentrations and these concentrations link directly to UWW loading per unit river flow. This is supported by estuaries with higher urban land cover having higher methane and nitrous oxide concentrations. Furthermore, methane and nitrous oxide concentrations are more strongly correlated to nitrite and ammonium than nitrate. Where estuaries experience very low oxygen conditions, higher concentrations of

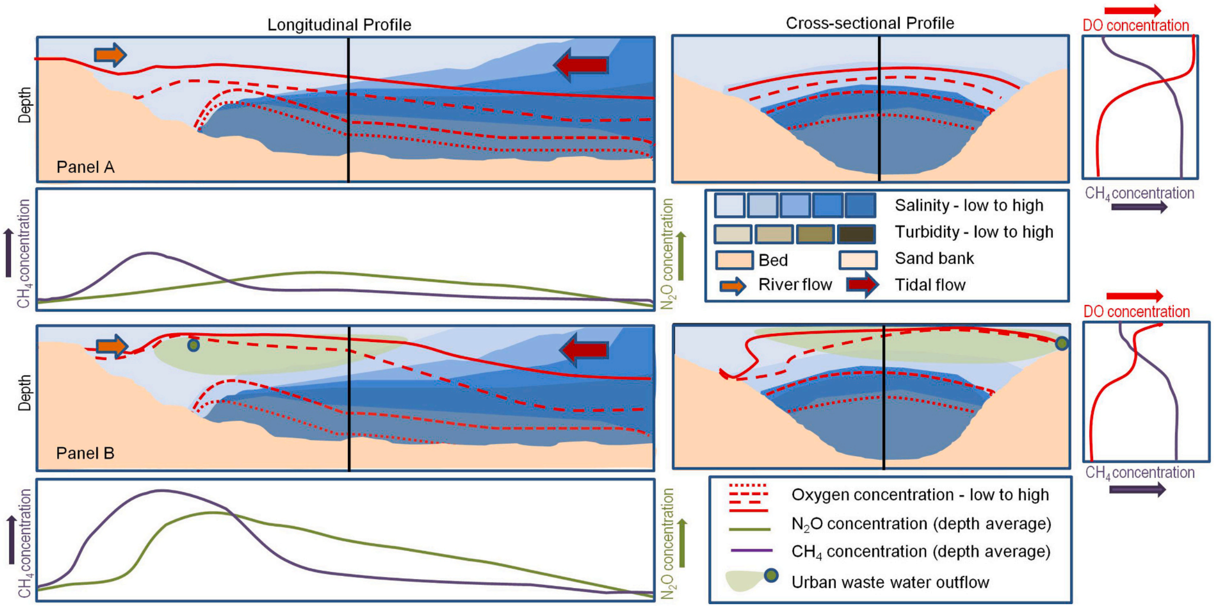

Fig. 8. Panel A: - Longitudinal and cross-sectional profiles of a highly stratified salt-wedge estuary at high tide, with the higher salinity water flowing shore-wards underneath the out-flowing river water.
The upper layer, from the river, would typically be oxygenated, but the lower layer would become lower in oxygen with no means of replenishment, as the oxygen is depleted with distance from the sea and time from low tide. The degree of stratification will change during the tidal cycle and with river and tidal conditions, but when the estuary is highly stratified, this will reduce diffusion of GHGs from the lower to upper layer trapping GHGs under the pycnocline. Methane generation in the bed is generally associated with the low salinity area of the estuary, significantly reducing when the water becomes highly saline. Oxic methane may be generated in the upper fresh water layer. Most methane (CH_4) oxidation would occur in the upper layer resulting in methane concentrations that are linked both to the water layer of generation and inversely related to the vertical oxygen profile. The specific relationship and location of the methane maximum is expected to change with river flow, tidal range and state of the tide, with surface methane concentration reducing on the ebb as more river water becomes available. Some dissolved inorganic nitrogen (DIN) may enter the estuary from the river, with DIN loading changing with river flow. Nitrous oxide (N_2O) concentration would be relatively low peaking at mid-salinity, compared to the methane peaking at low salinity, both reducing seawards due to dilution with sea water.
Panel B: - Longitudinal and cross-sectional profiles of a salt-wedge estuary at high tide including the introduction of urban wastewater concentrated in the low salinity upper layer due to limited mixing.
Introduction of UWW will result in additional nutrients trapped in the upper layer, causing oxygen depletion thereby inhibiting methane oxidation, resulting in higher methane concentrations and additional methane evasion. Ammonium derived from urban wastewater may significantly increase nitrous oxide production, near the source and in the mid salinity range. Most DIN will be trapped in the more oxygenated upper layer making nitrification, driven by DIN concentration, the main N_2O producing mechanism in this layer. N_2O production in the lower layer will be driven by denitrification, with the N_2O concentration increasing with lower oxygen levels further supported in estuaries that have long flushing times allowing DIN to mix or diffuse downwards. Oxygen depletion can result in a switch from nitrification to denitrification even in the surface layer.

both nitrous oxide, most likely generated via denitrification, and methane, in part due to reduced methane oxidation, can be detected. As enhanced nitrogen processing is favourably associated with mid-salinity conditions (Isnansetyo et al., 2014) and methane oxidation may be inhibited either directly or indirectly by higher ammonium concentrations, this makes the estuarine environment an unfortunate location for UWW disposal with respect to GHG emissions. Similarly nitrogen enrichment has been found associated with increased methane and nitrous oxide emissions from tidal flats (Hamilton et al., 2020) and higher methane emissions are now being associated with urban or anthropogenically influenced inland waters (Wang et al., 2021; Hao et al., 2021).

Estuary physio-chemical properties strongly influence methane and nitrous oxide concentrations. Stratified estuaries can experience significant oxygen depletion in the deeper more saline layer, with any legacy waste and associated oxygen sediment demand potentially exacerbating this effect. Additionally, inputs of UWW into a stratified estuary can result in further oxygen depletion in the upper layer due to nitrification of ammonium. Stratified estuaries experiencing low river flow, particularly in summer, when oxygen levels may already be low are even more susceptible to the impacts of UWW, as lower river flows will increase flushing times. Fully mixed estuaries, characterised by a low salinity and high turbidity maximum, can produce high levels of GHGs. The re-suspension of sediments can encourage high sediment oxygen demand (Mitchell et al., 1998), preventing oxidation of methane in the water column. This increase in methane concentration can be linked to tidal range and also possibly to urban or legacy waste.

The conceptual model presented in this paper hypothesises that higher concentrations of both methane and nitrous oxide occurs due to interactions between natural estuarine processes and anthropogenic factors. Low estuarine oxygen levels appear to be significant in causing high methane concentrations within the estuary environment and probably linked to increased methane production and reduced methane oxidation in the surface sediments and water column. Estuarine processes can cause low oxygen levels where they prevent oxygen from being brought to the estuary, for example during low river flows and at high temperatures. Additionally oxygen may not be replenished in the water column, for example when the estuary is stratified or particle residence times increased. Sediments re-suspension can result in BOD, when oxygen is consumed by mineralization of the degradable organic components in fine sediments. Oxygen can be further depleted by the interaction with anthropogenic factors; for example: the introduction of nutrients from UWW and where legacy pollution is contained in the sediment resulting in high SOD.

Use of this conceptual model enables us to predict that some stratified estuaries may experience elevated methane concentrations at high tide, upstream at the low salinity section of the estuary. It also suggests that fully mixed estuaries with significant SOD would experience

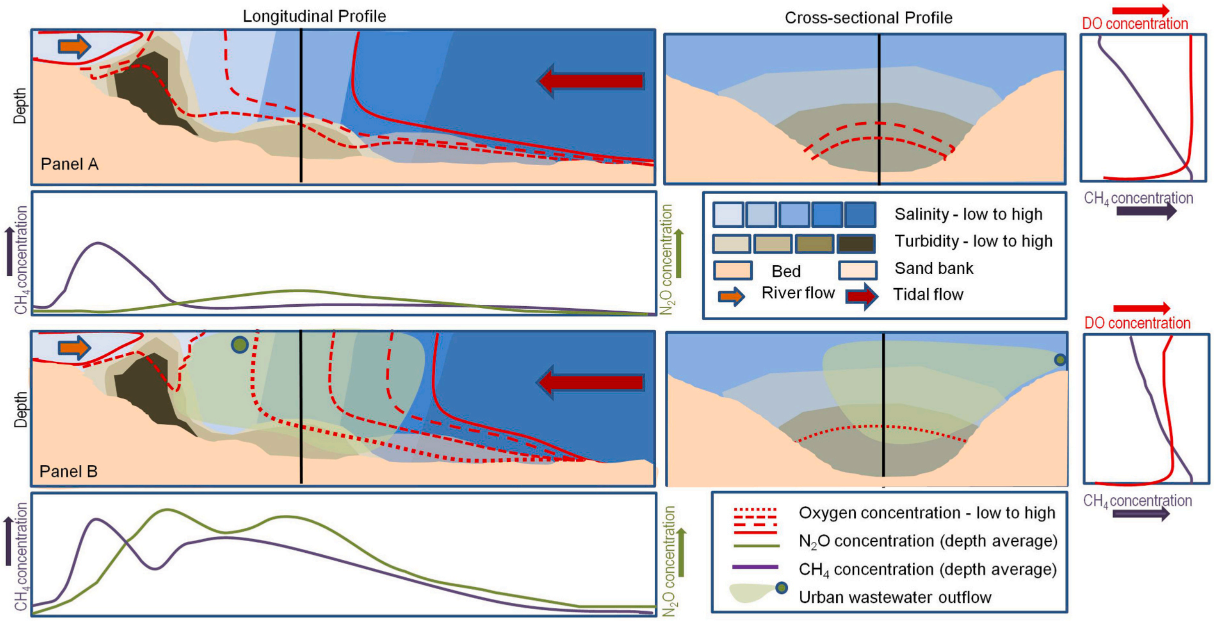

Fig. 9. Panel A: - Longitudinal and cross-sectional profiles of a fully-mixed estuary, with salinity and oxygen levels mixed vertically throughout the water column. Estuaries with high tidal mixing typically experience tidal asymmetry and the transport of fine marine sediments into the upper estuary resulting in a turbidity maximum at low salinity. These sediments are moved up the estuary on the flood and down the estuary of the ebb tide and can trap organic matter at the bed. Methane (CH_4) is mixed and oxidised throughout the water column resulting in little methane evasion in the unpolluted scenario. Any dissolved inorganic nitrogen (DIN) will likely be converted by the nitrification route due to the mixing and higher oxygen levels.
Panel B: - Longitudinal and cross-sectional profiles of a fully-mixed estuary, including the introduction of urban wastewater which is distributed throughout the water column due to effective mixing.
Introduction of urban wastewater (UWW) which will be mixed throughout the water column, will result in an interaction between the DIN and suspended sediments, allowing for both processing of nitrogen in the bed and water column, leading to higher nitrous oxide (N_2O) production. Where the UWW is sufficient to deplete oxygen levels through the water column dentification could occur. This can further act to increase methane if resulting in reduced oxygen levels and subsequent methane oxidation inhibition.

elevated methane concentrations during sediment suspension events, which are most often associated with high tidal range. However these events can also occur at low tide and if sediments are re-suspended in shallow water over estuarine mud, low oxygen and high GHG concentrations may result. The rate of nitrous oxide generation from nitrification is variable, dependent on the availability of electron acceptors and donors (Wrage et al., 2001), the salinity level (with optimum nitrification in the mid salinity range) and temperature (with increased production typical at higher temperatures). Where oxygen concentrations are low or variable, as is often the case in estuarine environments, denitrification may be triggered. This can further significantly increase nitrous oxide concentrations. Estuaries with high suspended sediment concentrations may also support nitrogen processing in the water column as well as at the bed, associated with, for example, a turbidity maximum.

The conceptual model presented here summarises the processes evident in several UK estuaries, but if relationships can be generated for different estuaries and related to both natural processes and anthropogenic perturbations then it may theoretically be applied elsewhere. A study in Chesapeake Bay, the largest estuary in the United States which is eutrophic with near bed hypoxia, also found that methane was associated with low oxygen conditions. Interestingly in this study methane built up under the thermocline and could be released by storm events that induced mixing and overturning (Gelesh et al., 2016). While our conceptual model considers only tidal stratification which lasts in the order of hours, this thermal stratification may last weeks and act to reduce methane diffusion to the surface. The only estuary in this study deep enough to form a thermocline in calm summer weather is the Forth estuary (Black Culm Ltd., 2018). Methane concentrations in the deeper, higher salinity part of the Forth (Upstill-Goddard and Barnes, 2016) were lower in summer, as such it is possible the formation of a thermocline may impact the surface methane signature and methane evasion estimates. GHGs evasion linked to large river plumes may also be dependent on offshore mixing, with higher GHG concentrations found in calm weather. Methane concentrations were measured in nine tidal estuaries in NW Europe including well-mixed, turbid estuaries with long particle residence times (Elbe, Ems, Thames, Scheldt, Loire, Gironde, and Sado) and salt-wedge estuaries with short particle residence times (Rhine and Douro) (Middelburg et al., 2002). While it is not clear how measurements were made relative to the phase of the tide or river flow, it is interesting that the stratified Rhine experienced high and highly variable methane concentrations as would be predicted by the conceptual model dependent on river flow and tidal range and phase. Conversely in well mixed estuaries methane was often highest at the low salinity end consistent with the turbidity maximum being important in methane production (Burgos et al., 2015).

While a single survey was available for the Thames (Middelburg et al., 2002) and some data for the Humber (see Table 1), these large complex estuaries with several contributing rivers and many UWW entry points were not included in the analysis and did not fit the model as well as the simpler estuaries. It is suggested that the large number of tributaries, distance between where tributaries enter the estuary and the large number of UWW treatment plants and the distance of these plants from the estuary make the results difficult to interpret. For example the outflow from 335 and 200 UWW treatment plants eventually enter the Humber and Thames estuaries respectively, some from over 200 km. It is likely that where UWW enters a river far from the estuary, that most nitrogen processing is completed within the typically well oxygenated riverine section reducing its influence within the estuary. Additionally, wide more exposed estuaries are likely to be mixed by wind helping oxygenation and increasing evasion, a process not explicit in this model.

8. Are estuaries a net carbon source or sink?

The flux of GHGs between estuaries and the atmosphere has been estimated by those authors considered herein. This flux is dependent on the dissolved gas concentrations (under consideration in this paper) and the gas transfer velocity (k), which is in turn dependent on in-water turbulence and wind speed (Wanninkhof, 1992; Clark et al., 1995). In estuaries the estimation of the gas transfer velocity associated with turbulence is complex, as turbulence is the result of tidal velocity and river flow interacting with friction from the bed bathymetry. As such salt-wedge estuaries, with lower turbulence compared to mixed estuaries may have a lower value of k. Wind speed, found to have the major impact on k (Clark et al., 1995), not only impacts diffusion at the interface but also wind induced waves which increase mixing. Estuaries that are wide and align with the prevailing wind direction and in topographies that increase wind exposure, are likely to evade a higher proportion of their GHGs to the atmosphere. Thus, k-values from a narrow, dredged, salt-wedge estuary may be less than from a fully-mixed, wide and exposed estuary, especially as GHGs in the lower layer will be less accessible. However, when the stratification is overturned or the stratified water becomes mixed, this may result in dynamic release of trapped GHGs to atmosphere. This process would be difficult to observe requiring detailed temporal monitoring, and emissions may be underestimated if only surface concentrations have been measured.

In addition to the direct atmospheric emissions, it is also important to understand whether estuaries are an overall carbon sink or source. The term 'Blue Carbon' is used to highlight the importance of the carbon sequestration capacity of coastal vegetated ecosystems (Santos et al., 2021). While there is currently insufficient data to understand the link between carbon sequestration and GHG concentrations, it has been hypothesised that discharges of high-nutrient but relatively low-carbon water generated by wastewater treatment can enhance carbon uptake from the atmosphere by affecting biogeochemical cycles in these system (Kuwae et al., 2016). While this is yet to be tested, this estimate focuses primarily on carbon dioxide and not nitrous oxide or methane. In contrast arable and (sub)urban estuaries were found to export, on average, 50% more dissolved organic carbon to coastal areas than they receive from rivers due to net anthropogenic derived organic matter inputs within the estuary, with the bioavailability of this dissolved organic matter promoting microbial production and degradation (García-martín et al., 2018). While beyond the scope of this paper, understanding where estuaries could act as carbon sinks and how this is impacted by anthropogenic inputs (in terms of micro-biome communities and bioavailability of nutrients) and activities (e.g. dredging) would be a beneficial area of study. The highly variable estuarine environments are likely to respond differently to enabling carbon sequestration both in terms of anthropogenic influences and estuarine processes.

9. The impact of survey design and areas of uncertainty

Where estuarine surveys are designed to produce an estimate of GHG concentrations it is important to consider the best approach to capture spatio-temporal variability. Based on data reviewed here we recommend the following approach for future studies:

a) use of fixed point transects with each point aligned to a particular area within the estuary and measurements taken upstream to the limit of the maximum saline intrusion
b) sufficient sampling undertaken to account for tidal range, stage of the tide, river flow and river flow history (for example periods of drought)
c) sufficient sampling undertaken to account for temperature ranges and seasonality, including the interaction of temperature and river flow
d) measurements to quantify the influence of any nutrient and pollution point sources within the estuary and to account for the different mechanisms of GHG production, for examples linked to: stratification, high turbidity and sediment oxygen demand, tidal flats, variation in salinity, legacy pollution and UWW
e) measurements of oxygen, turbidity and nutrients in addition to GHG concentrations
f) measurements to quantify GHGs in both layers where stratification occurs

Further measurements designed to quantify the specific impact of stratification, tide, temperature and river flow on GHG concentrations and emissions could help remove uncertainties in the conceptual models and further the objective of this paper in helping to identify and remediate estuaries that have high GHG concentrations, globally.

It can be difficult to distinguish between different anthropogenic factors, because areas which were the centres of past industrial activity still have high urban populations. Population density has been found to be significantly related to enrichment of sedimentary metals (Birch et al., 2015). As referred to previously, high levels of legacy pollution, particularly metals, may play a role in GHG emissions. Impairments to water quality can result in the creation of toxicologically stressful environments that may affect the microbiome community structure (Rodgers et al., 2020). This can have an impact on GHGs; for example methanogens use metals such as nickel within coenzymes (Lyu et al., 2018). At least four of the estuaries considered here have high legacy pollution, particularly heavy metals, including the Clyde (Rodgers et al., 2020; Balls et al., 1997), Forth (Lindsay et al., 1998), Tees and Tyne (Hall et al., 1996; Lewis, 1990). The Clyde and Tyne produce more methane than might be expected compared to the Tees and Forth. While this may be related to the Clyde and Tyne being physically restricted, narrow estuaries, it should be noted that the Clyde and Tyne estuaries are regularly dredged, while the upper Forth estuary has never been dredged and the Tees is only occasionally dredged (Marine Scotland, 2021; The Crown Estate, 2021). Dredging and straitening are likely to reduce bed friction and hence mixing. Dredging can re-suspend buried sediments associated with legacy heavy-metal pollution making it more available and leading to further anthropogenic interactions. A further uncertainty is the impact of temperature, salinity and nutrient levels on microbiome community structure and hence the balance between methane production and oxidation.

Expected changes in climate will also impact the estuary environment (Robins et al., 2016). This may act to further increase estuary GHG concentrations via a number of mechanisms. Increasing temperatures will reduce oxygen concentrations and increase nitrogen processing rates. Rising sea levels may increase sediment re-suspension and the extent of the saline intrusion, which could increase access to legacy waste. Changing rainfall patterns may increase the prevalence of drought conditions resulting in lower river flows and consequently lower oxygen and higher nutrient concentrations and reduced estuary flushing. Conversely more extreme rainfall events may lead to flooding which could result in flooding of land affected by legacy waste and nitrogen-rich agricultural land. All of these changes may act to further increase the susceptibility of estuaries to anthropogenic influences increasing GHG production.

10. Opportunities to reduce estuarine GHG emissions

Given that the estuary environment is a potentially significant source of GHG emissions, opportunities to manage and reduce emissions should be considered. Fundamental to the reduction of both nitrous oxide and methane emissions from estuaries is the lowering of DIN levels and removal of low oxygen conditions. Relating to the former, addition of nitrogen and phosphate removal technologies to existing UWW treatment systems outputting to estuaries should be considered. While estuary oxygenation has been trialled in a eutrophic estuary ((Larsen et al.,

2019) and some reservoirs (Gerling et al., 2014) its impact on the biome community and GHG production is unknown. This type of technology could be beneficial if powered by renewable technology. Our conceptual model may be applied to identify priority estuaries for this intervention. Additionally an improved understanding of processes associated with GHG generation could, in the interim, support the adoption of changed management practices, for example ensuring that outflows of UWW are not timed with conditions which may exacerbate estuarine GHG production. Applying our model to the Clyde estuary, we would expect the estuary to be well oxygenated (and hence have lower surface methane concentrations) during high river flows and during ebb tides. Hence, managing UWW outflow to avoid low oxygen conditions and timing outflows on the ebb tide rather than the flood tide could help reduce oxygen stress and methane and nitrous oxide emissions.

The annual nutrient loads to estuaries in the UK are comparatively small compared to reported figures for European and North African estuaries (Nedwell et al., 2002). As such, there may be even greater potential for excess GHG emissions, and reduction thereof, from estuaries at the global scale. With twenty two of the thirty two largest cities in the world are located on estuaries (NOAA, 2020), anthropogenically impacted estuaries may be hidden sources of GHG globally. The conceptual model could be applied to other estuaries globally, by considering both natural processes and anthropogenic perturbations. Furthermore with relatively little extra data, for example nutrients and oxygen (parameters that are often routinely measured) and an understanding of estuary dynamics (tide and river flow), this conceptual model could underpin both effective modelling of estuary GHG production and also provide a route for simpler monitoring of future improvements.

11. Considerations for policy makers

Estuaries are highly valuable as they are critical natural habitats and provide a wide range of ecosystem services. However they experience a wide range of anthropogenic stressors (Kennish, 2005). Estuaries have long been considered an effective location for the disposal of urban and industrial waste, because of their proximity to that waste generation and their perceived ability to flush this waste to the sea with its high dilution capability. However evidence shows that estuaries (both inner and outer) by their very nature: brackish water, low oxygen, stratification and high sediments loads, can become significant GHG sources, particularly when high levels of urban waste enter the estuary. Additionally seasonal changes in river flow, tide and temperature can further exacerbate this GHG generation.

As such criteria linked to GHG generation (not just eutrophication risk) should be included in legislation to further constrain waste water disposal. The mechanistic understanding of GHG generation in the estuarine environment and the associated conceptual model presented in this paper can be applied to help in the identification of estuaries which may act as significant GHG sources and also estuaries where interventions and reduction of anthropogenic influence could significantly reduce these emissions. Further research globally into estuary environments as a GHG source, together with research into mechanisms and the effectiveness of mitigations is still required.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank the authors of the papers and data sets used in this review and the two anonymous reviewers whose comments have helped improve the quality of this paper.

This works was funded by a Natural Environment Research Council (NERC) studentship through the IAPETUS Doctoral Training Partnership Grant No.: NE/S007431/1. AP's input was funded by the Natural Environment Research Council as part of the LOCATE project. CEH Grant No.: NEC05686, NOC Grant No.: NE/N018087/1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2021.113240.

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