A review of indirect N\textsubscript{2}O emission factors from artificial agricultural waters

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Abstract

Nitrous oxide (N\textsubscript{2}O) produced from dissolved nitrogen (N) compounds in agricultural runoff water must be accounted for when reporting N\textsubscript{2}O budgets from agricultural industries. Constructed (‘artificial’) water bodies within the farm landscape are the first aquatic systems that receive field N losses, yet emission accounting for these systems remains under-represented in Intergovernmental Panel on Climate Change (IPCC) emission factor (EF) guidelines and global N\textsubscript{2}O budgets. Here, we examine the role of artificial waters as indirect sources of agricultural N\textsubscript{2}O emissions, identify research gaps, and explore the challenge of predicting these emissions using default EFs. Data from 52 studies reporting dissolved N\textsubscript{2}O, nitrate (NO\textsubscript{3}) and EFs were synthesised from the literature and classified into four water groups; subsurface drains, surface drains, irrigation canals, and farm dams. N\textsubscript{2}O concentration varied significantly between artificial waters while NO\textsubscript{3} did not, suggesting functional differences in the way artificial waters respond to anthropogenic N loading. EFs for the N\textsubscript{2}O–N:NO\textsubscript{3}–N concentration ratio were highly skewed and varied up to three orders of magnitude, ranged 0.005%–2.6%, 0.02%–4.4%, 0.03%–1.33%, and 0.04%–0.46% in subsurface drains, surface drains, irrigation canals, and farm dams, respectively. N\textsubscript{2}O displayed a non-linear relationship with NO\textsubscript{3}, where EF decreased exponentially with increasing NO\textsubscript{3}, demonstrating the inappropriateness of the stationary EF model. We show that the current IPCC EF model tends to overestimate N\textsubscript{2}O production in response to NO\textsubscript{3} loading across most artificial waters, particularly for farm dams. Given their widespread existence, there is a need to: (a) constrain their global abundance and distribution; (b) include artificial waters in the global N\textsubscript{2}O budget, and (c) expand the study of N processing in artificial waters across a geographically diverse area to develop our biogeochemical understanding to the level that has been achieved for rivers and lakes.

1. Introduction

Anthropogenic inputs of nitrogen (N) have increased nitrous oxide (N\textsubscript{2}O) emissions from the world’s river networks by four-fold during the 21st century (Yao et al. 2020). Globally, agriculture contributes \textasciitilde60% (4.3 Tg N yr\textsuperscript{-1}) of anthropogenic N\textsubscript{2}O emissions (7.3 Tg N yr\textsuperscript{-1}), a result of increasing manure inputs within the pastoral sector and the widespread use of nitrogenous fertilisers on arable land (Tian et al. 2020). Agriculture contributes to N\textsubscript{2}O emissions as a result of the direct production of N\textsubscript{2}O within field soils (2.3 Tg N yr\textsuperscript{-1}), direct emissions from animal waste and manure management (1.5 Tg N yr\textsuperscript{-1}), and from N\textsubscript{2}O produced from inland waters (0.5 Tg N yr\textsuperscript{-1}) due to increased N loading from agricultural leaching and runoff (Tian et al. 2020). The incidental emissions from aquatic ecosystems, termed ‘indirect emissions’, are recognised as a key component of agricultural N\textsubscript{2}O inventories, due to \textasciitilde24% of terrestrial agricultural N inputs being lost via hydrological pathways (Hergoualc’h et al. 2019). A large proportion of indirect emissions are generated in water bodies located in close proximity.
Artificial aquatic ecosystems are designed ecosystems constructed for human purposes, and may be wholly engineered systems where no previous water body existed or physically modified natural waters (i.e. channelized stream) (Clifford and Heffernan, 2018). In agricultural landscapes, these artificial waters include channels constructed for subsurface and surface drainage, irrigation canals, and on-farm storage reservoirs (farm dams). These systems are designed to facilitate agricultural production and have human-defined hydrology. Some studies have demonstrated significant differences in dissolved N\textsubscript{2}O concentrations between natural and agricultural water bodies, concluding that the application of a single EF value is inappropriate for upscaling indirect aquatic emissions (Outram and Hiscock, 2012, Xiao et al., 2019). Although there has been an increase in studies measuring N\textsubscript{2}O and N loading in artificial waters, there remains a lack of quantitative understanding to guide predictions of indirect N\textsubscript{2}O emissions from these systems.

Currently, IPCC EFs for estimating indirect N\textsubscript{2}O emissions do not distinguish between artificial waters and natural surface waters (rivers, streams, and lakes) in agricultural landscapes. Agricultural surface waters such as drains, ditches, and canals are assigned the same EF as groundwater and headwater streams, yet represent 23\% of data determining the default emission value of EF\textsubscript{5r} (Tian et al., 2019). Farm dams and other small farm-scale impoundments fall under EF\textsubscript{5r} for rivers, lakes, and reservoirs, yet only represent \textasciitilde7\% of this category (Tian et al., 2019). This review aims to address these gaps by: (a) explicitly assessing the role of different artificial agricultural waters as sources of indirect agricultural N\textsubscript{2}O emissions; and (b) quantitatively evaluating their response to NO\textsubscript{3} loading in the context of the current IPCC indirect N\textsubscript{2}O EF estimates. We draw on available data from the published literature on artificial waters and review the knowledge of N\textsubscript{2}O production for each water type. We anticipate the findings in this review will lead to greater recognition, improved definition, and eventually, explicit inclusion of artificial waters in agricultural N\textsubscript{2}O budgets to help account for uncertainties in agricultural N\textsubscript{2}O accounting.

2. Methods

2.1. Literature search and classification

We employed a similar approach to that of Tian et al. (2019) in our literature search for studies reporting dissolved N\textsubscript{2}O and NO\textsubscript{3} concentrations in agricultural surface waters. The inclusion criteria was redefined to only include constructed, engineered, or modified water types located directly within the agricultural landscape (i.e. no rivers, natural creeks, or hydroelectric reservoirs). Data for EFs were gathered from studies included in the most recent IPCC update on EF\textsubscript{5g} and EF\textsubscript{5r} (Tian et al., 2019), and a
Google Scholar search was conducted using the key terms ‘EFs,’ or ‘dissolved N₂O concentrations’ combined with water definitions (‘wetland,’ ‘pond,’ ‘dam,’ ‘reservoir,’ ‘drainage,’ ‘storage,’ ‘canal,’ ‘ditch,’ ‘tile drain,’ ‘channel’) under the theme ‘agriculture.’ To be included, studies needed to (a) adequately define the water type to ensure it was an artificial or hydrologically modified system; (b) be located within an agriculturally dominant catchment; and (c) have an EF calculated from the N₂O–N/NO₃–N concentration ratio. We chose to focus on the N₂O–N/NO₃–N mass ratio method for calculating EFs as most studies lack the detailed mass balance information of N transport and N₂O flux measurement in their respective catchments required for EFs. Mean values from both temporal and spatial datasets were included if they reported N₂O and NO₃ concentrations. We opted not to include aquaculture ponds and flooded rice paddy waters as N₂O emissions from these systems would be considered direct agricultural emissions. Following this criteria, an additional 25 studies were collected on top of the 27 artificial water studies included in the current IPCC EF estimates (Tian et al 2019).

Table 1 describes the classification of agricultural surface waters considered in this review. Subsurface drains are drainage structures installed directly under agricultural fields to control groundwater levels and prevent waterlogging (Waller and Yitayew 2015). Originally known as tile drains, these structures often consist of a dense network of perforated pipes placed 1–2 m below the surface and which discharges into open collection drains. The concentration of nutrients is highest in these waters as they increase soil water infiltration and collect leached water directly from the soil surface. Surface drains are open waterways, such as ditches, that artificially remove excess water off the farm landscape. They include both on-farm zero-order field drains, main collection drains, and outlets. This infrastructure exists in flood prone areas such as wetlands, floodplains, and poorly draining soils, and acts to enhance agricultural productivity through improved efficiency, timing, and variety of farming operations (Christen et al 2001, Herzon and Helenius 2008). Canals represent engineered channel structures that can act as either supply or drainage channels for irrigated agricultural fields. These networks are often constructed in dryland agricultural regions and support intensive irrigated broad acre production of row crops and horticulture. Although drainage ditches and irrigation canals are structurally similar, being linear channels transporting flowing water, we decided to make a distinction here, largely because they represent inherently different farming systems (e.g. ditches located on farms where excess water is a limitation and canals located in dry regions where water needs to be artificially supplied).

On-farm dams are an integral part of the agricultural landscape that exist to store, control, recycle, and treat water on the farm. Here, we include all constructed waterbodies located directly in the farming landscape, including ponds and wetlands that have been modified or impacted by agriculture beyond their natural state. They exist across all areas of agriculture, including arable to livestock land and intensive commercial scale to small landholder scale (Chumchal et al 2016). In terms of nutrient cycling these water bodies behave functionally differently to drainage waters (as discussed below) and have been suggested as a management strategy to reduce surface N runoff (Siegfried et al 1994, Passy et al 2012).
2.2. Analysis

Data were categorised into four water groups: subsurface drains, surface drains, canals, and farm dams (table 1). To assess significant differences between water groups, means of N₂O, NO₃, and EFs were analysed using a one-way analysis of variance followed by a Tukey post-hoc test \((p < 0.05)\) performed in R version 3.6.3 (R Core Team 2020). N₂O, NO₃, and EF data were log₁₀-transformed prior to analysis after checking for skewness using the skewness function in R package e1071 (v1.7–3; Meyer et al 2019). EFs were converted to a percentage for plotting and represent the percentage of N₂O–N mg l⁻¹ relative to NO₃–N mg l⁻¹ present in the water.

To test the relationship between N₂O and NO₃, a Pearson’s least square regression for linear covariance \((p < 0.05)\), was applied to log₁₀-transformed data and assessed by water group. Models were compared with IPCC predictions by applying EF₅g and EF₅r (0.0060 and 0.0026) to NO₃ data collected in this review, and which assumes a linear increase in N₂O concentrations with increasing NO₃. Other environmental drivers that may be of importance in predicting aquatic N₂O emissions were also tested, given data availability. Variables included dissolved organic carbon (DOC), pH, annual N fertiliser applied, and precipitation.

Finally, artificial waters were compared with natural waters to assess whether artificial waters behave differently as sources of indirect N₂O emissions. Here, N₂O, NO₃, and EF data for natural waters collected in Tian et al (2019), for the 2019 IPCC refinement, were used, and included waters defined as groundwater, streams, rivers, and lakes in agricultural catchments.

3. Results

A total of 52 studies met the selection criteria for artificial waters defined in this review, which included 15 sub-surface drains, 22 surface drains, 11 farm dams, and 4 irrigation canals. Over half of studies were located in Europe, followed by 30% in Eastern to South-Eastern Asia, 13% in North America, and 8% in the Southern Hemisphere (figure S1 (available online at stacks.iop.org/ERL/16/043005/mmedia)). These included land uses such as arable systems which were mostly annual row-crops \((n = 19)\), pasture grazing for dairy and animal production \((n = 18)\), rice \((n = 6)\), irrigated land \((n = 3)\), palm oil plantations \((n = 2)\), and a mix of cropping and pasture \((n = 3)\).

Mean N₂O, NO₃ concentrations, and EFs across all studies ranged 0.27–108 µg N₂O–N l⁻¹, 0.13–57 mg NO₃–N l⁻¹, and 0.005%–4.37%, respectively (table S1, figure 1). In five studies, undersaturated N₂O concentrations relative to atmospheric equilibrium were reported, indicating potential negative emissions (figure 1). Within study variation...
was large, with up to one and two orders of magnitude between the minimum and maximum recorded values for N$_2$O and NO$_3$ concentrations, respectively. The largest variation observed was in drainage water from a heavy clay soil (Dowdell et al 1979), a small irrigation river for rice (Hasegawa et al 2000), and subsurface drainage from an onion field (Sawamoto et al 2003). This variation was attributed primarily to seasonal changes. For EFs, within study variation was as low as 0.04% in agricultural reservoirs holding water for irrigation (Wang et al 2017) and as high as 38% in a spatial survey of farm dams (Webb et al 2019a).

3.1. Differences between water groups
Significant differences between artificial waters were only observed for N$_2$O concentrations (figure 2). Sub-surface drains, surface drains, and farm dams were significantly different from each other with means of 13.04, 6.16, and 1.09 µg N l$^{-1}$, respectively for N$_2$O (table S1). Irrigation canals were significantly different from farm dams and had the highest mean N$_2$O concentration of 29.52 µg N l$^{-1}$, although this value was highly skewed by one high value (108 µg N l$^{-1}$). In contrast to N$_2$O concentrations, NO$_3$ and EFs did not vary significantly with water group. The highest mean NO$_3$ concentration was recorded in a sub-surface drainage site of a vegetable farm, in a region with high annual rainfall (Saitama Prefecture, Japan), while the lowest mean concentration was observed in an artificial lake collecting subsurface and surface drain discharge from dairy farms. In contrast, the sub-surface drainage site with the highest NO$_3$ loading reported the lowest mean EF of 0.005% (Hasegawa et al 2000).

3.2. N$_2$O and EF relationship with NO$_3$
Across all artificial waters, significant linear relationships for both log-transformed N$_2$O concentrations ($R^2 = 0.22$, $p < 0.05$) and EFs ($R^2 = 0.29$, $p < 0.05$) were observed with log-transformed NO$_3$ concentrations (figure 3). The rate of increase in N$_2$O concentrations with increasing NO$_3$ concentration was lower than that predicted by the IPCC EF$_5g$ and EF$_5r$ models (figure 3(A)). EFs demonstrated an inverse relationship with increasing NO$_3$ loading (figure 3(B)). When considering water groups separately, different responses to NO$_3$ were shown (figure S2), with only farm dams found to have a significant positive correlation between N$_2$O and NO$_3$ ($R^2 = 0.79$, $p < 0.05$). Subsurface drains, surface drains, and farm dams all had significant inverse relationships between EF and NO$_3$ (figure S3). Relationships were difficult to assess for irrigation canals due to the lack of observations ($n = 4$).

3.3. Relationships between N$_2$O concentration and other factors
Regression analysis with log-transformed mean N$_2$O concentrations revealed significant relationships with the DOC:NO$_3$ ratio, pH, and annual precipitation (figure S4), although these were limited by the number of studies that reported them. Lower N$_2$O concentrations were observed with either an increase in the DOC:NO$_3$ ratio ($R^2 = 0.2$, $p < 0.05$) or water pH ($R^2 = 0.24$, $p < 0.05$), while a weaker correlation ($R^2 = 0.07$, $p < 0.05$) with annual precipitation.
showed an increase in N₂O with higher precipitation. No significant relationship was found between N₂O concentrations and N inputs from fertilizer and manure.

4. Discussion

Significant differences in N₂O concentrations were observed between artificial waters, yet the large variability in NO₃ concentrations resulted in no distinct difference in EFs (figure 2). Seasonal variability presents a limitation in the current dataset analysis, with some studies reporting temporally resolved means and while others account for spatial variability (e.g. Webb et al 2019a), which could influence the lack of difference observed between some water types here. Given only ~50% of the dataset included seasonal measurements, future studies should examine seasonal impacts on EFs, as water temperatures affects gas dissolution and rainfall/drought events can influence NO₃ and substrate loadings (White et al 2021).

As reported in other studies and in the current dataset, N₂O concentrations do not linearly increase with increasing NO₃ concentration, which is the assumption taken when using stationary EFs for estimating indirect emission. This assumption does not take into account the different conditions that drive rates of N₂O production and consumption within each water type. The significant differences in N₂O but not NO₃ concentrations observed between subsurface drainage, surface channels, and farm dams supports the idea of mechanistic differences in N₂O processes. Here, we summarise the data and current understanding of mechanisms driving N₂O production in each artificial water type explored in this review.

4.1. Subsurface drains

Sub-surface drainage is used to protect soils from waterlogging and manage salinity in agriculture, and in some regions can occur across 80% of the cultivated landscape, often for annual row-crop production and perennial tree crops (Dinnes et al 2002). Sub-surface drains exist in tandem with surface drains as part of an integrated drainage system, including piped drains, field ditches, collection ditches, and an outlet drain. The global extent of subsurface drainage is unknown, however, it occurs in 10%–100% of agricultural soils across European countries and ~25% in Northern America (Herzon and Helenius 2008).

In this review, 15 studies had reported sub-surface drainage N₂O concentration measurements, installed at depths ranging from 0.5 to 1.6 m below the surface. Livestock agriculture was the main land use reported in addition to some mixed arable production. The majority of sites were located in the UK (n = 9), with the remaining from Japan (3), Canada (2), and Denmark (1) (figure S1). In almost all the studies, water was collected at the outlet of the subsurface drainage systems and, as a result, likely underestimated the true EF value due to rapid degassing of N₂O. This is one of the major limitations of sampling subsurface field drainage and requires consideration in future measurements (Roper et al 2013).

The mean EF of 0.52% for subsurface drains was significantly higher than other artificial water groups, and is comparable to the IPCC EF₅g recommendation of 0.60% for groundwater and drainage waters. The
higher \( \text{N}_2\text{O} \) concentrations observed within subsurface drains may be attributed to a number of factors (figure 2). Firstly, the key difference between these artificial waters with the others reviewed here is their lack of exposure to the open atmosphere, which regulates the rate of \( \text{N}_2\text{O} \) evolution from the water surface. Additionally, in situ production and consumption of \( \text{N}_2\text{O} \) is limited due to both the rapid delivery of drainage water once field water enters the drainage system and lack of bottom substrate to support microbial activity. If tile drains do develop any biofilm area, short water residence times may preclude any significant \( \text{NO}_3\text{-N} \) removal. Furthermore, supersaturated \( \text{N}_2\text{O} \) concentrations almost certainly originate from the same water source as shallow groundwater: leached soil pore water (Dowdell et al 1979). Therefore, subsurface drainage likely represents more of a passive pipe system, transporting dissolved \( \text{N}_2\text{O} \) produced in soil with little outgassing until water reaches a drainage outlet.

\( \text{N}_2\text{O} \) concentrations in subsurface drains are more closely linked to terrestrial characteristics, including soil type, land use and fertilizer practices. A UK study of an intensive arable catchment found that soil texture significantly influenced \( \text{N}_2\text{O} \) concentrations and the relationship with other water quality parameters in a subsurface field drain (Hama-Aziz et al 2017). Soils with poor drainage may provide more favourable conditions for \( \text{N}_2\text{O} \) production through increased anoxia and contact with the soil matrix (Hénault et al 2012, Jamali et al 2016), allowing for more \( \text{N}_2\text{O} \) to dissolve into leached soil water. The strong link with terrestrial \( \text{N} \) cycling processes is further supported by various studies demonstrating how subsurface drainage design can significantly influence soil \( \text{N} \) attenuation and direct \( \text{N}_2\text{O} \) emissions (Clagnan et al 2018).

### 4.2. Surface drains

Globally, artificial drainage exists in 130–200 million ha of cropland worldwide, and is increasing in extent and intensity (Schultz and De Wrachien 2002, Castellano et al 2019). Surface drains are part of the greater artificial drainage system, often co-existing with subsurface drains, yet are responsible for delivering eutrophying nutrients to natural aquatic and coastal ecosystems (Blann et al 2009). Here, 22 studies reported \( \text{N}_2\text{O}-\text{N}/\text{NO}_3\text{-N} \) concentration and EFs in surface drains, with water depths ranging from 0.06 to 0.6 m. Mixed arable production was the predominant land use followed by livestock, rice, and a palm oil plantation (supplementary data 1). Around 50% of studies were located in the UK, with others distributed across Europe, China, Japan, Indonesia, US, and New Zealand (figure S1). Mean EF was 0.46% (0.02%–4.37%), which is lower than the IPCC EF\textsubscript{3g} recommendation of 0.60% for groundwater and drainage waters.

Drain position and location within the network are likely important variables to consider when estimating \( \text{N}_2\text{O} \) EFs. Surface drains had significantly lower \( \text{N}_2\text{O} \) concentrations compared to subsurface drains, which supports observations in studies measuring surface drains and tile drains in connected artificial drainage systems (Sawamoto et al 2002, Reay et al 2004a). Variable physical gas transfer, discharge rate, dilution effects, and distance from point sources can substantially influence within-drain \( \text{N}_2\text{O} \) variability (Sawamoto et al 2002, Reay et al 2004a, Premaratne et al 2017). For example, open surface drains can support large atmospheric \( \text{N}_2\text{O} \) losses during the transport of field water, with dissolved \( \text{N}_2\text{O} \) reductions up to 80% (Reay et al 2003, 2004b). This is a result of the relatively high gas transfer velocity generated by field drain outfalls, weirs, and changes in discharge velocity based on the size or shape of a drain. As such, large changes in \( \text{N}_2\text{O} \) concentrations relative to \( \text{NO}_3\text{-N} \) concentrations can occur over small spatial scales which leads to large variability in EFs.

Adding to their complexity, some surface drains may receive water from a variety of land uses and sources, or have a more established benthic structure or vegetation environment dependent on stream hierarchy and channel morphology. Headwater agricultural channels can have exponentially higher \( \text{N}_2\text{O} \) emissions than higher-order waterways due to higher \( \text{N} \) loading, higher \( \text{N} \) processing rates, and less water volume dilution effects (Turner et al 2015). Headwater channels typically receive substantial sediment yields from agricultural fields, resulting in sediment storage with accumulation rates as high as \( \sim 90 \text{ kg m}^{-2} \text{ yr}^{-1} \) (Lecce et al 2006). This benthic environment can help attenuate agricultural nutrient loads through denitrification at the sediment-water interface, subsequently removing \( \text{NO}_3\text{-N} \) from the water column (Veraart et al 2017). The current assumption for these drainage systems within the IPCC EF\textsubscript{3g} model is that \( \text{NO}_3\text{-N} \) and \( \text{N}_2\text{O} \) are sourced from groundwater with little in-stream nitrification–denitrification. However, studies have shown strong denitrification activity in drainage ditches across a variety of land use and soil types (Veraart et al 2017, Soana et al 2019).

### 4.3. Irrigation canals

Globally, irrigation covers an area of over 300 million ha, which has doubled in the last 50 years and is expected to expand in developing countries (Schultz and De Wrachien 2002, Neumann et al 2011). Irrigation farming systems have some of the largest agricultural \( \text{N} \) losses from hydrological pathways, up to 46%–76% of total \( \text{N} \) applied to fields (Thorburn et al 2011, Perego et al 2012). Therefore, there is a need to characterise \( \text{N}_2\text{O} \) emissions from these dynamic systems, however, findings from this review reveal a severe lack of empirical data in this area.
Of the artificial waters collected in this review, only four recorded dissolved \( \text{N}_2\text{O} \) measurements within irrigation waters (table S1). The studies were distributed in the lower latitude regions including Japan, Australia, and Mexico where cotton, rice, and mixed livestock-rice were the main production types. Reported water depths ranged from 0.03 to 1 m. Irrigated farming systems are most prominent in semi-arid regions, with two thirds located in Asia (Molden 2007). Irrigation canals had a mean EF of 0.65% (0.03%–1.33%), which is comparable to the IPCC \( \text{EF}_{29} \) recommendation of 0.60%.

However, with such a limited number of studies, it remains difficult to draw conclusions on the difference in \( \text{N}_2\text{O} \) production from irrigation waters with other artificial waters. A large \( \text{N}_2\text{O} \) concentration range of 1.6–108 µg N l\(^{-1}\) in canals led to no significant difference when compared to subsurface and surface drains (figure 2). Although not shown here, irrigation canals have some key functional differences with surface drainage channels that may give rise to different \( \text{N}_2\text{O} \) emission estimates if the database for these systems increases. Field runoff collected by canals is largely driven by irrigation events rather than rainfall (Harrison et al. 2005). Further, irrigation canals can sometimes be free of both macrobenthic organisms and benthic macrophytes due to regular maintenance and concrete construction in some high value farming regions (Kitamura and Nakaya 2010). Finally, many on-farm irrigation canals undergo regular wetting and drying cycles with the irrigation regime, or remain flooded but have highly fluctuating water tables, which exposes bottom sediments or channel banks to the atmosphere. The indirect \( \text{N}_2\text{O} \) emissions released from the exposed sediment phase remains an area needing further investigation (Schwenke et al. 2020).

The timing and length of irrigation events control the supply of N from soils to the irrigation water and this will influence \( \text{N}_2\text{O} \) levels within irrigation canals collecting irrigation drainage. For example, an Australian cotton farm irrigation study speculated that low \( \text{N}_2\text{O} \) concentrations and EFs observed within the on-farm irrigation channels were due to a soil water deficit in preceding irrigation events and the short surface water application time (Macdonald et al. 2016). In addition, field water contact with groundwater may further alter the ratio of \( \text{N}_2\text{O} \) to \( \text{N}_2 \). Comparing two opposing studies reporting either no groundwater contact (Macdonald et al. 2016) or contact with groundwater (Hasegawa et al. 2000), the mean EF is two orders of magnitude higher in the groundwater-fed irrigation system. The mixed livestock and rice farm in Japan was an extreme case in terms of \( \text{N}_2\text{O} \) concentrations (7–407 µg \( \text{N}_2\text{O} \cdot \text{N} \cdot \text{l}^{-1} \)) within the irrigation group. In this case, high \( \text{NO}_3 \) groundwater from stock breeding areas flowed from altitude into rice paddies with high organic matter and fertiliser N inputs, which stimulated excessive \( \text{N}_2\text{O} \) production via denitrification in the receiving irrigation canal (Hasegawa et al. 2000).

### 4.4. Farm dams
On-farm dams are ubiquitous within the agricultural landscape, with several million across the globe used for water supply, irrigation, runoff control, and wastewater management (Verstraeten and Poesen 2000). They are highly abundant in agricultural regions within China, the North American Great Plains, and Australia, where densities often exceed 5 per km\(^2\) (Renwick et al. 2006, Grinham et al. 2018, Chen et al. 2019). Although agricultural dams have come into widespread existence since the 1940s (Renwick et al. 2006), research into the role of these small artificial lentic systems in GHG cycles has only very recently materialized (Grinham et al. 2018, Ollivier et al. 2019, Webb et al. 2019b). Here, 11 studies with \( \text{N}_2\text{O} \) concentration measurements were collected. Water depth ranged from 0.18 to 5.1 m and land use included irrigated crops, mixed arable, rice, pastures, and palm oil plantations. Studies were distributed across China, Australia, UK, France, Canada, and Indonesia (figure S1). Overall, a mean EF of 0.13% (0.04%–0.46%) was found, which is half the IPCC \( \text{EF}_{29} \) estimate of 0.26% for which these systems are included. Instead, the agricultural pond EF found here is comparable to the EF for lakes, ponds, and reservoirs of 0.12% found in a previous review for the refinement of IPCC guidelines (Tian et al. 2019). However, despite a significantly lower EF estimate compared to rivers (0.30%), lakes, ponds, and reservoirs were not assigned their own EF in the current IPCC \( \text{EF}_{29} \) guidelines.

In terms of \( \text{N}_2\text{O} \) concentrations, farm dams were significantly lower than all other artificial waters reviewed here (figure 2), reflecting findings found from a limited number of studies comparing different surface waters (Outram and Hiscock 2012, Xia et al. 2013, Xiao et al. 2019). Farm dams also had the only significant relationship with \( \text{NO}_3 \) out of the artificial waters (figure S2), where \( \text{N}_2\text{O} \) increased on a logarithmic scale with increasing \( \text{NO}_3 \), suggesting a closer alignment to steady state N processing conditions. These differences may be because farm dams are less hydrologically dynamic compared with drainage water bodies due to their role in water storage. Higher water residence times allow for more time for runoff N to be transformed into \( \text{N}_2\text{O} \), \( \text{NO}_3 \) or \( \text{N}_2 \) and can even be favourable for \( \text{N}_2\text{O} \) consumption processes (Webb et al. 2019a). For example, the development of strong thermoclines under steady hydrological conditions has been shown to be a strong influencing factor in supporting dissolved \( \text{N}_2\text{O} \) undersaturation (Webb et al. 2019a). Farm dams also have a lower gas transfer velocity compared to channels (Premaratne et al. 2017, Ollivier et al. 2019, Webb et al. 2019a), leading to slower gas exchange between the water–atmosphere surface and potentially less.
discrepancy between changes in N\textsubscript{2}O and NO\textsubscript{3} concentrations.

Introducing on-farm dams into intensive agricultural landscapes, especially those with a high density of tile drainage, may provide a measure to reduce potential N\textsubscript{2}O emissions further downstream. The strong reductive conditions enhanced due to low water velocity enables ponds to remove greater amounts of N than streams (Li et al. 2013, Garnier et al. 2014). This supports their ability to receive high inorganic N loads without the consequence of producing proportional N\textsubscript{2}O emissions (Webb et al. 2019a). The high density of streams and ponds scattered within the rice–paddy-dominated watersheds, characteristic of China, is an example of where high N input does not always lead to high N concentrations in the surface water (Xia et al. 2013, Xiong et al. 2015). Further, a study of the Orgeval watershed in France explored the role of pond implementation in drainage areas and predicted a 34%–47% reduction in surface water N export (Passy et al. 2012).

4.5. Low EF in waters with high N loading

Regression analysis between mean N\textsubscript{2}O concentrations and NO\textsubscript{3} concentrations revealed a significant positive-logarithmic rather than a linear response, and that in most cases EF\textsubscript{3g}\textsubscript{N} and EF\textsubscript{3r} models overestimated N\textsubscript{2}O concentrations for artificial waters (figure 3(A)). A stronger relationship between NO\textsubscript{3} and EF was found where EF scales inversely with higher NO\textsubscript{3} (figure 3(B)). This relationship was consistent across subsurface drains, surface drains, and farm dams (figure S3), and suggests that N\textsubscript{2}O emissions in most artificial waters are overestimated using standard EF\textsubscript{3} modelling. Non-linearity in the N\textsubscript{2}O concentration to NO\textsubscript{3} response has been observed in rivers, implying a limit on NO\textsubscript{3} processing and subsequent N\textsubscript{2}O production (Turner et al. 2016, Wang et al. 2018). Moving away from stationary EFs and developing a model that accounts for the inverse scaling of EF with higher N loading will greatly reduce N\textsubscript{2}O emission uncertainties from highly N polluted agricultural waters.

This pattern of lower N\textsubscript{2}O production with increasing NO\textsubscript{3} loading is consistent with data from previous studies, although the processes driving this trend remains unclear. In agricultural watersheds receiving high N loads, less N\textsubscript{2}O may be produced relative to NO\textsubscript{3} due to biological saturation (Mulholland et al. 2008, Beaulieu et al. 2011, Xiao et al. 2019). Alternatively, undersaturation of dissolved N\textsubscript{2}O in the presence of high NO\textsubscript{3} can occur if the right reductive conditions exist to facilitate complete denitrification, as seen in farm dams in Canada (Webb et al. 2019a). Furthermore, in open water systems any N\textsubscript{2}O produced in excess of atmospheric equilibrium will degas into the atmosphere more rapidly than microbial NO\textsubscript{3} transformations. If much of the N\textsubscript{2}O has already degassed, then discrepancies in the EF\textsubscript{3} method that derives ratios between actual measured fluxes of N\textsubscript{2}O and NO\textsubscript{3} versus dissolved concentrations will arise (Clough et al. 2006).

4.6. Artificial and natural waters in emission factor groups

To determine if artificial waters deserve recognition separate to natural waters for indirect N\textsubscript{2}O emission accounting, we compared N\textsubscript{2}O concentrations, NO\textsubscript{3}, and EFs from artificial waters collected in this study with natural waters contributing to the current EF\textsubscript{3g} and EF\textsubscript{3r} models. In this analysis, irrigation canals were included with the surface drainage group, renamed to surface channels, due to the small number of studies and the fact that no significance difference was detected in previous analyses (figure 2). Natural waters were divided into groundwater, lakes, rivers, and streams as defined in Tian et al. (2019). Despite finding significant differences in N\textsubscript{2}O concentrations, findings revealed no significant differences in EFs between artificial and natural waters (figure 4). This suggests that delineation of water groups into artificial and natural waters is unlikely to improve EF uncertainty within the current IPCC framework for assigning default EFs.

Mean N\textsubscript{2}O concentrations in farm dams were not significantly different between lakes, rivers, and streams, yet surface channels were significantly different to groundwater. Notable differences governing N\textsubscript{2}O concentrations in response to N loadings from artificial systems compared to natural waters have been found within agricultural watersheds. This included river N\textsubscript{2}O dynamics being more affected by heavy rainfall events than rice paddy ponds (Xiao et al. 2019), and differences in redox conditions and wind turbulence affecting N\textsubscript{2}O production between ditches and a river (Outram and Hiscock 2012). In contrast, both N\textsubscript{2}O and NO\textsubscript{3} concentrations for subsurface drainage were comparable to groundwater (figure 4), supporting the assumption that leached soil pore water is the primary source of supersaturated N\textsubscript{2}O in both waters (Well et al. 2005). On this basis, the IPCC EF grouping for EF\textsubscript{3g} is likely correct to include groundwater and subsurface drainage together, but not open water surface drainage (figure 4).

4.7. Limitations and future research

A number of competing factors that alter N\textsubscript{2}O and NO\textsubscript{3} concentrations, either separately or collectively, complicates the assumed linear response when estimating N\textsubscript{2}O emissions using default EFs. Some of these factors are more apparent in different artificial waters, such as higher gaseous losses in surface channels and where there is a greater capacity for N\textsubscript{2}O consumption, such as farm dams. As others have proven, a process-based model instead of revising default EFs will likely lead to the most noticeable improvements in estimating indirect aquatic N\textsubscript{2}O emissions.
of the environmental variables have been found to drive N$_2$O concentrations in artificial waters, including the DOC:NO$_3$ ratio, pH, fertilizer application, and precipitation, were tested across a subset of the artificial waters collected in this review (figure S4). The N$_2$O concentration was inversely related to both DOC:NO$_3$ and pH, while annual precipitation was less strong as a predictor and no relationship was found with total N application. Variables such as DOC and pH are often found to be strong drivers of aquatic N$_2$O dynamics, as at higher values they can represent conditions more favourable to microbial N reduction (Peacock et al 2017, Audet et al 2020). However, values for these factors could only be derived from 30% to 40% of studies reviewed here.

The large range in EFs within groups contributes to major uncertainty when applying default values to local sites. Grouping artificial waters into their respective groups also revealed a large range in EF, as well as a highly skewed distribution in N$_2$O, NO$_3$, and EF data (figure S5). Bias can arise when upsampling emissions using the mean statistic when the mean and median of a dataset are distinctly different, such as in surface drains with a mean and median EF of 0.46% and 0.11%, respectively (table S1). As discussed by others, care must be taken when extrapolating means derived from a skewed dataset to estimate GHG emissions (Grinham et al 2018; Rosentreter and Williamson 2020). Due to the low number of observations and geographical bias of studies collected here, the N$_2$O, NO$_3$, and EF datasets are unlikely to represent the ‘real-world’ distribution. In fact, ~50% of studies were located in the UK, which represents a notable limitation and a potentially sizeable source of error when extrapolating EFs globally. The choice of the arithmetic mean statistic in these cases may not provide a representative estimate for local-scale N$_2$O emissions and may explain why the IPCC default EFs are often found to be overestimated.

Default EFs that rely on the mass ratio of N$_2$O to NO$_3$ concentrations are also complicated by kinetic limitations introduced by variable gas exchange rates and water residence times across different water types. Open drains in particular represent complex aquatic systems for constraining N$_2$O emissions due to their dynamic hydrology and variable design. Where rapid gaseous N$_2$O losses occur within a water body, the N$_2$O:NO$_3$ ratio will be smaller as the biological processes consuming NO$_3$ operate at a slower time scale than physical evasion to the atmosphere. Additionally, water residence time introduces a hydrological constraint on the extent of in-system N transformations (Maavara et al 2019). Together, the physical constraints from gas transfer and hydrologic exchange result in a variable N$_2$O–N/NO$_3$–N concentration ratio that alters biological processing rates across different water types.

The IPCC provides two different methods for calculating indirect N$_2$O EFs, as presented in the
introduction, and it is important to be aware of the different EF values these two methods may produce. There can be large discrepancy between EFs estimated from mass N-fluxes and EFs estimated from N-concentrations ratios (as reviewed here), as reported in Clough et al. (2006) and Outram and Hiscock (2012), whereas at other times the two methods yield similar estimates (e.g. Hama-Aziz et al. 2017, Premaratne et al. 2017). In the few studies that reported EFs derived from both methods, or provided detailed information to allow the calculation, differences in the average EF ratio ranged from 0.00003 to 0.0469 in surface drainage systems and 0.0001 to 0.003 in subsurface drainage (supplementary table S3). Often, N₂O fluxes were calculated using gas exchange models, which can be a large source of uncertainty if not produced specifically for the local water system. Development of models for calculating gas transfer velocity across specific artificial water types will advance the field by enabling standardised emissions upscaling of dissolved N₂O concentrations. Some progress has been made by recent studies in this area, which report gas transfer coefficients of 3.8–6.6 m⁻¹ for surface drains (Premaratne et al. 2017) and 1–1.64 m⁻¹ for on-farm dams (Ollivier et al. 2019, Webb et al. 2019).

A hybrid modelling approach that integrates the biological and chemical controls of N₂O process rates with hydromorphological properties (e.g. Marzadri et al. 2020) of artificial waters, including their type, area, water residence time, and distance from farm fields or runoff source, is likely required to capture the complexity of these systems. However, until these local-scale processes for artificial waters can be upscaled in modelling efforts, scaling EFs with NO₃ loading may prove to be a promising first step to move away from the default EF approach. Significant inverse correlations were found across all water groups (excluding irrigation canals) between EF and NO₃, while only farm dams revealed NO₃ to be a significant driver of N₂O (figure S3). To develop this concept further, future research should explore N₂O production thresholds within high NO₃ environments to better understand the conditions that lead to the inverse EF to NO₃ relationship. Some studies have started progressing this area, by investigating denitrification rates/changes in ditches receiving greater NO₃ inputs (Veraart et al. 2017, She et al. 2018), and looking at stratification in farm dams supporting N₂O consumption under high NO₃ conditions (Webb et al. 2019a). Another variable worth investigating is the DOC/NO₃ ratio, which we also found to be a significant inverse driver of N₂O in artificial waters, as DOC/NO₃ can be a proxy for N limitation within aquatic ecosystems (Peacock et al. 2017).

Finally, it is difficult to assess the relative impact of artificial waters on regional and global indirect N₂O emissions until a database exists on the area and distribution these systems cover. The recent revised quantification of global N₂O sources and sinks attributes 0.5 Tg N yr⁻¹ to indirect anthropogenic emissions from streams, rivers, lakes, reservoirs (>0.1 km²), and estuaries, which is equivalent to 13% of total direct agricultural N₂O emissions. However, this estimate does not include small artificial waters. This gap presents an opportunity to refine the contribution of anthropogenic N₂O emissions in total global land emissions, where an estimated discrepancy of ∼1.8 Tg N yr⁻¹ exists between bottom-up and top-down land models (Tian et al. 2020). Explicitly including artificial waters in models for budget quantification will likely make a significant contribution to the agricultural N₂O budget in regions where artificial waterbodies have been densely created, such as the irrigation networks in the Mediterranean region of Spain and irrigation ponds in southern China (Aguilera et al. 2019, Chen et al. 2019). Development of national inventories are already underway in some regions (Aguilera et al. 2019, Malerba et al. 2021), yet a collective country-by-country effort is needed to quantify the global extent.

5. Conclusion

Our analysis of the available literature suggests that subsurface drains, surface drains, and on-farm dams function differently in terms of surface water N₂O production, while more studies are urgently needed to assess the role of irrigation canals. Studies showed that EFs vary largely in space and time within surface waters, which hinders detection of differences between artificial waters. The huge variability of EFs within water groups challenges the concept that N₂O production in downstream waters is proportional to agricultural NO₃ load. The current IPCC methodology using generalised EFs overestimates indirect N₂O production in waters receiving high NO₃ loading; a characteristic of many artificial waters. In fact, in these systems EFs scale downward with increasing N load. Improving the prediction of indirect N₂O emissions from agricultural surface waters likely requires a move away from stationary EFs and explicit inclusion of different artificial waters. On a global scale, the lack of accounting for artificial waters in the most recent global N₂O budget presents a significant gap in the quantification of indirect agricultural N₂O emissions from aquatic systems (Tian et al. 2020). As such, we suggest a need for a global database on the size, density, and distribution of artificial waters in agricultural landscapes, as well as a need to expand the global artificial waters N₂O dataset beyond the UK. Further, future field measurements should target different artificial waters across major agricultural industries to advance the biogeochemical understanding to the level that has been achieved for rivers and lakes (Lauerwald et al. 2019, Maavara et al. 2019).
Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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