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Widespread nitrous oxide undersaturation in farm waterbodies creates an unexpected greenhouse gas sink

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Nitrogen pollution and global eutrophication are predicted to increase nitrous oxide (\textsubscript{N}2\textsubscript{O}) emissions from freshwater ecosystems. Surface waters within agricultural landscapes experience the full impact of these pressures and can contribute substantially to total landscape \textsubscript{N}2\textsubscript{O} emissions. However, \textsubscript{N}2\textsubscript{O} measurements to date have focused on flowing waters. Small artificial waterbodies remain greatly understudied in the context of agricultural \textsubscript{N}2\textsubscript{O} emissions. This study provides a regional analysis of \textsubscript{N}2\textsubscript{O} measurements in small (<0.01 km\textsuperscript{2}) artificial reservoirs, of which an estimated 16 million exist globally. We show that 67% of reservoirs were \textsubscript{N}2\textsubscript{O} sinks (−12 to −2 \textmu m\textsubscript{ol} \textsubscript{N}2\textsubscript{O} m\textsuperscript{−2} d\textsuperscript{−1}) in Canada’s largest agricultural area, despite their highly eutrophic status (99 ± 289 \textmu g L\textsuperscript{−1} chlorophyll-a (Chl-a)). Generalized additive models indicated that in situ \textsubscript{N}2\textsubscript{O} concentrations were strongly and nonlinearly related to stratification strength and dissolved inorganic nitrogen content, with the lowest \textsubscript{N}2\textsubscript{O} levels under conditions of strong water column stability and high algal biomass. Predicted fluxes from previously published models based on lakes, reservoirs, and agricultural waters overestimated measured fluxes on average by 7- to 33-fold, challenging the widely held view that eutrophic N-enriched waters are sources of \textsubscript{N}2\textsubscript{O}. Nitrous oxide | agriculture | farm reservoirs | impoundments | greenhouse gases

Freshwater ecosystems are regarded as globally significant sources of nitrous oxide (\textsubscript{N}2\textsubscript{O}). Global emissions from rivers are estimated at 0.68 Tg \textsubscript{N}2\textsubscript{O}-N y\textsuperscript{−1}, while lakes and reservoirs contribute an additional ∼0.3 Tg \textsubscript{N}2\textsubscript{O}-N y\textsuperscript{−1} (1, 2). Combined, inland freshwaters may represent ∼15% of anthropogenic \textsubscript{N}2\textsubscript{O} emissions, although the global \textsubscript{N}2\textsubscript{O} budget has yet to include standing water bodies such as lakes, reservoirs, and wetlands (3). Current \textsubscript{N}2\textsubscript{O} emission estimates from lentic systems are limited by a lack of data, with only 309 global published reports of \textsubscript{N}2\textsubscript{O} measurements relative to 7,824 and 561 for CO\textsubscript{2} and CH\textsubscript{4}, respectively (2). Uncertainty in \textsubscript{N}2\textsubscript{O} levels in lentic systems is further exacerbated by a geographical bias in \textsubscript{N}2\textsubscript{O} measurements (4), the highly variable nature of freshwater \textsubscript{N}2\textsubscript{O} fluxes across temporal and spatial scales (5–7), and incomplete understanding of the drivers of \textsubscript{N}2\textsubscript{O} uptake at the freshwater surface (3).

Net flux of \textsubscript{N}2\textsubscript{O} from standing waters may be strongly affected by eutrophication, particularly with inorganic nitrogen (N) (8). Some of the highest \textsubscript{N}2\textsubscript{O} emission rates have been reported in agricultural drainage waters that receive excess N in runoff from manure and crop fertilizers (9–11). Drains, streams, and rivers within agricultural catchments can contribute from 4% to 45% of total landscape \textsubscript{N}2\textsubscript{O} emissions (12–14), indicative of a potentially important role for other agricultural waters in \textsubscript{N}2\textsubscript{O} emissions. Critically, landscape mass-balance models predict that nitrous oxide emissions from surface waters will nearly double with the forecast increases in N use and eutrophication (2, 15).

Agricultural landscapes contain large numbers of natural ponds, wetlands, and small constructed waterbodies (hereafter reservoirs). An estimated 16 million small (<0.01 km\textsuperscript{2}) artificial reservoirs exist globally (16), yet \textsubscript{N}2\textsubscript{O} data for these systems are lacking (2.6% of synthesized global lentic \textsubscript{N}2\textsubscript{O} measurements) (2). Many of these small systems are situated directly in agricultural catchments (17) and have proved to be of critical importance to landscape N cycling. For example, those sized between 0.001 and 0.1 km\textsuperscript{2} represent ∼25% of global lake and reservoir N removal from watersheds (18). Small farm water bodies also have a disproportionate influence on carbon cycling and CO\textsubscript{2} and CH\textsubscript{4} emissions (19, 20), yet their contribution to \textsubscript{N}2\textsubscript{O} emissions remains to be established. Constraining all \textsubscript{N}2\textsubscript{O} fluxes in agricultural systems is important given that terrestrial \textsubscript{N}2\textsubscript{O} emissions can offset >100% of CO\textsubscript{2} uptake associated with enhanced primary production in agriculture (21). Since agricultural reservoirs tend to be N rich and because elevated N influx favors \textsubscript{N}2\textsubscript{O} production, the omission of agricultural reservoirs may represent a key gap in global \textsubscript{N}2\textsubscript{O} budgets and greenhouse gas inventories.

To address these shortcomings, we provide an estimate of \textsubscript{N}2\textsubscript{O} concentrations in small agricultural reservoirs in one of the world’s largest agricultural regions, the Northern Great Plains of Nebraska, where agricultural reservoirs are highly concentrated. Data deposition: The data generated in this study are freely available on GitHub (https://github.com/simpson-lab/dugout-n2o) and Zenodo (DOI: 10.5281/zenodo.2636099).

Author contributions: J.R.W., G.L.S., P.R.L., and K.F. designed research; J.R.W. performed research; H.M.B. contributed new reagents/analytic tools; J.R.W. and N.M.H. analyzed data; J.R.W. wrote the paper; N.M.H., P.R.L., H.M.B., and K.F. contributed ideas; and G.L.S. developed models. The authors declare no conflict of interest. This article is a PNAS Direct Submission. This open access article is distributed under Creative Commons Attribution License 4.0 (CC BY).

Significance

Inland water bodies are currently considered to be nitrous oxide (\textsubscript{N}2\textsubscript{O}) sources to the atmosphere, based on limited studies on large lakes and reservoirs. However, emissions from small artificial waterbodies, such as farm reservoirs, are currently unaccounted for in global models. We present a regional-scale study of \textsubscript{N}2\textsubscript{O} in farm reservoirs and demonstrate that the majority of these waterbodies act as \textsubscript{N}2\textsubscript{O} sinks. Our findings contradict previously held assumptions that nitrogen-enriched and eutrophic surface waters within agricultural landscapes are strong sources of \textsubscript{N}2\textsubscript{O}. The underlying physical and chemical properties driving regional \textsubscript{N}2\textsubscript{O} consumption may be representative of another 16 million small artificial reservoirs that exist globally, potentially reducing their overall greenhouse gas impact.

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North America. Analysis of 101 small artificial waterbodies showed that the majority of farm reservoirs were atmospheric sinks of N\textsubscript{2}O, with 67% of all sites distinctly undersaturated despite mostly eutrophic waters which were rich in dissolved inorganic N. These findings suggest a need to reevaluate our mechanistic understanding of controls on N\textsubscript{2}O in lentic waters and indicate that farm reservoirs may provide a means of minimizing greenhouse gas (GHG) emissions in agricultural grasslands.

Results and Discussion

Nitrous oxide concentrations spanned three orders of magnitude (1.14–110 nM), with a median of 6.55 nM across all surveyed sites (SI Appendix, Table S1). Considering the average uncertainty in N\textsubscript{2}O samples (σ = 1.25 nM), 67% were undersaturated, 21% were supersaturated, and 12% were in relative equilibrium with the atmosphere (~8.83 nM). These agricultural reservoirs were usually eutrophic, nutrient-rich waterbodies, with concentrations of total dissolved nitrogen (TDN) (417–14,280 μg N L\textsuperscript{-1}), dissolved inorganic nitrogen (DIN) (32–7,688 μg N L\textsuperscript{-1}), and chlorophyll-\textalpha{} (Chl-\textalpha{}) (2.2–2,484 μg L\textsuperscript{-1}) varying two to three orders of magnitude. Average reservoir TDN (3,082 μg N L\textsuperscript{-1}) and phytoplankton abundance (Chl-\textalpha{}, 99 μg L\textsuperscript{-1}) greatly exceeded global averages (~800 μg N L\textsuperscript{-1} and ~20 μg L\textsuperscript{-1}, respectively) observed in prior N\textsubscript{2}O studies of lakes and reservoirs (2, 4). As such, these reservoirs represent some of the most nutrient-rich and eutrophic systems where N\textsubscript{2}O measurements have been carried out and challenge the assumption that N-enriched surface waters are potent N\textsubscript{2}O sources (4, 8).

Reservoir N\textsubscript{2}O concentrations are the result of complex interactions among potential pathways of N\textsubscript{2}O production and consumption (Fig. 1). To evaluate the potential importance of controls on reservoir N\textsubscript{2}O concentrations, we assessed the relationship between dissolved gas concentrations and common environmental variables known to influence N\textsubscript{2}O. Predictor variables included surface- and bottom-water O saturation, pH, ratios of TDN to soluble reactive phosphorous (SRP), Chl-\textalpha{}, sediment C:N ratio, maximum buoyancy frequency (BF), and DIN concentration. As previous studies have demonstrated that simple linear regressions are often inadequate for predicting freshwater N\textsubscript{2}O concentrations and fluxes (5, 22), we used generalized additive models (GAMs) capable of modeling nonlinear and nonmonotonic relationships to quantitatively assess the effect of environmental conditions and develop a predictive model for our reservoir N\textsubscript{2}O concentrations (Materials and Methods).

Analysis with GAMs showed that N\textsubscript{2}O concentrations were predicted well by a combination of maximum buoyancy frequency and dissolved inorganic nitrogen (P < 0.001), surface dissolved oxygen levels (P < 0.05), and Chl-\textalpha{} content (P < 0.05) but not by other measured parameters (SI Appendix, Table S2). The use of a GAM allowed us to detect nonuniform trends in predictor variables, resulting in a model that explained ~85% of deviance in N\textsubscript{2}O concentrations (SI Appendix, Table S2). The lowest N\textsubscript{2}O concentrations occurred under strongly stratified conditions and during periods of high phytoplankton abundance and primary productivity (Fig. 2). Elevated DIN content boosted N\textsubscript{2}O concentrations only when reservoirs were unstratified (BF = 0 s\textsuperscript{-2}) or weakly stratified (BF = 0.01 s\textsuperscript{-2}) (Fig. 2A).

Our finding demonstrates that elevated DIN content does not invariably result in supersaturation of water-column N\textsubscript{2}O in small reservoirs and depends instead on the degree of water-column stratification. Strong stratification influenced the degree of N\textsubscript{2}O undersaturation across low to high DIN concentrations, with elevated N\textsubscript{2}O levels only in reservoirs that had high DIN and lacked strong stratification (Fig. 2A). This interactive effect suggests that denitrification, a two-step process capable of both producing and consuming N\textsubscript{2}O, is switching between production and consumption below the thermocline (Fig. 1). First, weak stratification may allow for a more spatially variable oxic–anoxic interface in response to diurnal heating and cooling cycles. This enhanced interaction between reduced and oxidized solutes can support coupled nitrification–denitrification under the presence of high DIN (Fig. 1) (23, 24). Second, strong and persistent stratification often promotes N\textsubscript{2}O undersaturation via complete denitrification in hypolimnetic waters that exhibit persistently low O\textsubscript{2} (23, 25). Alternately, strong stratification may physically limit transfer between the epilimnion and the hypolimnion (25). However, epilimnetic N\textsubscript{2}O consumption is rarely observed in lakes (26) and the precise mechanism remains unknown.

The significant negative response of N\textsubscript{2}O to O\textsubscript{2} supersaturation and elevated Chl-\textalpha{} concentrations may indicate a degree of nutrient competition between primary producers and N\textsubscript{2}O-producing microorganisms in the epilimnion (Fig. 2 B and C) as well as nutrient productivity (Fig. 2D) and DIN consumption (Table 1) are limiting any N\textsubscript{2}O production via nitrification, a process that is constrained to the surface layer where oxic conditions prevail (Fig. 1). The negative effect of increasing surface DO above saturation also supports this theory of competition, although the highest levels of DO saturation did not correlate with the highest algal abundance. Dissolved O\textsubscript{2} can fluctuate greatly over shorter time scales and may represent alternate controlling processes. A diel effect of O\textsubscript{2} on N\textsubscript{2}O levels has been observed in previous freshwater studies, where lower concentrations coincide with DO peaks (22, 28), although N\textsubscript{2}O remains supersaturated in that research. Thus, the mechanisms linking low N\textsubscript{2}O content to O\textsubscript{2} supersaturation in our reservoirs remain unexplained and require further research.

Evidence of N\textsubscript{2}O consumption has been reported in some other small productive lentic systems and has been attributed to limiting N conditions which support complete denitrification (29, 30). For example, ponds used for microalga cultivation (29) experience N\textsubscript{2}O undersaturation as NO\textsubscript{2} becomes limiting (Fig. 3), while small, strongly stratified, hypereutrophic lakes exhibit only trace N\textsubscript{2}O concentrations below the thermocline (30). The observation of strong N\textsubscript{2}O consumption below the stratified layer in the column supports our findings for a primary role of water-column stratification as a regulator of N\textsubscript{2}O processes and concentration gradients. If N\textsubscript{2}O consumption is occurring below the thermocline, then a diffusion gradient of N\textsubscript{2}O between the epilimnion and the hypolimnion can be strong enough to deplete...
N$_2$O in the surface layer (30, 31). Further research into how the physical and biological controls interact to support or limit mechanisms of N$_2$O consumption in small, N-enriched waters is required.

Complex interactions between stratification intensity and N content may help explain inconclusive relationships between eutrophication, nutrient status, and N$_2$O emissions seen elsewhere (25–28). In other small lentic systems, high N$_2$O concentrations have been found to be elevated NO$_x$ or NH$_4$ concentrations (32), high algal abundance (2, 33), or spatial variation in redox conditions (34). However, some studies report a negative relationship between NO$_2$ and N$_2$O (35), others suggest either high or low redox conditions support N$_2$O production (12, 34, 36), while the presence of algal biomass has been proposed to either enhance or limit N$_2$O production in surface waters (29, 34). We believe results of our GAM analysis help resolve these contrasts by identifying the nonlinear relationships between N$_2$O concentrations and environmental conditions (Fig. 2). Specifically, we show that physical stratification appears to interact with DIN content to either inhibit or promote N$_2$O production, depending on the strength of thermal or chemical stratification.

Our finding that N-enriched small agricultural reservoirs were undersaturated in N$_2$O may have broader implications for the N$_2$O source or sink behavior of the 16 million other small artificial reservoirs that exist globally (16). Comparing our sites across a limited number of N$_2$O measurements made in similar-sized systems, we demonstrate that undersaturation of N$_2$O is not universal in small waterbodies (Fig. 3). Indeed, some of the highest N$_2$O concentrations are observed at NO$_2$ concentrations >400 µg N L$^{-1}$; however, variability within and between systems for both N$_2$O (1–3,930 nm) and NO$_2$ (0.1–5,500 µg N L$^{-1}$) is large and no significant relationship exists across all studies (Fig. 3). Interestingly, most of our sites remained undersaturated in N$_2$O at NO$_2$ ranges that typically support highly supersaturated N$_2$O concentrations in other small lentic systems (Fig. 3). This pattern clearly illustrates the need for further work in small ecosystems. Given that our study contains the largest dataset to date on N$_2$O measurements in small waterbodies, we provide substantial evidence that not all waterbodies act as N$_2$O sources under elevated DIN.

Taking the average of measured reservoir-specific gas transfer velocity (Materials and Methods) and extrapolating to all 101 sites, calculated N$_2$O fluxes were small (median = −4.03 µmol m$^{-2}$ d$^{-1}$), with most acting as sinks rather than large sources of N$_2$O (SI Appendix, Table S1). For those sites with N$_2$O uptake (69 sites), calculated fluxes ranged from −12 to −2 µmol m$^{-2}$ d$^{-1}$, whereas sites which were sources (20 sites) varied in strength from 2.21 to 166 µmol m$^{-2}$ d$^{-1}$. Fluxes from the remaining sites (12 sites) that were close to atmospheric equilibrium could not be considered as distinct sinks or sources (−1.37 to 1.38 µmol m$^{-2}$ d$^{-1}$). Few studies have reported negative N$_2$O fluxes in lentic systems (range −60 to −0.08 µmol m$^{-2}$ d$^{-1}$), and those that do are often characterized as low N environments (5, 37, 38). In contrast, flowing waters in agricultural catchments tend to act as strong N$_2$O sources (93–2,500 µmol m$^{-2}$ d$^{-1}$) (12–14), a pattern which is consistent with the observation that agricultural ponds and wetlands have significantly lower N$_2$O emissions (three- to ninefold) than flowing waters (12, 36).

While our comprehensive spatial study provides baseline evidence for the role of these systems as N$_2$O sinks, research is needed to quantify the temporal variability in N$_2$O content in artificial waterbodies among different seasons. It is likely that our late-summer sampling period represents a time when small waterbodies are N$_2$O sinks, as both primary productivity and water-column stratification are greatest at this time. Limited studies have assessed the temporal variation of N$_2$O concentrations in small artificial waterbodies, yet those that have report conflicting seasons when emissions peak (34–36). This lack of pattern may reflect the differences in regional climate among studies or local variation in physicochemical conditions that regulate O$_2$ conditions and organic N availability. For example, in the Northern Great Plains, the duration of N$_2$O influx is likely governed by the length of stable stratification and autotrophic activity, a period which normally lasts approximately 5 mo (39, 40).

Application of previously published empirical relationships (2, 4, 41) to our reservoirs overestimated potential N$_2$O emissions by 7.5- to 33-fold (Fig. 4). Other studies have developed predictive models using water-body area, Chl-a, and NO$_2$ for global lakes and impoundments (2, 4). Those models often overestimated N$_2$O fluxes in our reservoirs when observed fluxes were negative, with differences between calculated and model-predicted values ranging from −0.27 to 13 mg N$_2$O-N d$^{-1}$. For example, the Intergovernmental Panel on Climate Change (IPCC) methodology for agricultural GHG inventories predicts N$_2$O emissions will increase linearly with NO$_2$ emissions across all regions (41). Applying the average 11-fold overestimate of N$_2$O fluxes predicted by the IPCC to agricultural reservoirs throughout Saskatchewan produces an estimated 10,530 tonnes (T) CO$_2$ equivalent emissions y$^{-1}$, whereas the actual mean measured
N$_2$O fluxes totaled only 968 t C equivalent emissions y$^{-1}$ (42). These observations suggest that global models may not apply universally to similarly designed small artificial waterbodies.

Additional measurements of N$_2$O in other agricultural waterbodies are required to further assess their ability to reduce agricultural emissions. Small reservoirs are common in many agricultural regions of the globe, with over 3 million in the United States (43, 44), India (45), Australia (46–48), and Saskatchewan (49) alone, ranging in density from 0.1% to 6% of agricultural land area (17). With a high density of 10 reservoirs on a 1-km$^2$ block of farmland in Saskatchewan, agricultural reservoirs have the ability to reduce up to 1–4% of soil N$_2$O emissions (0.68–0.95 kg N$_2$O-N ha$^{-1}$ y$^{-1}$) (50) as CO$_2$ equivalents (42) if all were acting as strong sinks. Although the total effect of agricultural reservoirs on integral greenhouse gas emissions is potentially limited by their small landscape area, our key finding remains that these artificial waterbodies do not contribute to significant N$_2$O emissions characteristic of other water bodies. For example, if small farm reservoirs in Saskatchewan exhibited N$_2$O effluxes as high as other eutrophic systems on farms such as drainage canals (8 mg N$_2$O-N·m$^{-2}$·d$^{-1}$) (12), these basins would account for as much as 66–73% of total farm N$_2$O emissions.

In summary, we add an additional 101 sites (~32%) to the sparse global dataset of lake and reservoir N$_2$O measurements. Importantly, this study provided regional-scale insight into the functioning of agricultural water bodies as N$_2$O sinks. Given that millions of small agricultural reservoirs exist worldwide, yet have rarely been studied for GHG emissions, we highlight a call to action for further N$_2$O measurements in countries with large agricultural areas. This work reveals that in contrast to many lake and reservoir studies, the majority of our agricultural reservoirs act as N$_2$O sinks despite having elevated N concentrations, with N$_2$O fluxes as much as 33-fold lower than model predictions for lakes and reservoirs in agricultural regions. Nonlinear relationships between stratification, DIN, and N$_2$O content reveal the need to reassess the role of small waterbodies as N$_2$O sources and consider the environmental controls leading to freshwater N$_2$O sinks. Despite their shallow nature and perceived unimportance of vertical structure, stratification in particular should be considered in other small waterbodies when investigating N$_2$O dynamics. Inclusion of small reservoirs in agricultural basins may provide an important means of anthropogenic N retention, while providing a potential avenue to reduce net GHG emissions in agriculture.

Materials and Methods

Sampling Sites. A spatial survey of 101 constructed agricultural reservoirs was conducted in a 5-wk period from July to August 2017 across southern Saskatchewan in Canada, covering a total area of 235,000 km$^2$ (SI Appendix, Fig. S1). Sites were selected from a database of farm reservoirs collected by a survey of regional landowners, as well as from sites on federal lands. Site selection was refined by ensuring a relatively even spatial distribution across the study area, while also considering ease of access. Sites spanned latitudinal and longitudinal ranges of 49° 2′ 25″ to 52° 43′ 9″ and −109° 51′ 6″ to −103° 22′ 42″, respectively. We sampled a diversity of sites that ranged in size from 90 to 13,900 m$^2$ and that covered broad land-use types including grassland, pasture, and crop land. The sample area is dominated by intensive agriculture (80%) (51) which contains >110,000 manmade agricultural reservoirs (“dugouts”) (49) to provide onsite surface water storage. The region experiences a subhumid to semiarid climate (Köppen Dfb classification), with an average annual rainfall ranging from 200 to 500 mm across the prairie ecoregion of the province (52). The cultivated plains are characterized by countless shallow lakes and small pond-like water bodies, most of which are highly evaporative and generally receive most of their surface water from spring snow melt (53). Soils consist of glacial till composed of carbonates derived from limestone bedrock, which leads to the hard-water properties observed in many of the surface waterbodies in the region (39, 54).

Buoyancy Frequency. The Brunt–Väisälä buoyancy frequency was used as a measure of thermal stratification strength to provide an indication of water column stability. Buoyancy frequency was calculated from temperature profiles based on the density gradient using the package “lakeAnalyzer” (57) in R (58). We then used the maximum buoyancy frequency for each site in our analysis.

N$_2$O Concentrations and Flux. Samples for N$_2$O were collected at ~0.3 to 0.5 m below the surface at the deepest point of each reservoir by filling a 1.2-L glass serum bottle using a subsurface pump. Atmospheric air was added (60 mL) to the sealed bottle to create a headspace and it was shaken vigorously for 2 min. Two analytical replicates of the equilibrated headspace were extracted with an airtight syringe and dispensed to 12-mL evacuated Exetainer vials with double wadded caps. A sample for atmospheric air was also taken at each site and used to back calculate the original N$_2$O concentration in the water. Headspace concentrations were measured using gas chromatography with a Scion 456 Gas Chromatograph (Bruker Ltd.) and calculated using standard curves. Dry N$_2$O molar fractions were converted to concentrations as a function of added atmospheric N$_2$O concentration, local atmospheric pressure, and N$_2$O solubility at the measured water temperature and salinity (59).

Average daily fluxes ($f_{N_2O}$) were calculated using water-column N$_2$O concentration ($C_{w,atm}$) and average reservoir gas transfer velocity ($k_{res}$) using the equation

$$f_{N_2O} = k_{res} (C_{w,atm} - C_{air})$$

where $f_{N_2O}$ is the flux of N$_2$O (mmol·m$^{-2}$·d$^{-1}$) and $C_{air}$ is the concentration of N$_2$O in the water at atmospheric equilibrium. The average global mixing ratio for the sampling period of 0.33 ppm was used for calculating equilibrium concentrations (Mauna Loa NOAA station, June–August 2017). A series of floating-chamber (0.23 m$^2$ area, 0.046 m$^3$ total volume) measurements were carried out at a subset of sites (10) to derive a reservoir-specific gas transfer velocity ($k$). Briefly, a total of 30 incubations were taken, with changes in gas
concentration recorded by taking five gas samples every 2.5 min for 10 min using a 30-mL syringe, and injected into preevacuated 12-mL vials. The five concentrations were then used to calculate the flux for each incubation using linear regression,

$$f_{\text{gas}} = \frac{SV}{MV} \cdot t,$$

where \(s\) is the slope of the of the gas change in the chamber (\(\mu\text{atm} \cdot \text{min}^{-1}\)), \(V\) is the volume of the chamber (L), \(S\) is the chamber surface area (m\(^2\)), \(m\) is the molar volume of the gas at current atmospheric pressure, and \(t\) is a conversion factor from minutes to day.

Due to small \(N_2O\) fluxes measured at our chosen sites, a change in concentration was often too low to be detected with confidence over a 10-min incubation period. \(N_2O\) fluxes were determined to be unacceptable due to either the change in chamber \(N_2O\) ppm concentration being within the analysis accuracy (2%) or having an \(r^2\) value < 0.7 in the linear regression (60). Instead, the measured \(CH_4\) flux was used for deriving estimates of \(k\) due to a stronger detection in the gas accumulation rate. Excluding those incubations that displayed step-like jumps in gas accumulation, which suggests an ebullition event, a total of 23 measurements were used. \(k_{\text{CH}_4}\) (m\(^3\) d\(^{-1}\)) was calculated using the inverted equation of Fick’s law for gas diffusion,

$$k_{\text{CH}_4} = \frac{f_{\text{CH}_4}}{k_w(P_{\text{CH}_4\text{water}} - P_{\text{CH}_4\text{air}})},$$

where \(f_{\text{CH}_4}\) is the measured \(CH_4\) flux (mmol m\(^{-2}\) d\(^{-1}\)), \(k_w\) is Henry’s constant, and \(P_{\text{CH}_4\text{water}}\) and \(P_{\text{CH}_4\text{air}}\) are the \(CH_4\) partial pressures (\(\mu\text{atm}\)) in the water and ambient air, respectively. The average global mixing ratio for the sampling period of 1.85 \(\mu\text{atm}\) was used for \(P_{\text{CH}_4\text{air}}\) (Mauna Loa NOAA station, June–August 2017). All \(CH_4\) values required for this calculation were collected and analyzed from the same sample as described for \(N_2O\) above. From \(k_{\text{CH}_4}\), the gas transfer velocity was converted to \(k_{\text{NO}_3}\) by using their respective Schmidt numbers \((SC_{\text{NO}_3} \text{ and } SC_{\text{CH}_4})\), assuming a Schmidt exponent of 0.67 as follows:

$$k_{\text{NO}_3} = \frac{SC_{\text{NO}_3}}{SC_{\text{CH}_4}} \cdot k_{\text{CH}_4}.\]  

The average \(k_{\text{NO}_3}\) calculated from the floating-chamber incubations was 1.64 ± 1.24 m\(^3\) d\(^{-1}\). The original data generated in this study are freely available on GitHub and Zenodo (61).

**Statistical Methods.**

**Variable selection.** To assess the predictability of environmental drivers on controlling \(N_2O\) concentrations, we selected a range of variables known to affect \(N_2O\) production and consumption pathways. Fig. 1 provides an overview of the assumed processes potentially influencing \(N_2O\) in our artificial agricultural reservoirs. We included both surface and bottom water dissolved oxygen (DO) saturation. Dissolved oxygen represents the extent of oxic and anoxic conditions in the water column, which has been shown to exert strong controls over consumption and production processes including nitrification, incomplete and complete denitrification, and dissimilatory nitrate reduction to ammonium (DNRA) in aquatic environments (62). Sediment C:N ratio was used as a proxy for carbon substrate availability, which is a key energy source to heterotrophic communities such as denitrifiers and those facilitating DNRA (63). Chlorophyll-a was included as a measure of phytoplankton abundance and trophic status (2). The amount of production by algal biomass can serve as an indicator for N loading and, if especially abundant, may compete for inorganic carbon and nitrogen substrates in the upper water column (Fig. 1). Reservoir pH (measured at the surface) was included as low pH has been shown to limit nitrification rates and stimulate \(N_2O\) sink behavior (5). TDN to SRP ratio (mg mg\(^{-1}\)) was included to provide a measure of N limitation, as well as the concentration of inorganic nitrogen species (DIN = NH\(_4\) + NO\(_3\)) that are directly involved in all \(N_2O\) processes (Fig. 1). Finally, Brun-Vaissàlå buoyancy frequency was included as a physical control for surface water and bottom water mixing. Physical stratification can promote the development and persistence of anoxic conditions in the hypolimnion, allowing more opportunity for \(N_2O\) consumption to persist throughout the water column (23, 26).


