# Terrestrial and Aquatic Nitrous Oxide Emissions

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# Abstract

Agriculture has emerged as the foremost source of nitrous oxide ($N_2O$), a potent greenhouse gas and the dominant ozone depleting substance, in response to the widespread application of nitrogen (N) fertilizer.  Globally, the magnitude of this source is well constrained based on long-term trends in atmospheric $N_2O$ [*Crutzen et al.*, 2008]. However, large uncertainties remain at regional-scales where discussions around the development of scalable mitigation practices and policies will be implemented.

To estimate national or regional emissions, bottom-up emission inventories are created that predict $N_2O$ losses by applying an emission factor (EF) to individual land-use activities.  However, recent top-down validation exercises – performed using tall towers and aircraft, have determined that regional bottom-up models significantly underestimate North American agricultural emissions.  As a result, benchmarking the success of widespread mitigation practices is hampered.  The goals of this dissertation are, therefore, twofold: 1) isolate and revise the EF that is responsible for biasing the bottom-up $N_2O$ emission inventory; and, 2) identify the underlying mechanisms that control emissions to help guide mitigation practices.

The emission factor for N leaching and runoff from agricultural fields ($EF_{5r}$) is one of the most uncertain components included in bottom-up inventories.  Here, a full stream network approach shows that $N_2O$ emissions decline exponentially with increasing Strahler stream order.  This function was used to upscale emissions and revise the $EF_{5r}$, which determined that the default $EF_{5r}$ had been underestimated by as much as 9-fold in bottom-up emission inventories.  This correction brings regional bottom-up

inventories in line with top-down models, improving our confidence in these budgets when the riverine component is properly accounted.

However, uncertainty remains in the river biochemical conditions necessary to promote high aquatic emissions. Towards this end, data were collected using a novel gas equilibrator coupled to flow-through water quality sensors [*Crawford et al.*, 2015] to identify complex biochemical relationships. This freshwater data set, the world's largest and the first measurements from the Mississippi River, shows that dissolved $N_2O$ concentrations plateau at high nitrate ($NO_3^-$) concentrations. The decreasing $N_2O$ response at higher $NO_3^-$ concentrations is likely the result of environmental limitations on N processing – including, turbidity, dissolved oxygen, and carbon. However, this relationship suggests that if river models are accurate, the projected doubling of riverine $NO_3^-$ export could amplify $N_2O$ emissions by as much as 40%. Yet, this response could be diminished if environmental limits on N processing were imposed – including, decreased turbidity, highlighting an important tool to mitigate indirect $N_2O$ emissions.

Mitigation of direct emissions from soils, the largest single component of the agricultural source, have been heavily discussed in the literature. However, due to the variability of $N_2O$ production, the success of practices designed to mitigate emissions have been mixed. Here, two techniques to mitigate direct emissions were assessed. The first explored the effect that a kura clover living mulch had on $N_2O$ emissions in a corn – soybean rotational field. Alternative management practices are becoming more common, yet their impact on $N_2O$ emissions is not well understood. As a legume, kura clover provides a N-credit to the crop, allowing farmers to reduce their application of synthetic

fertilizer, which may reduce $N_2O$ losses.  Contrary to our hypothesis, elevated emissions from the kura clover treatment during periods of soil disturbance, plant stress, and post-anthesis significantly increased $N_2O$ losses relative to the non-kura clover treatment.

Lastly, the importance of emission "hotspots" in the field-scale $N_2O$ budget was assessed by resolving $N_2O$ emissions at a high spatial resolution using geospatial analyses.  These data and analyses determined that hotspots were responsible for a disproportionate share of the field-scale emissions, despite occupying a limited area of the field.  From these measurements, targeted management of $N_2O$ hotspots could be used to efficiently reduce field-scale emissions by as much as 17%.  The findings presented here provide a roadmap for policy makers and farm managers to proactively address and mitigate agricultural $N_2O$ emissions.

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# Chapter 1
# Introduction

Advancements in technology have stimulated global crop productivity to unprecedented levels that are now capable of supporting the basic needs of more than seven billion people annually. One innovation, the manufacture of synthetic nitrogen (N) fertilizers *via* the Haber-Bosch process, has been credited with averting a *Malthusian* crisis [*Trewavas*, 2002] by removing the N limitation and thereby promoting high yielding crops. Despite modernization efforts that have made food production more efficient than ever, global demand for N continues to rise at rate of 1.8 Tg N yr$^{-1}$ [*FAO*, 2015]. Agroecosystems also receive N from atmospheric deposition and organic sources, such as manure and legume species. Cumulatively, these sources (synthetic + organic) exceed 170 Tg N yr$^{-1}$ globally [*Smil*, 1999]. However, as much as 70% can be lost to the water and atmosphere [*Galloway et al.*, 2003], of which 4% [*Crutzen et al.*, 2008] is converted to nitrous oxide ($N_2O$), a powerful greenhouse gas [*Hartmann et al.*, 2013] and stratospheric ozone depleting substance [*Ravishankara et al.*, 2009].

Consequently, the ambient concentration of $N_2O$ has risen steadily, up 20% from the pre-industrial estimate [*Hartmann et al.*, 2013]. This rise is largely attributed to agricultural systems, which account for between 60-80% of the anthropogenic $N_2O$ emission budget [*Davidson*, 2009; *Davidson and Kanter*, 2014; *US Department of State*, 2014]. Therefore, strong emissions occur where climate allows for efficient crop production. For instance, the United States Corn Belt, one of the most intensively cultivated areas on Earth, produces 40% of the world's grain [*NRCS*, 2012] and consumes nearly 60% (7 Tg N yr$^{-1}$) of the national fertilizer budget. Here, measurements from tall-towers note ambient $N_2O$ concentrations that are up to 3 ppb greater than non-

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cultivated locations [*Griffis et al.*, 2013].  The agricultural signal can also be seen globally; a latitudinal tropospheric $N_2O$ gradient has emerged whereby Northern Hemisphere concentrations are 2 ppb higher than those in the Southern Hemisphere [*Hartmann et al.*, 2013] in response to the strong agricultural sources in North America, Europe, and Asia.

Signatories to the United Nations Framework Convention on Climate Change are obligated to create a national $N_2O$ emission inventory.  These "bottom-up" inventories are generated using emission factors (EFs)[1] to estimate the cumulative emissions given a limited set of activity data [*De Klein et al.*, 2006].  These EFs have been constrained from field and laboratory experiments with national-scale integration in mind.  Because bottom-up emission inventories are necessary tools for treaty benchmarking and objective policy assessment, their accuracy is essential.  However, top-down emission constraints – including those from tall-towers [*Miller et al.*, 2012; *Griffis et al.*, 2013; *Zhang et al.*, 2014; *Chen et al.*, 2016] and aircraft [*Kort et al.*, 2008], indicate that bottom-up emission inventories significantly underestimate the agricultural $N_2O$ source.  To reconcile bottom-up and top-down inventories, many hypothesize that one or more EFs are underestimated [*Griffis et al.*, 2013; *Zhang et al.*, 2014].  Yet, the episodic and spatially variable nature of $N_2O$ fluxes has made the determination of which EF is biased, and to what extent, challenging.

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[1] Emission factors provide a first-approximation of annual $N_2O$ emissions given known land-use and activity data.

The goals of this dissertation are therefore to: 1) quantify the strength of indirect $N_2O$ emissions from leaching and runoff and revise the EF ($EF_5$) accordingly; and, 2) identify the underlying mechanisms that control direct and indirect emissions in order to help guide $N_2O$ mitigation practices. The findings presented here provide a roadmap for policy makers and farm managers to address agricultural $N_2O$.

In Chapter 2, the indirect emission factor for leaching and runoff ($EF_5$), the most uncertain EF included in bottom-up inventories [*Nevison*, 2000], is assessed. This EF describes the quantity of $N_2O$ emitted offsite in response to agriculturally linked N that flows through groundwater ($EF_{5g}$), rivers ($EF_{5r}$), and eventually into estuaries ($EF_{5e}$). Of these components, the accuracy of the $EF_{5r}$ is the most contentious, as some suggest it may underestimate $N_2O$ emissions in agricultural areas [*Beaulieu et al.*, 2011; *Outram and Hiscock*, 2012]. The large uncertainty in the $EF_{5r}$ has been caused by a paucity of studies[*Clough et al.*, 2006] and a wide range of river morphology types [*Beaulieu et al.*, 2008]. Although river morphology, semi-quantitatively described by the Strahler stream order, directly effects the turbulent exchange of mass across the air – water interface [*Butman and Raymond*, 2011], its relationship with the flux of $N_2O$ has not yet been assessed. Here, a portable floating chamber system is used to measure emissions across a Strahler stream order gradient in a dense agricultural region. These measurements, coupled with high-resolution stream network and fertilizer data sets, are used to provide a robust revision of the $EF_{5r}$. This chapter concludes with an upscaling exercise to estimate total riverine emissions from the United States Corn Belt.

Constraining which variables regulate $N_2O$ emissions from agriculturally impacted rivers in the United States Corn Belt is a necessity for policy and emission model forecasting. This heavily modified agricultural region is largely drained by the Upper Mississippi River. Consequently, the effects of excess nitrate ($NO_3^-$) here have been studied extensively [*Turner and Rabalais*, 1991], yet $N_2O$ dynamics in the Upper Mississippi River have not yet been observed. Towards this end, data collected using a novel flow-through sensor platform are presented in Chapter 3 to describe regional $N_2O$ patterns and their biochemical controls in the Upper Mississippi River. These data and analyses provide insight into mechanisms that may limit indirect $N_2O$ emissions and provides insights regarding future emissions given specific $NO_3^-$ modelling projections and policy targets.

Chapter 4 addresses direct $N_2O$ emissions from agricultural soils, one of the largest individual sources included in bottom-up emission inventories [*Davidson*, 2009]. The mitigation of direct emissions generally focuses on improving field-scale nitrogen management practices, including fertilizer timing and source optimization. Although alternative management practices, like living mulches, which provide N benefits are experiencing greater use. A living mulch is a technique whereby a perennial cover crop is grown with the crop, and is capable of reducing $NO_3^-$ leaching [*Ochsner et al.*, 2010] while fixing additional N [*Baker*, 2012]. However, $N_2O$ measurements from these systems are rare and must be explored so farmers can manage with respect to $N_2O$ emissions. Here, the first $N_2O$ measurements from a kura clover based living mulch are reported, which allow for a thorough exploration of direct emissions in these systems.

Static chambers are the most common method to measure soil $N_2O$ emissions, yet the accuracy of a field-scale budget is limited by $N_2O$ production mechanisms that vary widely throughout a field. As a result, $N_2O$ measurement campaigns yield a high degree of uncertainty, due in large part to emission "hotspots". Such sources generally appear in low-lying areas [*Ambus and Christensen*, 1995] where flow paths converge [*McClain et al.*, 2003] to support disproportionately high rates of denitrification. In Chapter 5, emission and soil sample data sets are coupled with geospatial analyses, to resolve $N_2O$ emissions at a high-spatial resolution. These data and analyses highlight the options available to mitigate agricultural $N_2O$ hotspots and an estimation of their potential emission benefits.

# Chapter 2

# Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order

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Overview

Nitrous oxide ($N_2O$) is an important greenhouse gas and the primary stratospheric ozone depleting substance. Its deleterious effects on the environment have prompted appeals to regulate emissions from agriculture, which represents the primary anthropogenic source in the global $N_2O$ budget. Successful implementation of mitigation strategies requires robust bottom-up inventories that are based on emission factors (EFs), simulation models, or a combination of the two. Top-down emission estimates, based on tall-tower and aircraft observations, indicate that bottom-up inventories severely underestimate regional and continental scale $N_2O$ emissions, implying that EFs may be biased low. Here, we measured $N_2O$ emissions from streams within the US Corn Belt using a novel chamber-based approach and analyzed the data as a function of Strahler stream order ($S$). $N_2O$ fluxes from headwater streams often exceeded 29 nmol $N_2O$-N $m^{-2}$ $s^{-1}$ and decreased exponentially as a function of $S$. This relation was used to scale up riverine emissions and to assess the differences between bottom-up and top-down emission inventories at the local to regional scale. We found that the Intergovernmental Panel on Climate Change (IPCC) indirect EF for rivers ($EF_{5r}$) is underestimated up to 9-fold in southern Minnesota, which translates to a total Tier 1 agricultural underestimation of $N_2O$ emissions by 40%. We show that accounting for zero-order streams as potential $N_2O$ "hotspots" can more than double the agricultural budget. Applying the same analysis to the US Corn Belt demonstrates that the IPCC $EF_{5r}$ underestimation explains the large differences observed between top-down and bottom-up emission estimates.

## Significance

N₂O emissions from riverine systems are poorly constrained, giving rise to highly uncertain indirect emission factors that are used in bottom-up inventories. Using a novel, non-steady-state flow-through chamber system, N₂O fluxes were measured across a stream order gradient within the US Corn Belt. The results show that N₂O emissions scale with the Strahler stream order. This information was used to estimate riverine emissions at the local and regional scales and demonstrates that previous bottom-up inventories based on the IPCC default values have significantly underestimated these indirect emissions.

## Introduction

$N_2O$ is projected to remain the dominant stratospheric ozone depleting substance of the 21$^{st}$ century [*Ravishankara et al.*, 2009] and is a powerful greenhouse gas (GHG) that currently accounts for about 6% of the net radiative forcing associated with long-lived anthropogenic GHGs [*Hartmann et al.*, 2013]. The detrimental environmental impacts of $N_2O$ have stimulated appeals to regulate emissions from agricultural lands [*Ravishankara et al.*, 2009; *Kanter et al.*, 2013], which account for nearly 80% of the global anthropogenic $N_2O$ budget [*Crutzen et al.*, 2008; *Davidson*, 2009]. The successful regulation and mitigation of $N_2O$ emissions requires a sound understanding of the direct and indirect emission processes and reduced uncertainty regarding the emission factors (EFs) [*Shcherbak et al.*, 2014].

The IPCC Tier 1 approach uses EFs to provide first-order approximations of

annual $N_2O$ emissions based on mechanistic and empirical information that have been

constrained by field studies. These EFs are widely used in bottom-up inventories such as

the Emission Database for Global Atmospheric Research[2] (EDGAR) and the Global

Emissions Initiative[3] (GEIA). These inventories are essential tools for tracking country

specific emission trends, assessing thresholds for international treaties, and for evaluating

the impacts of mitigation policies. Recent independent top-down estimates note large

discrepancies with these bottom-up inventories.

Tall-tower and aircraft-based top-down studies use atmospheric concentration

data to estimate landscape $N_2O$ fluxes. Several studies using these approaches

demonstrate that bottom-up inventories underestimate $N_2O$ emissions by up to 9-fold in

the Midwest United States Corn Belt [*Kort et al.*, 2008; *Miller et al.*, 2012; *Griffis et al.*,

2013; *Zhang et al.*, 2014], implying that some EFs are too small. An important problem,

therefore, is determining which EFs are biased low and how to reduce their uncertainty.

Bottom-up $N_2O$ emission inventories include direct and indirect emission

pathways. Direct emissions describe the loss of $N_2O$ produced in soils by microbial

processes (e.g. nitrification and denitrification). This source is arguably well-constrained

as a consequence of more than 1000 chamber-based emission studies [*Stehfest and

Bouwman*, 2006; *Shcherbak et al.*, 2014]. Plant $N_2O$ fluxes, although neglected in direct

emissions inventories, appear to be negligible [*Zhang et al.*, 2014]. The relatively low

direct emission uncertainty range (0.4 – 3.8 Tg N yr$^{-1}$) [*Nevison*, 2000] suggests that this

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EF (0.003 – 0.03) [*De Klein et al.*, 2006] is well constrained.

Indirect emissions represent the aggregate of $N_2O$ production from leaching and runoff, human sewage, and atmospheric deposition of reactive nitrogen. Global indirect emission estimates range from 0.23 – 11.9 Tg N $yr^{-1}$ [*Mosier et al.*, 1998] and represent nearly two thirds of the uncertainty in the total global $N_2O$ budget [*Nevison*, 2000]. In fact, the EF for leaching and runoff (IPCC emission factor: $EF_5$), which includes emissions from groundwater ($EF_{5g}$), rivers ($EF_{5r}$), and estuaries ($EF_{5e}$), is the single largest source of uncertainty in the bottom-up inventory [*Nevison*, 2000]. In the 2006 IPCC Emission Guidelines report, the $EF_5$ value was reduced from 0.025 to 0.0075 by reducing both the $EF_{5g}$ and $EF_{5r}$ to 0.0025 in response to two studies from New Zealand and the United Kingdom [*De Klein et al.*, 2006]. Although recent studies [*Beaulieu et al.*, 2011; *Outram and Hiscock*, 2012; *Hinshaw and Dahlgren*, 2013; *Yu et al.*, 2013] suggesting riverine $N_2O$ loss is underestimated by up to 3-fold notably contradict the $EF_{5r}$ reduction.

Uncertainty in the $EF_{5r}$ can be attributed to a scarcity of studies [*Clough et al.*, 2006, 2007], poorly constrained water-air gaseous exchange relationships [*Cole and Caraco*, 1998; *Beaulieu et al.*, 2012], and high variability in river morphology [*Beaulieu et al.*, 2008; *Wang et al.*, 2009]. Further, the $EF_{5r}$ assumes a linear relation between nitrate in water and $N_2O$ emissions [*Nevison*, 2000], the validity of which is the subject of considerable debate [*Rosamond et al.*, 2011, 2012; *Xia et al.*, 2013; *Venkiteswaran et al.*, 2014]. Finally, $N_2O$ fluxes derived from simple gas exchange models have been shown to underestimate the flux if stream channel hydraulics (i.e. stream flow velocity) are

ignored [*Reay et al.*, 2003], highlighting that stream chemistry alone is not an accurate predictor of $N_2O$ fluxes.

We posit that the indirect $N_2O$ fluxes in agricultural landscapes are highly dependent on stream hierarchy, which is semi-quantitatively represented with the Strahler stream order (*S*), a numerical classification system. Here, we demonstrate that with detailed knowledge of *S*, $N_2O$ fluxes can be scaled up to the region and help to resolve the discrepancy between top-down and bottom-up $N_2O$ emission estimates in the US Corn Belt.

## Results and Discussion

N2O fluxes in southeastern Minnesota were measured in streams of varying S over a two year period. A total of nineteen stream systems, representing nine stream orders, were sampled. An exponential function was used to describe the relationship between observed N2O fluxes (F, nmol $N_2O$-N $m^{-2}$ $s^{-1}$) and S,

$$F = b_0 exp^{(-b_1 * S)} \qquad \text{(Equation 2.1)}$$

where $b_0 = 34 \pm 10.2$ (95% confidence interval), $b_1 = 0.73 \pm 0.2$, with $R^2 = 0.95$ and 0.58 for binned ($n = 9$) and raw data ($n = 200$), respectively (Figure 2.1). Fluxes ranged from below the chamber system detection limit of 0.018 nmol $N_2O$-N $m^{-2}$ $s^{-1}$ (i.e. for the Mississippi River; $S = 9$) to a maximum observed flux of 34.5 nmol $N_2O$-N $m^{-2}$ $s^{-1}$ in a headwater stream ($S = 1$). A Kruskal-Wallis significance test revealed a significant mean rank difference ($p < 0.05$) in fluxes for headwater streams versus all other stream orders. Further, there was a significant rank difference between fifth – ninth-order streams while

there was no rank difference detected in second – fifth-order streams.  The differences

were greatest when testing non-sequential stream orders.

We hypothesize that the exponential decline in $N_2O$ flux is the result of both

weakened concentration gradient and lower piston velocities ($k$) in higher order streams.

Riverine $N_2O$ fluxes are a product of the concentration gradient between the surface

water and the overlying atmosphere and a physical gas transfer coefficient [*Raymond and

Cole*, 2001].  We propose two possible mechanisms underlying the emergent pattern

shown in Figure 2.1 including: 1. Decreased *in-situ* $N_2O$ production and loading; and, 2.

Decreased gas exchange rates.

*Mechanism 1*: Headwater streams form from surface and subsurface runoff that,

in regions with a high density of row crop agriculture, have high nitrate and ammonium

loads and as a consequence, approximately 45-50% of a watershed's inorganic nitrogen

transport can occur in these systems [*Peterson et al.*, 2001; *Alexander et al.*, 2007].

Nitrogen is rapidly transformed *via* nitrification and removed through denitrification

[*Mulholland et al.*, 2008] in headwater streams [*Peterson et al.*, 2001] and these

processes can quickly produce a surplus of $N_2O$ in the water column.  However, the

average first-order rate of nitrogen loss within stream channels declines by as much as

90% down the stream order continuum [*Alexander et al.*, 2000].  Therefore, production

potential declines as stream order increases.  Accordingly, we observed a decline in

surface water $N_2O$ concentrations from super-saturated (>1000%) in second-order

streams to near equilibrium with atmospheric $N_2O$ in fourth-order streams.  Groundwater

dissolved gas inputs are an additional $N_2O$ source and are most impactful in low flow

headwater systems [*Jones and Mulholland*, 1998]. However, groundwater loading has less of an effect on stream water chemistry with rising stream order (i.e. due to the water volume dilution effect) [*Jones and Mulholland*, 1998]. Collectively, with increasing stream order, $N_2O$ production potential and loading progressively decline, which could account for the pattern shown in Figure 2.1.

     *Mechanism 2*: Exchange across the water-atmosphere interface of supersaturated gases is governed by $k$, which describes the turbulent nature of the stream. An inverse relationship between $k$CO$_2$ and $S$ has been observed [*Butman and Raymond*, 2011; *Raymond et al.*, 2012, 2013; *Crawford et al.*, 2013] and as a consequence, the highest $k$CO$_2$ values are frequently observed in headwater streams [*Butman and Raymond*, 2011; *Wallin et al.*, 2011; *Crawford et al.*, 2013; *Raymond et al.*, 2013]. The same relationship after adjusting for the Schmidt number should be applicable to $N_2O$, implying that $k$N$_2$O increases with declining stream order. Localized areas with high $k$ values (i.e. riffles) have been shown to be strong emission sources [*Reay et al.*, 2003] if streams are supersaturated (e.g. Mechanism 1). However, if the stream is not supersaturated, a high $k$ value alone cannot generate a large flux. Further, a lower $k$ implies a longer total residence time (age) and therefore, a greater probability of $N_2O$ reacting with nitrous oxide reductase (*nos*), the enzyme that catalyzes the final step in the denitrification reaction sequence – the reduction of $N_2O$ to $N_2$ [*Maier et al.*, 2009]. Although this has not been documented in river systems, this potential mechanism merits further research to determine its importance and its ability to weaken the water-atmosphere $N_2O$ concentration gradient. We posit that these two mechanisms, individually or combined,

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account for the relationship observed in Figure 2.1 and require further study in order to elucidate their relative importance.

In our study, the variability of $N_2O$ flux (i.e. the standard deviation) scaled with stream order, leading to a tightly constrained relation for high order systems (Figure 2.1). These observations imply a robust constraint on high order (fifth-order and higher) emissions and that this pattern could be applied to similar systems [*Beaulieu et al.*, 2010]. Conversely, much larger uncertainty in low ordered systems [*Hasegawa et al.*, 2000; *Harrison and Matson*, 2003] exists, indicating that caution must be taken before generalizing our scaling function outside of the US Corn Belt. Headwater streams displayed the greatest uncertainty and their high variability has also been noted in $CO_2$ evasion work [*Crawford et al.*, 2013]. Low order streams receive tile drainage outflow and groundwater from springs giving rise to localized "hotspots" of $N_2O$ loss [*Hasegawa et al.*, 2000], similar to those seen in methane evasion work [*Crawford et al.*, 2013].

To test the appropriateness of the default IPCC $EF_{5r}$ value, we used Equation 1 to up-scale emissions within the observed concentration footprint (50 km radius) of our tall-tower $N_2O$ flux station [*Griffis et al.*, 2013]. Land use in this study area consists of 70% crops and pasture, 14% mixed vegetation, 11% forest, 3% developed, 2% open water and is representative of the US Corn Belt. Streams in the area represent only a small fraction (0.16%) of the total surface area. Using default IPCC EFs for direct and indirect emissions, we provide a conservative estimate of the local agricultural $N_2O$ budget in addition to our up-scaled riverine emissions.

Whole-river emissions are the product of our scaling function and river area over a predicted ice-free period. We estimated the annual riverine $N_2O$ loss by coupling Equation 1 with detailed geospatial datasets on stream length and width. Headwater streams ($S = 1$) were the strongest sources, emitting 60% of the riverine budget. The remaining streams in the study area ($S = 2$ through 5) contributed 14%, 8%, 10%, and 8% to the up-scaled riverine emission budget, respectively. This disproportionate flux distribution was a result of a 3-fold greater mean flux density from headwater streams (17.1 nmol $N_2O$-N $m^{-2}$ $s^{-1}$) than second-order streams (5.7 nmol $N_2O$-N $m^{-2}$ $s^{-1}$).

Using the IPCC Tier 1 methodology [*De Klein et al.*, 2006], the total agricultural (direct + indirect) $N_2O$ emissions from the tall-tower footprint were 0.2 Gg $N_2O$-N $yr^{-1}$ which corresponds to a flux density of 0.25 (0.08 – 0.6) nmol $N_2O$-N $m^{-2}$ $s^{-1}$. Indirect and direct sources contributed 22% and 78%, respectively to the Tier 1 budget. Here, the default $EF_{5r}$ predicts that rivers emitted 0.01 Gg $N_2O$-N $yr^{-1}$, which represents just over 5% of the total $N_2O$-N emissions. Our scaling method predicted a riverine source of 0.09 (0.04 – 0.18) Gg $N_2O$-N $yr^{-1}$ (Figure 2.2a), an estimate that is 9 times greater than the source predicted by the default $EF_{5r}$, signaling a significant bottom-up bias in the $EF_{5r}$. Replacing the $EF_{5r}$ with our scaling function suggests that the total Tier 1 bottom-up agricultural emissions have been underestimated by 40%. Accounting for this potential bias increases the predicted bottom-up flux density within the tall-tower source footprint to 0.36 nmol $N_2O$-N $m^{-2}$ $s^{-1}$ (Figure 2.2c). This estimate is in excellent agreement with the top-down tall-tower measured ensemble flux of 0.35 (0.3 – 0.4) nmol $N_2O$-N $m^{-2}$ $s^{-1}$ [*Griffis et al.*, 2013], indicating that top-down and bottom-up budgets can be reconciled

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by applying our stream order scaling function. Our study suggests that an appropriate EF$_{5r}$ for the tall-tower source footprint should be closer to 2%, assuming the average application rate of nitrogen fertilizer[4] (88.8 kg N ha$^{-1}$), which is in agreement with a recent independent investigation [*Outram and Hiscock*, 2012].

Based on the Tier 1 methodology, we estimated the agricultural N$_2$O budget of the US Corn Belt at 58 (15 – 256) Gg N$_2$O-N yr$^{-1}$, of which 6% or 3.5 Gg N$_2$O-N yr$^{-1}$ emanates from rivers (Figure 2.2b). In this region, watersheds with high agricultural land use (>40%) occupy 93 million ha (58 million ha under active row-crop cultivation). Applying Equation 1 to these watersheds and using river area data, we obtained a riverine emission of 19.5 (9.3 – 41.2) Gg N$_2$O-N yr$^{-1}$. Our findings suggest that riverine N$_2$O emissions are underestimated by at least 16 Gg N$_2$O-N yr$^{-1}$ for the Corn Belt and on average by 29 kg N$_2$O-N km$^{-2}$ yr$^{-1}$ in watersheds whose cropland fractions are greater than 40% (Figure 2.3). This translates to a 27% increase in the total Tier 1 emission estimate from 58 to 75 Gg N$_2$O-N yr$^{-1}$ (Figure 2.2b). These results indicate that a more appropriate regional EF$_{5r}$ is closer to 1.5% (0.7% - 3%) if the average nitrogen inputs, agricultural coverage[5], and runoff scaling factor [*De Klein et al.*, 2006] are used.

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[4] Potter P, Ramankutty N, Bennett EM, Donner SD (2011) Global Fertilizer and Manure, Version 1: Nitrogen Fertilizer Application. Palisades, NY: NASA Socioeconomic Data and Applications Center (SEDAC). http://dx.doi.org/10.7927/H4Q81B0R. Accessed 29 August 2014.

[5] Fry J, et al. 2011 Completion of the 2006 National Land Cover Database for the Conterminous United States, *PE&RS*, Vol. 77(9):858-864.

It is important to note that our revised $EF_{5r}$ may not be applicable to areas that are nitrogen limited. Our conservative land use threshold of > 40% cropland was chosen because the corn and soybean systems prevalent in the US Corn Belt indirectly identify areas of high nitrogen loading. While average nitrogen application rates vary, from 1994-2001 the average applied to all arable lands within the US Corn Belt was 48 kg N ha^{-1} [*Potter et al.*, 2011]. As such, we propose that agriculturally dominated watersheds receiving rates greater than 48 kg N ha^{-1} will be subject to similar indirect emissions and emission factors as observed in this study. We believe that the majority of the annual riverine $N_2O$ budget will originate from those watersheds and that their total area globally exceeds 235 million ha. Following the United States (93 million ha), the largest regions meeting these criteria are China (69 million ha), Europe (43 million ha), and India (30 million ha). The remaining watersheds are likely to be small $N_2O$ sources and the default 2006 IPCC $EF_{5r}$ value should be appropriate for these cases [*Dong et al.*, 2004].

The application of our methodology to the global scale is limited by two main factors. First, the scaling relation described in Figure 2.1 is likely applicable to watersheds that are dominated by cropland systems with nitrogen inputs greater than 48 kg N ha^{-1}. Second, our stream order width was estimated using methodologies limited to the contiguous United States and Africa [*Downing et al.*, 2012]. At this time, we are unaware of an existing accurate global river width dataset and this represents an important limitation for application of our method to other regions. We believe this is an important research need, especially in countries with significant agricultural production including corn (e.g. China, India, Brazil, and others).

The above analyses did not consider the role of fine-scale drainage features. Zero-order streams, or microflow stream channels, extend upland of headwater streams, are highly episodic, and are likely "hotspots" of nitrogen processing [*McClain et al.*, 2003]. Zero-order stream systems form at the intersection of terrestrial and aquatic environments. However, because of their episodic nature and low spatial coverage, $N_2O$ flux observations are severely lacking. Advancements in LiDAR remote sensing have made it possible to identify episodic microflow paths that may activate following snowmelt and precipitation events. The microflow paths are produced from high resolution (1 m) elevation maps that predict surface water movement. From these data, zero-order streams represent the most common stream order. We estimate that their length is 33 times that of first-order streams in the tall-tower footprint. By extrapolating Equation 1 to include zero-order streams, we suggest that they exert a significant influence on the $N_2O$ budget by increasing the local emissions to 0.41 Gg $N_2O$-N $yr^{-1}$ in the tall-tower footprint, or 101% greater than the default IPCC estimate. Scaling zero-order streams to the Corn Belt increases indirect emissions to 82 Gg $N_2O$-N $yr^{-1}$ while the total emissions double to 129 Gg $N_2O$-N $yr^{-1}$. However, the uncertainty in $N_2O$ emissions related to zero-order streams is large because we lack direct observational data, the reactivation timing is uncertain, and the microscale watershed threshold necessary to form a zero-order stream is highly variable. Regardless, there appears to be growing evidence of their importance in closing the gap between bottom-up and top-down emission estimates for the US Corn Belt.

## Materials and Methods

### $N_2O$ Flux Sampling

$N_2O$ fluxes were measured in the field using a flow-through non-steady-state chamber system adapted for deployment in rivers.  The floating chamber consisted of an aluminum lid with a pressure equilibration vent buoyed by foam insulation and covered with reflective material.  The chamber enclosed a surface area of 0.145 $m^2$ with a headspace volume of approximately 0.0147 $m^3$.

Headspace gas was pulled through a Teledyne gas filter correlation $N_2O$ analyzer (Model M320EU2, Teledyne Instruments API, City of Industry, California, USA) and the dry mole fraction was recorded at a sampling frequency of 1 Hz using a data-logger (model 23X, Campbell Scientific Inc., Logan, Utah, USA).  The analyzer was powered in the field by deep cycle 12 VDC batteries wired in parallel to a DC-to-AC inverter.  The chamber system has a minimum detectable flux of 0.028 nmol $N_2O$ $m^{-2}$ $s^{-1}$ [*Fassbinder et al.*, 2013].  The analyzer was calibrated at the beginning of the season using an analytical grade standard and zeroed two times per month using $N_2$ gas.  The concentration precision of the analyzer was 1.5 nmol $mol^{-1}$ and the flux measurement precision was 0.003 nmol $m^{-2}$ $s^{-1}$ [*Fassbinder et al.*, 2013].

The raw data were processed in Matlab (Matlab, Version R2012a, Mathworks, Natick, Massachusetts, USA).  Fluxes were calculated according to:

$$F = \frac{\rho V \Delta}{A} \qquad \qquad \text{(Equation 2.2)}$$

where $\rho$ (mol m$^{-3}$) is the molar density of dry air, $A$ (m$^2$) is the surface area enclosed by the chamber, $V$ (m$^3$) is the chamber volume, and $\Delta$ (nmol N$_2$O mol$^{-1}$ s$^{-1}$) is the rate of change of N$_2$O concentration in the chamber headspace determined from linear regression [*Fassbinder et al.*, 2013]. Prior to calculating the chamber N$_2$O fluxes, a wavelet de-noising technique was applied to the raw concentration data. This reduced the effect of instrument noise and improved the signal to noise ratio [*Fassbinder et al.*, 2013]. We eliminated all chamber flux data when the linear regression R$^2$ value was less than 0.9.

Upscaling

Nonlinear regression analysis was performed using the "fitnlm" function in Matlab. Local stream order data were downloaded from the Minnesota Department of Natural Resources. Mean North American stream order width [*Downing et al.*, 2012] was used to generate stream area. Stream order areal estimates were applied to our nonlinear function to predict river emissions over a 214 day period (DOY 91-305).

The extent of the Corn Belt is subjective and lacks boundaries. Our definition was determined by selecting HUC12 sub-watersheds[¶] with greater than 40% agriculture from 13 states in the Midwest (ND, SD, NE, KS, MN, IA, MO, AR, WI, IL, OH, IN, MI). Regional stream order data (NHDPlus) was used in our nonlinear model. The regional dataset is at a lower resolution than the local stream order and as a consequence

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[¶] NHDPlus V.2, Horizon Systems Corp., Herndon, Virginia, USA, http://www.horizon-systems.com/NHDPlus/

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underestimated stream length.  A comparison of Minnesota streams determined a scaling factor (1.4) was appropriate to apply to the regional data to correct for this underestimation.

Default Tier 1 IPCC methodologies were used to estimate $N_2O$ emissions [*De Klein et al.*, 2006].  This budget included direct emissions from soils from synthetic and organic nitrogen application, indirect emissions from the volatilization of synthetic and organic fertilizer, rivers, and groundwater.  We did not account for emissions from natural systems, industry, grazing livestock, organic soils, crop residues and legumes. Annual rates of synthetic and organic fertilizer application were used.

Zero-order streams were estimated from LiDAR data provided by the Minnesota Geospatial Information Office that was processed using ArcMap.  A threshold of 250 $m^2$ was set before a stream would "activate".  We assumed a period of 2 months of active emissions which would include spring thaw and periodic precipitation events.  Zero-order width was estimated using a regression equation from North American stream width data [*Downing et al.*, 2012].

## Acknowledgements

Minnesota Supercomputing Institute for Advanced Computational Research

(https://www.msi.umn.edu/).

$$y = 34 *exp^{(-0.73 *S)}$$
$$R^2 = 0.95$$
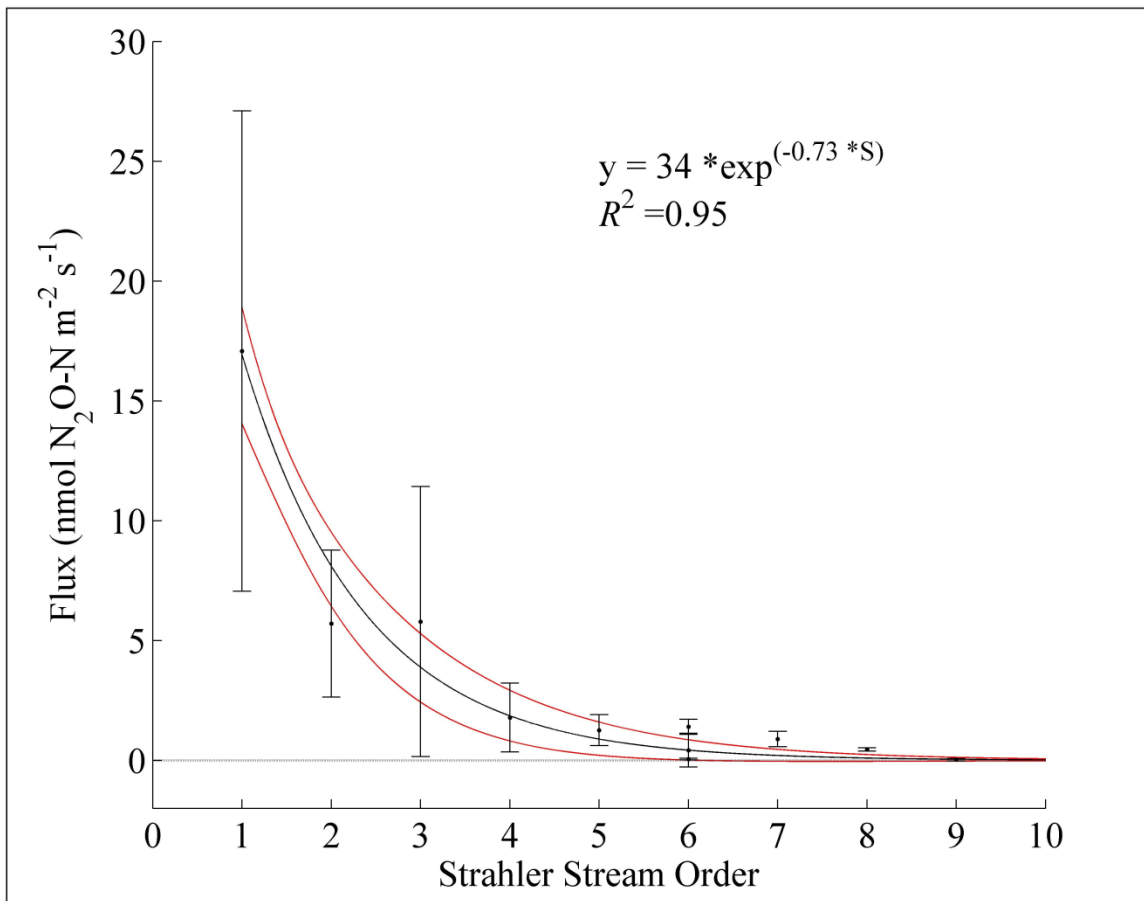
**Figure 2.1.** The relation between $N_2O$ flux and the Strahler stream order in southeastern Minnesota. The black line represents the best fit of an exponential function to the mean flux values measured at each stream order. Red lines represent the 95% confidence interval of the model fit and error bars indicate one standard deviation from the mean.
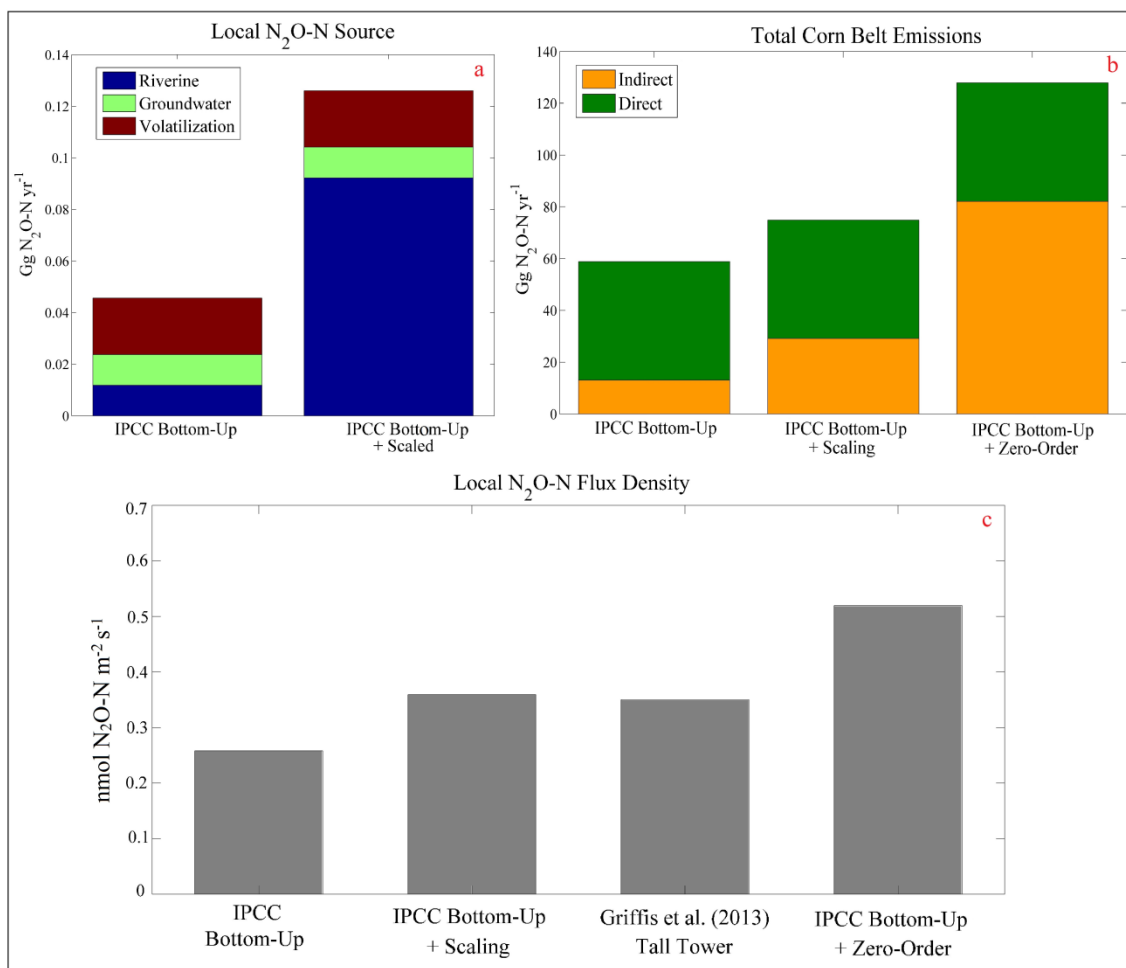
**Figure 2.2.** Results from upscaling N$_2$O emissions. a) A comparison of local indirect N$_2$O-N sources from default IPCC EFs and our scaling method. b) Total US Corn Belt emissions from the three methods. c) The flux densities from the tall-tower source footprint for each method.
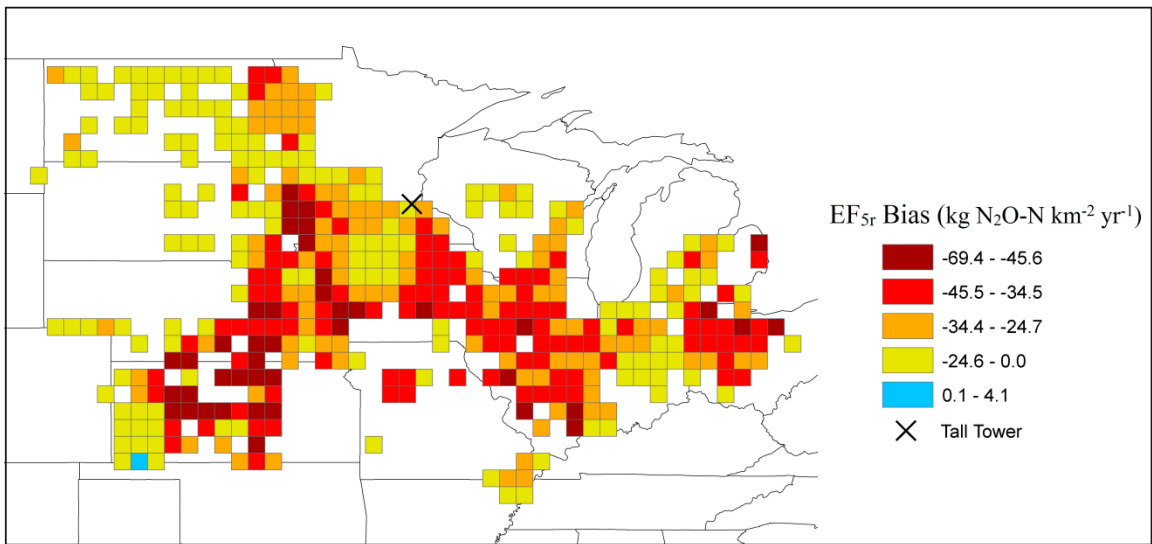
**Figure 2.3.** The first-order default EF$_{5r}$ underestimation from the Corn Belt region. The bias is defined as the difference between IPCC EF$_{5r}$ emissions and the results from stream order scaling.

## Appendix

Stream $N_2O$ flux observations were taken from locations scattered throughout southern Minnesota, U.S.A. during the 2013-2014 ice-free seasons. The seasonal and spatial distribution of sample dates and sites are described below.

| Latitude | Longitude | Date | Stream |
|----------|-----------|------|--------|
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.696 | -93.076 | 06 17 2013 | 1st Order |
| 44.695 | -93.075 | 06 17 2013 | 1st Order |
| 44.695 | -93.075 | 06 17 2013 | 1st Order |
| 44.695 | -93.075 | 06 17 2013 | 1st Order |
| 44.695 | -93.075 | 06 17 2013 | 1st Order |
| 44.674 | -93.076 | 06 17 2013 | 1st Order |
| 44.674 | -93.076 | 06 17 2013 | 1st Order |
| 44.674 | -93.076 | 06 17 2013 | 1st Order |
| 44.674 | -93.076 | 06 17 2013 | 1st Order |
| 44.590 | -93.116 | 06 20 2014 | 1st Order |
| 44.590 | -93.116 | 06 20 2014 | 1st Order |
| 44.590 | -93.116 | 06 20 2014 | 1st Order |
| 44.590 | -93.116 | 06 20 2014 | 1st Order |
| 44.361 | -93.204 | 07 03 2013 | 1st Order |
| 44.361 | -93.204 | 07 03 2013 | 1st Order |
| 44.361 | -93.204 | 07 03 2013 | 1st Order |
| 44.360 | -93.204 | 07 03 2013 | 1st Order |
| 44.360 | -93.204 | 07 03 2013 | 1st Order |
| 44.360 | -93.204 | 07 03 2013 | 1st Order |
| 44.361 | -93.204 | 07 12 2013 | 1st Order |
| 44.361 | -93.204 | 07 12 2013 | 1st Order |
| 44.361 | -93.204 | 07 12 2013 | 1st Order |
| 44.360 | -93.204 | 07 12 2013 | 1st Order |
| 44.360 | -93.204 | 07 12 2013 | 1st Order |
| 44.360 | -93.204 | 07 12 2013 | 1st Order |
| 44.360 | -93.204 | 07 12 2013 | 1st Order |

| Latitude | Longitude | Date | Stream |
|----------|-----------|------|--------|
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.360 | -93.205 | 07 12 2013 | 1st Order |
| 44.022 | -94.319 | 08 29 2013 | 1st Order |
| 44.022 | -94.319 | 08 29 2013 | 1st Order |
| 44.022 | -94.319 | 08 29 2013 | 1st Order |
| 44.022 | -94.319 | 08 29 2013 | 1st Order |
| 44.539 | -93.100 | 06 20 2014 | 2nd Order |
| 44.539 | -93.100 | 06 20 2014 | 2nd Order |
| 44.539 | -93.100 | 06 20 2014 | 2nd Order |
| 44.572 | -93.024 | 06 24 2014 | 2nd Order |
| 44.572 | -93.024 | 06 24 2014 | 2nd Order |
| 44.572 | -93.024 | 06 24 2014 | 2nd Order |
| 44.486 | -93.215 | 07 15 2014 | 2nd Order |
| 44.486 | -93.215 | 07 15 2014 | 2nd Order |
| 44.486 | -93.215 | 07 15 2014 | 2nd Order |
| 44.539 | -93.100 | 07 18 2014 | 2nd Order |
| 44.539 | -93.100 | 07 18 2014 | 2nd Order |
| 44.539 | -93.100 | 07 18 2014 | 2nd Order |
| 44.539 | -93.100 | 07 18 2014 | 2nd Order |
| 44.539 | -93.100 | 06 20 2014 | 3rd Order |
| 44.539 | -93.100 | 06 20 2014 | 3rd Order |
| 44.539 | -93.100 | 06 20 2014 | 3rd Order |
| 44.539 | -93.100 | 06 20 2014 | 3rd Order |
| 44.555 | -92.975 | 06 24 2014 | 3rd Order |
| 44.555 | -92.975 | 06 24 2014 | 3rd Order |
| 44.555 | -92.975 | 06 24 2014 | 3rd Order |
| 44.522 | -93.247 | 07 15 2014 | 3rd Order |
| 44.522 | -93.247 | 07 15 2014 | 3rd Order |
| 44.522 | -93.247 | 07 15 2014 | 3rd Order |
| 44.539 | -93.100 | 07 18 2014 | 3rd Order |
| 44.539 | -93.100 | 07 18 2014 | 3rd Order |
| 44.539 | -93.100 | 07 18 2014 | 3rd Order |
| 44.539 | -93.100 | 07 18 2014 | 3rd Order |
| 44.507 | -93.130 | 06 20 2014 | 4th Order |
| 44.507 | -93.130 | 06 20 2014 | 4th Order |

| Latitude | Longitude | Date | Stream |
|---|---|---|---|
| 44.515 | -93.232 | 07 15 2014 | 4th Order |
| 44.515 | -93.232 | 07 15 2014 | 4th Order |
| 44.515 | -93.232 | 07 15 2014 | 4th Order |
| 44.507 | -93.130 | 07 18 2014 | 4th Order |
| 44.507 | -93.130 | 07 18 2014 | 4th Order |
| 44.507 | -93.130 | 07 18 2014 | 4th Order |
| 44.093 | -94.108 | 08 29 2013 | Blue Earth River |
| 44.093 | -94.108 | 08 29 2013 | Blue Earth River |
| 44.093 | -94.108 | 08 29 2013 | Blue Earth River |
| 44.093 | -94.108 | 08 29 2013 | Blue Earth River |
| 44.488 | -93.128 | 08 01 2013 | Cannon River |
| 44.489 | -93.119 | 08 01 2013 | Cannon River |
| 44.492 | -93.113 | 08 01 2013 | Cannon River |
| 44.495 | -93.108 | 08 01 2013 | Cannon River |
| 44.496 | -93.100 | 08 01 2013 | Cannon River |
| 44.499 | -93.093 | 08 01 2013 | Cannon River |
| 44.506 | -93.074 | 08 01 2013 | Cannon River |
| 44.509 | -93.065 | 08 01 2013 | Cannon River |
| 44.510 | -93.059 | 08 01 2013 | Cannon River |
| 44.513 | -93.056 | 08 01 2013 | Cannon River |
| 44.515 | -93.050 | 08 01 2013 | Cannon River |
| 44.516 | -93.020 | 08 01 2013 | Cannon River |
| 44.640 | -93.757 | 08 20 2013 | Minnesota River |
| 44.644 | -93.758 | 08 20 2013 | Minnesota River |
| 44.645 | -93.749 | 08 20 2013 | Minnesota River |
| 44.649 | -93.734 | 08 20 2013 | Minnesota River |
| 44.659 | -93.716 | 08 20 2013 | Minnesota River |
| 44.668 | -93.710 | 08 20 2013 | Minnesota River |
| 44.672 | -93.695 | 08 20 2013 | Minnesota River |
| 44.683 | -93.684 | 08 20 2013 | Minnesota River |
| 44.684 | -93.683 | 08 20 2013 | Minnesota River |
| 44.694 | -93.657 | 08 20 2013 | Minnesota River |
| 44.695 | -93.646 | 08 20 2013 | Minnesota River |
| 44.899 | -93.191 | 08 15 2013 | Mississippi River |
| 44.895 | -93.186 | 08 15 2013 | Mississippi River |
| 44.894 | -93.179 | 08 15 2013 | Mississippi River |
| 44.894 | -93.171 | 08 15 2013 | Mississippi River |
| 44.896 | -93.161 | 08 15 2013 | Mississippi River |
| 43.783 | -92.032 | 08 28 2013 | Root River |

| Latitude | Longitude | Date | Stream |
| --- | --- | --- | --- |
| 43.783 | -92.032 | 08 28 2013 | Root River |
| 43.783 | -92.032 | 08 28 2013 | Root River |
| 43.783 | -92.032 | 08 28 2013 | Root River |
| 43.783 | -92.032 | 08 28 2013 | Root River |
| 43.840 | -92.197 | 08 28 2013 | Root River |
| 43.840 | -92.197 | 08 28 2013 | Root River |
| 44.674 | -93.075 | 06 20 2013 | Vermillion River |
| 44.674 | -93.075 | 06 20 2013 | Vermillion River |
| 44.674 | -93.075 | 06 20 2013 | Vermillion River |
| 44.026 | -94.229 | 08 29 2013 | Watonwan River |
| 44.022 | -94.319 | 08 29 2013 | Watonwan River |
| 44.046 | -94.195 | 08 29 2013 | Watonwan River |
| 44.047 | -94.168 | 08 29 2013 | Watonwan River |
| 44.047 | -94.168 | 08 29 2013 | Watonwan River |
| 44.319 | -92.701 | 08 27 2013 | Zumbro River |
| 44.319 | -92.701 | 08 27 2013 | Zumbro River |
| 44.306 | -92.761 | 08 27 2013 | Zumbro River |
| 44.306 | -92.761 | 08 27 2013 | Zumbro River |
| 44.257 | -92.494 | 08 27 2013 | Zumbro River |
| 44.257 | -92.494 | 08 27 2013 | Zumbro River |
| 44.257 | -92.493 | 08 27 2013 | Zumbro River |
| 44.320 | -92.127 | 08 27 2013 | Zumbro River |
| 44.320 | -92.127 | 08 27 2013 | Zumbro River |

# Chapter 3

# Regional-scale controls on dissolved nitrous oxide in the Upper Mississippi River

Peter A. Turner, Timothy J. Griffis, John M. Baker, Xuhui Lee, John T. Crawford, Luke C. Loken, and Rodney T. Venterea (2016), *Geophysical Research Letters*, 43 (9), 4400-4407, doi: 10.1002/2016GL068710

## Overview

The U.S. Corn Belt is one of the most intensive agricultural regions of the world and is drained by the Upper Mississippi River (UMR), which forms one of the largest drainage basins in the U.S. While the effects of agricultural nitrate ($NO_3^-$) on water quality in the UMR have been well documented, its impact on the production of nitrous oxide ($N_2O$) has not been reported. Using a novel equilibration technique, we present the largest dataset of freshwater dissolved $N_2O$ concentrations and examine the controls on its variability over a 350-km reach of the UMR. Driven by a supersaturated water column, the UMR was an important atmospheric $N_2O$ source that varies non-linearly with $NO_3^-$, which should be considered in emission inventories. Our analyses indicated that a projected doubling of $NO_3^-$ by 2050 would cause dissolved $N_2O$ concentrations and atmospheric emissions to increase by about 40%.

## Introduction

The Upper Mississippi River (UMR) drains nearly 492,000 $km^2$ of the U.S. Corn Belt [*NRCS*, 2012], one of the most intensively cultivated regions on the planet. Within the UMR basin, more than half of the U.S. share of nitrogen (N) fertilizers are applied [*Griffis et al.*, 2013; *FAO*, 2015] to produce 40% of the nation's corn [*NRCS*, 2012]. These activities have amplified river N loading, mainly as nitrate ($NO_3^-$) [*Turner and Rabalais*, 1991; *Panno et al.*, 2006]. Much effort has focused on the effects of excessive N on water quality [*Rabalais*, 2002] and the ability of the UMR to reduce downstream

transport [*Richardson et al.*, 2004; *Strauss et al.*, 2004, 2011] to estuary systems.

However, measurements of nitrous oxide ($N_2O$), the dominant stratospheric ozone

depleting substance [*Ravishankara et al.*, 2009] and an important greenhouse gas

[*Hartmann et al.*, 2013], in the UMR are conspicuously absent in the literature,

representing a significant knowledge gap in our understanding of the regional controls on

dissolved $N_2O$ concentrations and emissions in heavily modified agricultural rivers.

Rivers are globally significant sources of $N_2O$ to the atmosphere [*Beaulieu et al.*,

2011; *Turner et al.*, 2015], responsible for 10% – 17% of the anthropogenic budget

[*Beaulieu et al.*, 2011; *Syakila and Kroeze*, 2011].  Yet, rivers remain one of the most

uncertain $N_2O$ sources [*Nevison*, 2000], largely due to low spatiotemporal sampling

resolution that is unable to resolve the high variability of surface water $N_2O$

concentrations caused by dynamic production and consumption processes.  Nitrous oxide

production *via* denitrification and nitrification in the water column [*Beaulieu et al.*, 2010]

and sediments [*Boyer et al.*, 2006; *Marzadri et al.*, 2014] causes rivers to become

saturated with $N_2O$ that is emitted to the atmosphere.  Generally, the degree of $N_2O$

saturation increases with the concentration of $NO_3^-$ and ammonium ($NH_4^+$), indicating

that emissions from large rivers are derived from *in-situ* $N_2O$ production [*Beaulieu et al.*,

2010], rather than terrestrial delivery.  Global model simulations suggest a doubling of N

loading in rivers by the year 2050 [*Seitzinger et al.*, 2002], implying that $N_2O$ emissions

from rivers, including the UMR, will likely increase.  However, the relationship between

dissolved $N_2O$ concentrations in rivers and N loading is poorly constrained because

obtaining these types of data is logistically challenging and, consequently, observations are very limited.

Recent studies indicate that surface water $N_2O$ concentrations behave non-linearly, plateauing in response to a number of environmental drivers, including dissolved oxygen concentration [*Rosamond et al.*, 2012] and water temperature [*Venkiteswaran et al.*, 2014]. Observations that $N_2O$ concentrations increase at a decreasing rate is likely caused by the inverse relation between N loading and removal efficiency [*Mulholland et al.*, 2008]. This non-linearity implies that $N_2O$ emissions will not increase proportionally with N loading projections, especially as a river becomes N-saturated. Characterizing the $N_2O:NO_3^-$ mass ratio should provide an upper constraint on $N_2O$ concentrations in N-rich systems and provide insights regarding how these rivers may respond under business-as-usual nitrogen use scenarios.

Here, we present the largest freshwater dissolved $N_2O$ concentration dataset to date and the first $N_2O$ surface water concentration measurements from the UMR to: 1) explore the biochemical factors that control the degree of riverine $N_2O$ saturation; 2) identify $N_2O$ hotspots; and 3) predict how $N_2O$ concentrations will respond to future N loading.

## Materials and Methods
### Site Description

For this study, we considered a portion of the UMR that extends from Minneapolis, MN through Pool 8 (near La Crosse, WI). Along this stretch, eight lock

and dam combinations have been installed to facilitate navigation. The river is organized into pools to describe river sections between two neighboring dams. In addition to the main channel, a pool includes impounded waters, side channels, and backwaters [*Strauss et al.*, 2011]. The seasonal (10 April, 16 June, 4 August, and 13 October) and spatial dynamics of $N_2O$ concentration were observed in Pool 8, a 104 $km^2$ section of the UMR upstream of Lock and Dam 8. From 1-3 August 2015, a 350 km reach from Minneapolis, Minnesota to Pool 8 provided a regional-scale assessment of $N_2O$ concentration patterns in the UMR.

Water Sampling

We used a boat-mounted flow-through sampling system [*Crawford et al.*, 2015] to continually measure surface water $N_2O$ and other limnological parameters. In brief, we pumped surface water (0.3-m) to a series of sensors and stripped the dissolved gases using a sprayer-type equilibration device [*Crawford et al.*, 2015]. This type of equilibrator has a fast response time [*Santos et al.*, 2012; *Yoon et al.*, 2016] and has been used in oceanic $N_2O$ campaigns [*Bange et al.*, 1996; *Arévalo-Martínez et al.*, 2013, 2015; *O'Reilly et al.*, 2015] but has never been used to measure $N_2O$ in freshwater systems. Equilibrator headspace air was drawn through a desiccant tube before entering a Teledyne gas filter correlation $N_2O$ analyzer (Model M320EU2; Teledyne Instruments, City of Industry, CA, USA) [*Fassbinder et al.*, 2013; *Turner et al.*, 2015]. A circular loop was created by returning sample air back to the equilibrator device. A data-logger

(Model 23X; Campbell Scientific, Logan, UT, USA) stored the $N_2O$ analyzer output at 1 Hz for processing.

This system, the Fast Limnology Automated Measurement (FLAMe) platform has been used extensively to monitor dissolved $CO_2$ and $CH_4$ on the Mississippi River [*Crawford et al.*, 2016].  The FLAMe instrument panel consisted of a YSI sonde (Model EXO2; Yellow Springs, OH, USA), an optical $NO_3$ sensor (Model SUNA V2, Satlantic, Halifax, NS, Canada), and a GPS device.  The FLAMe platform measured water temperature (*T*), dissolved oxygen (DO), pH, turbidity, specific conductivity, Chl-*a*, and fluorescent dissolved organic matter (fDOM).  Higher fDOM values are related to terrestrially derived organic matter [*Spencer et al.*, 2013] and are a proxy for dissolved organic carbon [*Crawford et al.*, 2015].  Spatial coordinates were recorded semi-continuously at 1 Hz while measurements of $NO_3^-$ were stored at 0.1 Hz.

Data Processing

The raw $N_2O$ concentration data (*n* = 101,862) were processed using Matlab (R2013b; Mathworks, Natick, MA, USA) software.  To georeference the FLAMe and $N_2O$ data, we determined the hydraulic and sensor response time lags using a series of step-change experiments [*Crawford et al.*, 2015].  The hydraulic and sensor lag describes the time required for the instrument to detect a step change (42.3-s) caused by tube length, instrument responsivity, and equilibrator lag.  The sensor responsivity of the $N_2O$ analyzer was estimated using an equilibrator time constant $\tau$ (61.6-s) that describes the time required for a 63% step change to occur.  A wavelet denoising technique was

applied to the $N_2O$ concentration data to improve the signal to noise ratio of the instrument [*Fassbinder et al.*, 2013]. For convenience of data processing and statistical analyses, all of the data streams were subjected to 30-s block averaging resulting in a data series of $n = 3,667$.

The surface water $[N_2O]$ (mol $N_2O$ $L^{-1}$) was calculated from:

$$[N_2O] = [N_2O_*] \times F(T, p) \qquad \text{(Equation 3.1)}$$

where $[N_2O_*]$ is the equilibrator concentration, and $F(T, p)$ is the solubility function at the given surface water temperature (T) and pressure (p) [*Weiss and Price*, 1980; *Grefe and Kaiser*, 2014]. The theoretical equilibrium $N_2O$ concentration ($[N_2O_{amb}]$, mol $N_2O$ $L^{-1}$) assuming water-atmosphere equilibrium was calculated similarly:

$$[N_2O_{amb}] = [N_2O_{amb*}] \times F(T, p) \qquad \text{(Equation 3.2)}$$

where $[N_2O_{amb*}]$ is the ambient atmospheric concentration reading by the $N_2O$ analyzer, and T and p are ambient water temperature and air pressure, respectively at the time of measurement. The ambient concentration was measured every 2-hrs. The analyzer was zeroed and spanned using analytical grade standards (Specialty Gases of America, Toledo, OH, USA) before each measurement campaign. The concentration precision of the analyzer after wavelet denoising is 1.5-nmol mol$^{-1}$ [*Fassbinder et al.*, 2013]. These two metrics, $[N_2O]$ and $[N_2O_{amb}]$, are water temperature dependent. Therefore, we use their ratio to standardize the measurements with respect to the in-situ water temperature:

$$N_2O_{sat} = \frac{[N_2O]}{[N_2O_{amb}]} \qquad \text{(Equation 3.3)}$$

A novel aspect of the FLAMe platform is its capacity to incorporate spatial coordinates to identify spatial patterns driving $N_2O_{sat}$ across large spatial distances. A Getis-Ord G* analysis of each dataset identified clustering of statistically significant high and low $N_2O_{sat}$ and $NO_3^-$ values relative to neighboring points [*Ord and Getis*, 2010]. A 99% significance threshold was used to determine $N_2O_{sat}$ and $NO_3^-$ hotspots and coldspots (Arcmap v.10.3; ESRI, Redlands, CA, USA).

Using $CO_2$ piston velocity ($k$) measurements from the UMR [*Crawford et al.*, 2016], we estimated the mean ($n = 22$) $k$ using the temperature adjusted $N_2O$ Schmidt number [*Wanninkhof*, 1992]. Nitrous oxide fluxes (nmol $N_2O$-N m$^{-2}$ s$^{-1}$) from the UMR were calculated as:

$$\text{Flux}_{N2O} = k \times ([N_2O] - [N_2O_{amb}]) \qquad \text{(Equation 3.4)}$$

We assumed that variations in the evasion coefficient would be negligible within the UMR because of minimal channel geometry change and consequently, $N_2O_{sat}$ and $\text{Flux}_{N2O}$ would be most sensitive to in-situ production and consumption mechanisms. We estimated that $N_2O_{sat}$ ratios greater than 1.2 and less than 0.8 were indicative of active production and consumption zones, respectively, while $N_2O_{sat}$ values within this window were classified as zones of negligible production and consumption [*Beaulieu et al.*, 2015].

Ensemble Regression Trees

The controls on riverine $N_2O_{sat}$ were identified independently for each river section using ensemble ($n = 500$) binary bagged regression trees with the Matlab *fitensemble* function (v.2015.b, Mathworks, Natick, MA, USA).  This supervised learning method does not require an assumption of normality and the bootstrap aggregation technique reduces prediction variance [*De'ath and Fabricius*, 2000; *Sutton*, 2005] making it a powerful tool for better understanding the controls on $N_2O$ saturation [*Baulch et al.*, 2011; *Venkiteswaran et al.*, 2014; *Lundy et al.*, 2015].  The relative predictor importance (RPI) of each explanatory variable on the corresponding $N_2O_{sat}$ response was computed by summing the change in mean square error from splitting each predictor and dividing by the number of nodes.  The importance was normalized with respect to the largest value [*Lundy et al.*, 2015]; a response of 1 recognizes the independent variable with the greatest impact on the $N_2O_{sat}$ and a value of zero indicates no influence.  The variance of the ensemble regression model was determined by calculating the pseudo $R^2$ value of model predicted and observed $N_2O_{sat}$ concentrations.

Results and Discussion

The UMR was supersaturated with $N_2O$ throughout the ice-free measurement period, indicating it was an important atmospheric source (Figure 3.1, 3.2a).  Across all sampling locations and dates, the mean (standard deviation) $N_2O_{sat}$ was 2 (0.9) times the atmospheric saturation (Table 3.1).  The regional mean flux was 0.5 (0.3) nmol $N_2O$-N $m^{-2}$ $s^{-1}$, which is comparable to observations from nearby corn fields [*Griffis et al.*, 2013]

and within the range observed in other large rivers [*McMahon and Dennehy*, 1999; *Cole and Caraco*, 2001; *Hinshaw and Dahlgren*, 2013].  Since groundwater and most tributary flows are negligible in a river of this size, and because of the short residence time of upstream dissolved gases, our data indicate that the UMR actively produces $N_2O$ throughout the year.

During the June Pool 8 campaign, an instrument issue prevented $N_2O_{sat}$ measurements greater than 4.8.  Since we can only state that $N_2O_{sat}$ was equal to or above 4.8, they were not included in the following analyses.  However, the high $N_2O_{sat}$ in Pool 8 in June is consistent with recent top-down measurements and modeling that found total emissions (direct + indirect) [*Miller et al.*, 2012; *Griffis et al.*, 2013] and indirect emissions from leaching and runoff [*Chen et al.*, 2016] to be highest during this period, likely because of the recent application of N fertilizers.

Spatial analyses, based on the Getis-Ord G* statistic [*Ord and Getis*, 2010], identified four $N_2O_{sat}$ hotspots along this section of the UMR (Figure 3.2b).  Hotspots were generally within close proximity to municipal wastewater treatment plants (WWTP).  These hotspots dissipated rapidly, presumably because of dilution, over relatively short distances suggesting that care should be taken when sampling nearby. The strength of these hotspots reflects differences in effluent discharge and river volume. Since $NO_3^-$ hotspots were not observed downstream of each WWTP (Figure 3.2c), it is likely that $N_2O$ was produced during wastewater processing prior to discharge into the UMR [*Kampschreur et al.*, 2009].  However, WWTPs are relatively minor contributors to the total N in the UMR, with greater than 70% being from agricultural sources [*Wall et*

*al.*, 2013].  Our analyses identified five $N_2O_{sat}$ coldspots along this reach that were collocated with $NO_3^-$ coldspots (Figure 3.2c), indicating that $NO_3^-$ concentrations are an underlying requirement for $N_2O$ production.

Overall, the surface water $NO_3^-$ (RPI = 1) concentration was the most important explanatory variable driving regional fluctuations in UMR $N_2O_{sat}$ (Figure 3.3a), whereas across seasons, temperature (RPI = 1) and $NO_3^-$ (RPI = 0.86) were the most important predictors (Figure 3.3b).  The strong relation with $NO_3^-$ throughout the UMR was expected because it is linked to both nitrification and denitrification.  These processes are well documented in rivers [*Strauss et al.*, 2002; *Beaulieu et al.*, 2011], lakes [*Wang et al.*, 2009], reservoirs [*Beaulieu et al.*, 2015], and estuaries [*Owens*, 1986; *Murray et al.*, 2015].  In a well-oxygenated river such as the UMR, the strong relation between $NO_3^-$ and $N_2O_{sat}$ suggests that nitrification is a likely $N_2O$ production pathway [*Beaulieu et al.*, 2015].  Further, we argue that the $NO_3^-$ concentration in the surface water is also an indirect measure of the $NO_3^-$ available for diffusion into hypoxic sediments [*Rosamond et al.*, 2012], i.e. the sediment denitrification potential.  However, the kinetics of $NO_3^-$ processing and concurrent $N_2O$ production are affected by secondary environmental factors – including turbidity (RPI = 0.4), pH (RPI = 0.3), fDOM (RPI = 0.18), and DO (RPI = 0.14) that may limit or enhance reaction rates (production *via* nitrification and consumption *via* denitrification).

We posit that these secondary factors indirectly dampen the $N_2O_{sat}$ response by reducing the efficiency of $NO_3^-$ removal (i.e. $N_2O$ production potential) at high solute concentrations [*Mulholland et al.*, 2008].  This response has been attributed to limits on

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denitrification – including, dissolved oxygen and carbon [*Mulholland et al.*, 2008] that

were also identified by our ensemble regression tree model.  These data also classified

pH as an important predictor, likely because it affects the rates of denitrification

[*Knowles*, 1982] and nitrification [*Strauss et al.*, 2004].  We hypothesize that the positive

relation identified between turbidity and $N_2O_{sat}$ in the model reflects the fact that

nitrifying bacteria bind to suspended particles in the water column [*Beaulieu et al.*, 2010].

Together, these factors affect the fraction of $NO_3^-$ converted to $N_2O$ at N saturation

[*Beaulieu et al.*, 2011] that underlies the horizontal asymptote observed for dissolved

$N_2O$ concentrations in the UMR (Figure 3.4).

Using Michaelis-Menten kinetics [*García-Ruiz et al.*, 1998; *Boyer et al.*, 2006],

we describe the weakening $N_2O$ response to N saturation as:

$$[N_2O] = \frac{V_{max} \times [NO_3]}{K_m + [NO_3]}$$
(Equation 3.5)

with the parameters estimated using a nonlinear least squares fitting function (*enzkin*;

v.R2013B; Mathworks, Natick, MA, USA).  Here, the $[N_2O]$ (mg $N_2O$-N $L^{-1}$) can be

derived from the $[NO_3^-]$ (mg $NO_3^-$ $L^{-1}$) with a $V_{max}$ of 0.0011 (95% CI; $\pm 4.1 \times 10^{-5}$) mg

$N_2O$-N $L^{-1}$ and a $K_m$ of 1.36 ($\pm 0.11$) mg $NO_3^-$ $L^{-1}$.  The $V_{max}$ represents the system's

maximum $[N_2O]$ and the $K_m$ is the $[NO_3^-]$ required to reach 50% of the $V_{max}$.  The non-

linearity of Figure 3.4 implies that increasing $NO_3^-$ concentrations will have a

progressively weaker effect on $N_2O$ concentrations in the UMR.  In North America, river

models project a doubling of the $NO_3^-$ exported to estuaries by the year 2050 [*Seitzinger

et al.*, 2002].  Using the relation shown in Figure 3.4, a doubling of $NO_3^-$ would increase

N$_2$O emissions from the UMR by about 42% (95% CI; 32-52%). Conversely, the U.S. Environmental Protection Agency has established a goal to reduce N export by 45% by 2035. If this goal were achieved, N$_2$O concentrations in the UMR would be decreased by about 32% (26-38%), implying a significant reduction in N$_2$O emissions. However, because our regression tree models indicated that N$_2$O$_{sat}$ was influenced by secondary factors, these forecasts could be diminished – for instance, a reduction in turbidity (decreased substrate for nitrifying bacteria) would lower N$_2$O$_{sat}$ and therefore these forecasts should represent an upper estimate.

While automated soil N$_2$O measurement systems have become more common in recent years, techniques for continuous measurement of riverine N$_2$O concentrations have lagged behind. The techniques applied in this study have potential to address this problem worldwide and could significantly reduce the uncertainty in riverine N$_2$O emissions and the riverine emission factor (EF$_{5r}$) provided by the Intergovernmental Panel on Climate Change (IPCC). For instance, stationary *in-situ* sampling platforms located at strategic locations within a stream network could be used for emission upscaling [*Turner et al.*, 2015] to develop regionally appropriate, Tier II EF$_{5r}$ values. Further, such data could be used to improve our understanding of the inter-annual variability and long-term dynamics of dissolved riverine N$_2$O and emissions.

## Conclusions

Our data and analyses demonstrate that the UMR is supersaturated with N$_2$O during the ice-free period and is an important source of atmospheric N$_2$O. The regression

tree models evaluated in this study indicate that $NO_3^-$ is the dominant control on $N_2O$ concentrations, but that other environmental variables may limit $NO_3^-$ processing. Given the significant non-linear relation between $NO_3^-$ and $N_2O$ in the UMR, we expect that a doubling of N loading is likely to cause a substantial (32-52%) rise in dissolved $N_2O$ concentrations and atmospheric emissions.

## Acknowledgments
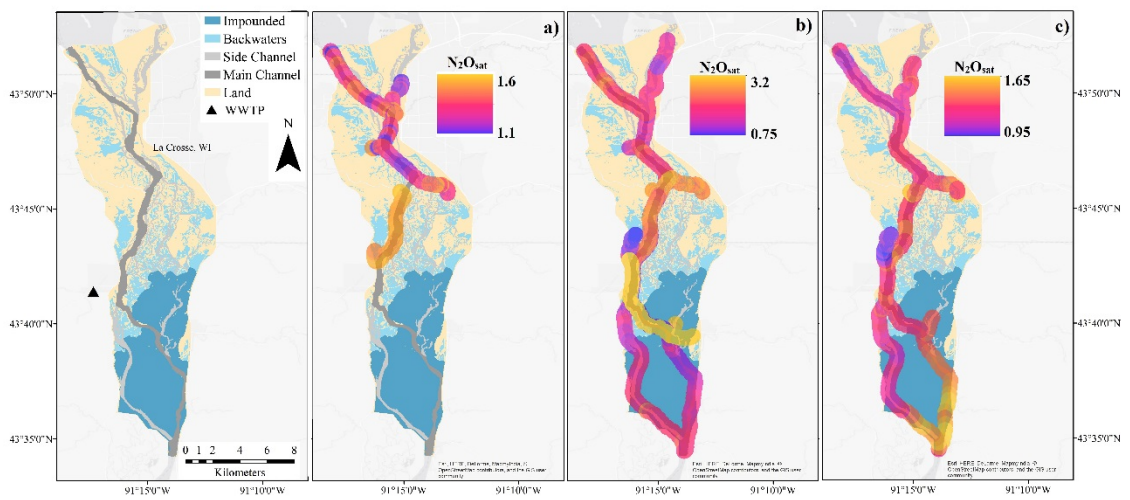
**Figure 3.1.** The seasonal and spatial dynamics of $N_2O_{sat}$ in Pool 8 of the UMR in a) April ($n = 298$), b) August ($n = 828$), and c) October ($n = 514$).
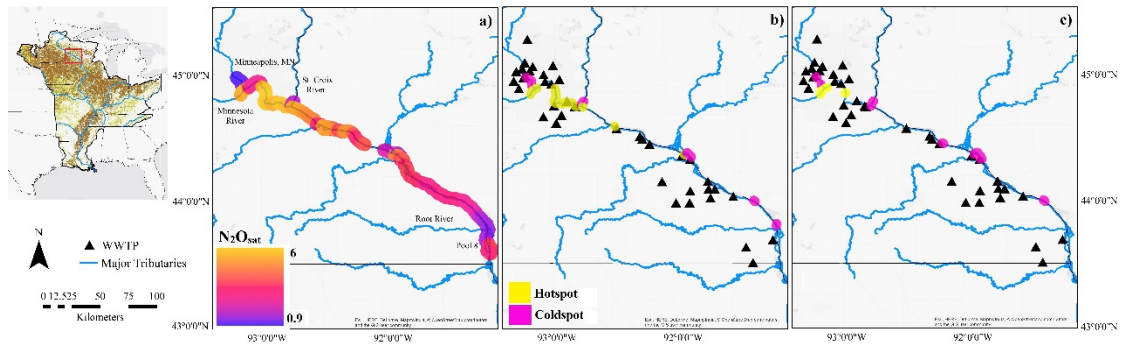
**Figure 3.2.** Inset) Agricultural land use within the UMR basin.  Row-crop (brown) and pasture (yellow) were drawn using information from the National Land Cover Database (2011).  a). The regional-scale variability of $N_2O_{sat}$ in the UMR ($n$ = 1,553).  Hotspots and coldspots of b) $N_2O_{sat}$ and c) $NO_3^-$.
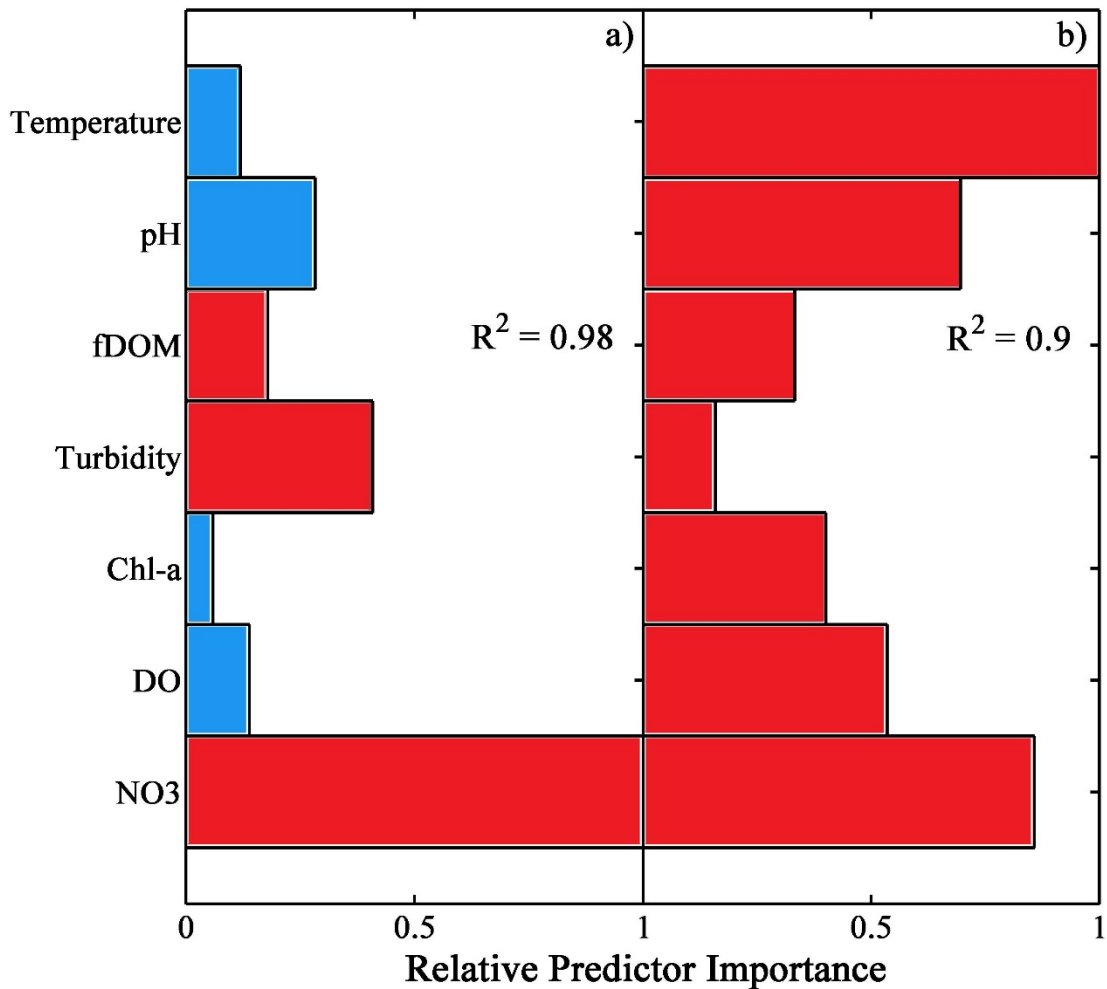
**Figure 3.3.** Relative predictor importance (RPI) determined using ensemble ($n = 500$) regression trees to predict $N_2O_{sat}$ observations. Red and blue bars denote positive and negative relationships, respectively. The variable importance describes the explanatory power of a predictor on the $N_2O_{sat}$ response. The pseudo $R^2$ was determined from an observed $N_2O_{sat}$ vs. predicted $N_2O_{sat}$ determined from the ensemble regression model. Each value was normalized to the most important predictor in each system where a) is the RPI of the regional-scale measurements, b) is the seasonal (April, August, October) RPI from Pool 8.
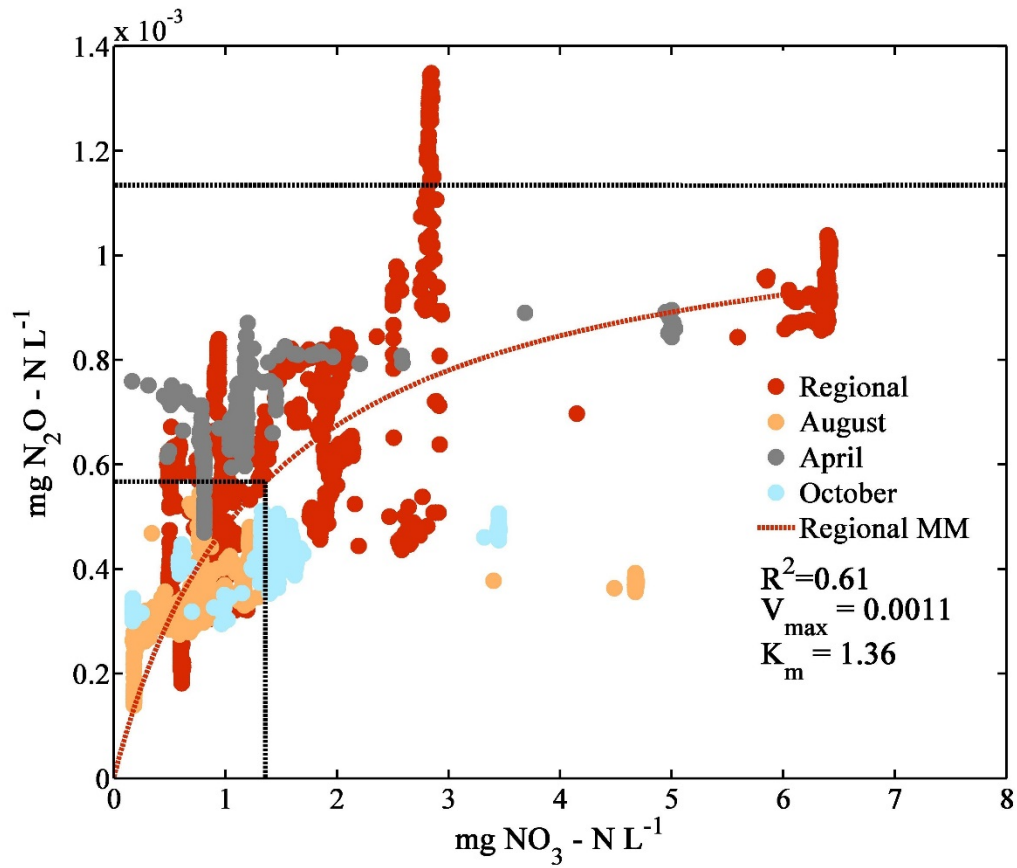
**Figure 3.4.** Measurements of N₂O and NO₃⁻ from the UMR basin. The dashed line is the Michaelis-Menten function derived from the regional-scale campaign ($n = 1,553$).

# Chapter 4

# The Impact of Kura Clover Living Mulch on Nitrous Oxide Emissions in a Corn/Soybean System

Peter A. Turner, John M. Baker, Timothy J. Griffis, and Rodney T. Venterea (2016),

## Overview

Nitrous oxide ($N_2O$), produced primarily in agricultural soils, is a potent greenhouse gas and the dominant ozone depleting substance. Efforts to reduce $N_2O$ emissions are underway, but mitigation results have been inconsistent. The leguminous perennial kura clover (*Trifolium ambiguum* M. Bieb.) can grow side-by-side with cash crops in rotational corn (*Zea mays* L.) – soybean (*Glycine max* L.) systems. With biological nitrogen fixation, kura clover (KC) provides land managers an opportunity to reduce external fertilizer inputs, which may diminish problematic $N_2O$ emissions. To investigate the effect of a KC living mulch on $N_2O$ emissions, automated soil chambers coupled to a $N_2O$ analyzer were used to measure hourly fluxes from April through October in a 2-yr corn-soybean rotation. Emissions from the KC treatment were significantly greater than those from the conventional corn-soybean (CS) treatment, despite the fact that the KC treatment received substantially less inorganic nitrogen (N) fertilizer. A seasonal tradeoff was observed with the KC treatment wherein emissions prior to strip-tillage were reduced but were surpassed by high losses following strip-tillage and also post-anthesis. These results represent the first-reported measurements of $N_2O$ emissions from a KC -based living mulch. The findings cast doubt on the efficacy of KC for mitigating $N_2O$ loss in corn-soybean systems. However, if KC reduces nitrate leaching losses, as has been reported elsewhere, it may result in lower indirect (offsite) $N_2O$ emissions.

Introduction

Nitrous oxide ($N_2O$) is an important greenhouse gas [*Hartmann et al.*, 2013] and the primary ozone depleting substance [*Ravishankara et al.*, 2009]. In the United States, approximately 74% of the anthropogenic $N_2O$ source is linked to agriculture [*USEPA*, 2015], placing tremendous pressure on the agricultural community to reduce $N_2O$ emission while simultaneously increasing grain yields. Most often, the discussion to reduce $N_2O$ emission revolves around modifying traditional crop and N management practices. Efforts have included optimizing fertilizer timing [*Venterea and Coulter*, 2015] source [*Halvorson et al.*, 2014], and depth of application [*Maharjan and Venterea*, 2014]; amendments of biochar [*Lin et al.*, 2014]; and alternative tillage techniques [*Bavin et al.*, 2009; *Jin et al.*, 2014]. However, the success rates of these practices have been inconsistent and conflicting, in part because of the complex site specific soil and meteorological interactions governing $N_2O$ production [*Decock*, 2014].

Because N fertilizers stimulate $N_2O$ production, the N rate is often the best predictor of $N_2O$ emissions [*Stehfest and Bouwman*, 2006]. Notably, recent work suggests that emissions may respond exponentially to increasing N application rates [*Hoben et al.*, 2011; *Shcherbak et al.*, 2014], especially beyond the agronomic optimum application rate [*van Groenigen et al.*, 2010]. Correspondingly, $N_2O$ emissions can be reduced most effectively by simply reducing the N rate, but this practice can reduce yield. To minimize yield loss in response to N rate reduction, a legume can be used to supplant N through biological nitrogen fixation (BNF). This process releases N over time and at lower concentrations than those initially observed following fertilizer application that

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could improve synchronization with crop N needs [*Crews and Peoples*, 2004] while affecting $N_2O$ emissions. Commonly grown legumes include soybeans and cover crop (CC) species such as alfalfa, red clover, and hairy vetch. A long-term alternative is a perennial living mulch management system. This approach provides the BNF benefit of a leguminous CC, minimizing the need for external N fertilizers, which could concurrently reduce $N_2O$ emissions without harming yields.

A living mulch is an alternative cropping system in which a CC grows year round with a commodity crop planted into it. Living mulches provide numerous environmental benefits to the community and land managers by reducing soil erosion [*Wall et al.*, 1991], increasing soil organic matter [*Farahbakhshazad et al.*, 2008], reducing nitrate ($NO_3^-$) leaching [*Ochsner et al.*, 2010], and improving the field's pest resilience [*Enache and Ilnicki*, 1990]. The leguminous perennial KC can grow alongside corn and, when managed correctly, may only minimally impact grain yield [*Zemenchik et al.*, 2000]. We have successfully grown soybeans interseeded into KC as well [*Baker*, 2012], so it has the potential to be a perennial living mulch for corn-soybean rotational systems. However, for farmers to make informed management decisions relative to total environmental impact, the $N_2O$ advantages or disadvantages of living mulches must also be considered.

The impacts of CCs on agricultural $N_2O$ emissions are poorly understood because studies have been sparse and conflicting [*Basche et al.*, 2014]. Leguminous CCs have been reported to either increase [*Gomes et al.*, 2009] or have no effect [*Alluvione et al.*, 2010; *Barton et al.*, 2011] on the $N_2O$ budget. Leguminous production of $N_2O$ is driven

by the decomposition of N-rich residues [*Rochette and Janzen*, 2005], rather than the process of BNF [*Zhong et al.*, 2009]. Residues of legume CC species generally have low ($< 25:1$) carbon (C):N ratios [*Gomes et al.*, 2009] that permit rapid decomposition and nitrification of biotic N, creating an abundance of $NO_3^-$ for $N_2O$ production. Because living mulch systems are not terminated, proper management of these perennial systems could curtail the $N_2O$ losses observed following the termination of a CC [*Basche et al.*, 2014], which are amplified at low C:N residue ratios [*Huang et al.*, 2004]. However, the effects of KC management and root turnover on $N_2O$ emissions are unknown. There is hope that agricultural producers can play an important role in climate change mitigation, but that requires a better understanding of the impact of alternative management practices on greenhouse gas emissions. Toward that end, our objective was to compare $N_2O$ emission budgets from a conventional CS system to one that included a KC living mulch in a strip-tilled, irrigated field over two growing seasons.

## Methods and Materials

### Site Description and Experimental Design

The experiment was conducted in a 17-ha field on the University of Minnesota Rosemount Research and Outreach Center near Rosemount, MN (44°42' N 93°06' W) over the 2013 and 2014 growing seasons. The soil is a Waukegan silt loam consisting of a silt loam surface layer of 0.4 - 0.7-m depth overlying a layer of outwash sand and gravel > 20-m thick. It is well drained and the surface layer has an organic matter content

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of 5.2% and a pH of 6.4 [*Baker*, 2012].  This location has been under nearly continuous cultivation for 125 years, primarily in corn and soybeans since the 1950's [*Griffis et al.*, 2007].

Kura clover was established vegetatively in the summer of 2010, with the primary intent of comparing corn and soybean production in a living mulch versus conventional production [*Baker*, 2012].  The field is equipped with a center pivot.  The field was split into four blocks (quartered), and each block was subdivided into four 1-ha plots: irrigated CS, irrigated KC, rain-fed conventional CS, and rain-fed KC.  Our instruments were housed on the border between an irrigated CS plot and an irrigated KC plot. Measurements reported here were taken only from the irrigated plots.  For the past four years, the entire field has been in a corn-soybean rotation, with soybean in even years and corn in odd.  Each year the entire field is strip-tilled immediately before planting using an Othman 6-row unit.  This implement has a single shank with fluted row cleaners in front of the shank and wavy coulters on either side.

Glyphosate (N-(phosphonomethyl)glycine)-resistant seed was planted on DOY 154 (Corn; Pioneer P9917R) and 151 (Soybean; Pioneer 22T69R) in 2013 and 2014, respectively.  In late spring following strip-tillage and planting, during the crucial germination and early growth period for corn and soybeans, the KC remaining in the inter-row grows vigorously, competing with the young crop for light and resources [*Baker*, 2012].  To minimize these impacts, the KC was mowed to a height of 0.05-m shortly after planting on DOY 165 and DOY 163 in 2013 and 2014, respectively, with the residue left to decompose [*Baker*, 2012].  Weed control in both treatments was

accomplished with a glyphosate application at a rate of 1.04 kg ae ha$^{-1}$ on DOY 176 and 175 in 2013 and 2014, respectively.  This rate has been tailored to suppress rather than to kill the KC [*Zemenchik et al.*, 2000], while also controlling weeds. To minimize water stress, the field received 12.5-mm from the center pivot irrigator on 7 and 3 occasions in 2013 and 2014, respectively.

To capitalize on the BNF benefit provided by the KC, the N rate was reduced (-43%) during the corn phase (2013) in the KC relative to the CS treatment.  We anticipated that labile KC residues created by tillage and mowing would release mineralizable N in the root zone to support crop requirements.  On DOY 154, a broadcast pre-plant N, P, K starter fertilizer (9-18-9) provided 6.7 kg N ha$^{-1}$ to the entire field.  The whole field was side-dressed with a 28% urea and ammonium nitrate (UAN) solution at a rate of 57.1 kg N ha$^{-1}$ on DOY 171.  The remainder, 76.2 (DOY 200) and 15.7 (DOY 203) kg N ha$^{-1}$, was applied to the CS and KC treatment, respectively as 28% UAN through the center pivot irrigator.  Fertilizer was not applied to the soybean crop in 2014.

Nitrous Oxide Emissions

Soil N$_2$O fluxes were measured with automated soil chambers (Model LI8100-104; Li-Cor Inc., Lincoln, NE, USA) controlled by a datalogger (Model 23X; Campbell Scientific, Logan, UT, USA) connected to a multiplexer controlling two sets of solenoids (Clippard Inc., Cincinnati, OH, USA) [*Fassbinder et al.*, 2013; *Baker et al.*, 2014].  All soil chambers ($n = 8$) were vented, finished with white enamel to minimize solar heating, and installed onto PVC collars.  The collars were placed at the center of the inter-row and

inserted 0.05-m into the soil.  A rubber gasket and weather stripping prevented ambient

dilution during chamber closure.  Each chamber was activated for 7-min at one hour

intervals during which headspace air was pulled through a column of desiccant before

entering a $N_2O$ analyzer (Model M320EU2; Teledyne Instruments API, San Diego, CA,

USA).  A nafion dryer within the Teledyne removes remaining $H_2O$ vapor before the

sample air enters the measurement cell.  Fluxes ($n$ = 31,539 and 28,972 for 2013 and

2014, respectively) were calculated using:

$$F = \frac{PV\Delta}{ART} \hspace{4cm} \text{(Equation 4.1)}$$

$P$ is air pressure (Pa), $V$ is the chamber volume (0.004 m$^3$), $A$ is the chamber footprint

(0.032 m$^2$), $R$ is the molar gas constant (J mol$^{-1}$ $^{\circ}$K$^{-1}$), $T$ is the air temperature at the time

of measurement ($^{\circ}$K), and $\Delta$ is the slope of $N_2O$ concentration change over time in the

chamber headspace.  Prior to slope calculation, the raw $N_2O$ concentration data were

passed through a wavelet de-noising algorithm to improve the signal to noise ratio

[*Fassbinder et al.*, 2013].  The slope was calculated from a 90-s window beginning 150-s

after chamber closure.  All data were processed using Matlab software (Version R2013b;

Mathworks, Natick, MA, USA).

Climate, Soil, and Plant Analyses

Precipitation was measured at a micrometeorology tower located 1.6-km east of

the experimental field.  Soil temperature and volumetric water content were measured in

each plot at 0.05, 0.1, 0.2, 0.3, and 0.4-m (5TM; Decagon Devices Inc, Pullman, WA,

USA) at 30-min intervals (EM-50; Decagon Devices Inc, Pullman, WA, USA).  Each

chamber was equipped with a thermocouple (Type E) to measure soil temperature at 0.05-m depth.  In August 2015, aboveground KC biomass was collected and samples ($n =$ 21) were dried and pulverized before total carbon and nitrogen were calculated with an elemental analyzer (VarioMax; Elementar, Hanau, Germany).  At crop maturity, corn and soybean grain from 6-m row sections in each plot were hand-harvested, dried, and weighed to obtain grain yields.

Data Analysis and Statistics

The 24-h cumulative area-scaled $N_2O$ emissions were determined by integration of the daily mean flux for each plot.  The cumulative emission budget was calculated for each plot as the sum of the daily area-scaled emissions during the measurement periods (196 and 151-d in 2013 and 2014, respectively).  Missing data due to instrument downtime (3% and 17% in 2013 and 2014, respectively) were not gap filled and therefore the cumulative emissions represent a conservative estimate.  Yield-scaled emissions were determined by dividing the annual cumulative area-scaled emissions by the dry grain yield.  Normality was evaluated using a Kolmogorov–Smirnov test.  The daily cumulative area-scaled $N_2O$ emissions were log transformed to improve normality [*McSwiney et al.*, 2010].  Treatment significance was assessed using a two-factor analysis of variance (ANOVA) [*Jarecki et al.*, 2009] of log transformed cumulative area-scaled daily $N_2O$ emission data, treatment, and year.  Automated chambers provide a temporally rich dataset that was used to evaluate emissions associated with different field activities (e.g., strip-tilling, mowing, and spraying) and periods (prior to strip-tilling and post-

anthesis) using paired $t$-tests ($\alpha = 0.01$) of log transformed daily area-scaled $N_2O$

emissions.  Photographs from 2013 were used to estimate the onset of crop anthesis

(DOY 226).  For consistency, DOY 226 was used in our 2014 analyses.

## Results and Discussion

Overall, daily average $N_2O$ fluxes were significantly influenced by the treatment

(KC > CS; $p < 0.001$) and year (2013 > 2014; $p < 0.005$).  The year effect is most likely a

result of fertilizer application that only occurred during the corn phase (2013), rather than

a meteorological difference.  Average air temperature and precipitation during the

measurement period in each year were 17ºC and 606-mm and 17.5ºC and 818-mm in

2013 and 2014, respectively (data not shown).  Corn (2013; $p = 0.08$) yields were 11.1 ±

0.9 and 9.7 ± 0.9 Mg (dry) ha$^{-1}$ while soybean (2014; $p = 0.03$) yields were 2.51 ± 0.11

and 2.11 ± 0.18 Mg ha$^{-1}$ in the CS and KC treatments, respectively.

### 2013 – Corn

Presence of the KC living mulch significantly affected $N_2O$ emissions during the

corn phase (Figure 4.1).  Cumulative area-scaled and yield-scaled emissions were, 2.3 ±

0.1 kg N ha$^{-1}$ and 233 ± 112 g N Mg$^{-1}$ grain, respectively in KC, and 1.3 ± 0.1 kg N ha$^{-1}$

and 118 ± 137.6 g N Mg$^{-1}$ grain in the CS, respectively.  During the entire measurement

period, the average volumetric water content and soil temperature at 0.05-m depth was

0.24 ± 0.02 and 16.5 ± 6.6 ºC, respectively, from the KC treatment and 0.22 ± 0.02 and

14.5 ± 6.5 ºC, from the CS respectively (data not shown).

2014 – Soybeans

The KC living mulch increased $N_2O$ emissions during the soybean phase (Figure 4.1). Area-scaled and yield-scaled emissions were $1.6 \pm 0.1$ kg N ha$^{-1}$ and $765 \pm 65$ g N Mg$^{-1}$ grain, respectively from the KC treatment, and $0.7 \pm 0.1$ kg N ha$^{-1}$ and $291 \pm 58$ g N Mg$^{-1}$ grain from the CS treatment, respectively. Intermittent problems with our soil moisture and temperature probes prevented a full assessment of the treatment effects on the microclimate during 2014.

Prior to Strip-Tillage

The available data suggest that the KC living mulch may have marginally reduced $N_2O$ emissions in the spring, prior to strip-tillage (Table 4.1). Although the treatment effect was not significant, the CS treatment emitted 9.3 mg $N_2O$-N m$^{-2}$ and 12 mg $N_2O$-N m$^{-2}$ more than the KC treatment in 2013 and 2014, respectively (Table 4.1). This trend may have resulted from greater residual soil N in the CS treatment, which the presence of a CC has been shown to reduce [*Nair and Lawson*, 2014]. This benefit, known as N "scavenging", is the result of greater plant N demand, especially outside of the growing season. The KC living mulch removes N that would otherwise be available for $N_2O$ production in the spring, contrary to the CS plots that were left fallow between growing seasons. The presence of an over-winter CC can result in lower spring $N_2O$ emissions relative to fallow conditions [*Wagner-Riddle and Thurtell*, 1998]. The amount of residual N scavenged by a CC is variable and depends on the CC species [*Nair and Lawson*, 2014] and management decisions [*Komatsuzaki and Wagger*, 2015]. In Iowa,

uptake estimates of 20 kg N ha$^{-1}$ are common from rye CCs [*Nair and Lawson*, 2014] while rates as high as 80 kg N ha$^{-1}$ under legume CCs have been observed in the Philippines [*George et al.*, 1994]. Importantly, N scavenging can improve the field's overall nitrogen use efficiency by assimilating and recycling N [*George et al.*, 1994] that could be lost through leaching and runoff. In addition to N scavenging, the additional surface residue alters the KC soil microclimate by insulating the surface from solar radiation. However, we did not observe significant differences in soil temperature or volumetric water content between treatments during this period in 2013 (temperature: $p = 0.8$; moisture: $p = 0.5$) or 2014 (temperature: $p = 0.9$; moisture: N/A).

Strip-Tilling and Planting

Area-scaled $N_2O$ emissions increased immediately after strip-tillage (Figure 4.1). Emissions from the KC treatment were up to 2.6-fold higher than the CS treatment in 2013 (Table 4.1). An even stronger $N_2O$ emission response was observed in 2014 after tillage and planting where total $N_2O$ losses from the KC treatment were 3.6-fold greater than the CS treatment (Table 4.1). Since strip-tillage and planting are disruptive activities, damage to the KC root system, coupled with incorporation of above-ground vegetation, may have caused the release of mineralizable N.

Mowing

Immediately following KC mowing, emissions were not significantly different between treatments in 2013 or 2014 (Table 4.1). However, cumulative $N_2O$ emissions from the KC treatment were 1.5 and 1.6-fold larger than the CS treatment during 2013

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and 2014, respectively (Table 4.1).  This may represent a direct response of mowed KC

residue mineralization as others have also observed high $N_2O$ emissions coinciding with

CC decomposition [*Brozyna et al.*, 2013; *Mitchell et al.*, 2013; *Basche et al.*, 2014].  The

application of residue on the surface has resulted in a positive effect on $N_2O$ emissions

[*Baggs et al.*, 2003] that are amplified at low C:N residue ratios [*Huang et al.*, 2004].

Leaving the clippings in place can alleviate the denitrification carbon limitation creating

an opportunity for high $N_2O$ production [*Mitchell et al.*, 2013].  Kura clover biomass

samples show that the C:N ratio was 14.4:1, which is considerably lower than corn stover

(>50:1) [*Baker et al.*, 2014], with an average of 2.8% N.  The low C:N ratio of the KC

clippings would allow for rapid decomposition and nitrification, boosting soil $NO_3^-$

content for $N_2O$ production.  Further, rapid decomposition would deplete oxygen,

creating a more conducive environment for denitrification.  Although CC residues may

also immobilize soil N [*McSwiney et al.*, 2010], our results suggest that the KC clippings

had a positive, but minor effect on $N_2O$ emissions (Table 4.1).

Suppression Spraying

   After herbicide application, $N_2O$ emissions from the KC treatments were elevated

(1.9-fold) above the CS treatments in 2013 (Table 4.1).  Likewise, KC $N_2O$ emissions

were substantially greater (2.6-fold) in the period after suppression and prior to anthesis

in 2014.  The amplification of KC emissions following herbicide application may have

been in response to KC mineralization.  Suppression spraying can release N from the root

system [*Zemenchik et al.*, 2000] that would be an important source of inorganic N for the

crop. Moreover, the mineralization of KC root exudates may partially explain the $N_2O$ emission pulse observed on DOY 180 in 2013.

Fertilizer Application

The $N_2O$ emissions from the KC treatment were 1.8-fold greater than the CS treatment following side-dressing, which was possibly bolstered by plant stress caused by KC mowing or the recent decomposition of mowed KC residue (Table 4.1). Similarly, plant stress brought about by the recent application of herbicides may partially explain why KC emissions were 3-fold greater than the CS treatment following fertigation (Table 4.1). By increasing N and C availability while depleting $O_2$, the rapid decomposition of residues and plant stress may enhance KC $N_2O$ emissions, a response that becomes even more pronounced when N fertilization follows these events. Further, the comparatively low $N_2O$ emission response from the CS treatment could indirectly signal optimal N application timing that facilitated rapid uptake by actively growing corn. A reduction in $N_2O$ emissions has been observed in fertigated vegetable systems [*Kennedy et al.*, 2013] as N is applied more in line with crop needs.

Post-Anthesis Mineralization

In 2013 and 2014, a substantial proportion of the cumulative KC emissions occurred after anthesis (Figure 4.1). Emissions from the KC treatment were 2.4-fold greater than the CS treatment from DOY 226 through the end of the 2013 measurement campaign, likely in response to post-senescence kura mineralization (root turnover +

exudates).  This late season pulse was responsible for 28% of the cumulative KC $N_2O$

budget while 20% of the CS budget was lost during the same period (Table 4.1).

The post-anthesis burst in 2014 was sufficiently large to offset the significant

modest early season $N_2O$ reductions provided by KC N scavenging.  Kura clover losses

here accounted for 49% of the cumulative $N_2O$ budget, but only 17% of losses from the

CS (Table 4.1).  Since we did not observe a similar pulse from the CS treatment, this

would indicate that post-harvest mineralization of N from soybean residues must have

been minimal.  However, because measurements were seasonally limited to spring,

summer, and fall, it is possible that low winter emissions from the KC treatment could

counterbalance our observations [*Basche et al.*, 2014].

## Irrigation

There were emission pulses following irrigation events in 2013 on DOY 186 (1st

irrigation event) and DOY 233 (5th irrigation event), where the CS system lost 63 and

43% more $N_2O$, respectively than the KC treatment (data not shown).  Greater levels of

available N earlier in the season that are progressively depleted through the growing

season may have been responsible for the pulse observed on DOY 186.  The remaining

five irrigation events in 2013 exhibited a negligible effect on emissions, possibly because

either the standard 12.5-mm irrigation event was insufficient to saturate soils and

promote denitrification or because of low residual N.  Further, the emission response

following irrigation on DOY 233 may have been made possible because an irrigation

event 5-d prior "primed" the soil microbe community. There was not an $N_2O$ emission response to irrigation from either treatment during the 2014 (soybean) period.

Indirect Emissions

We did not consider the role of indirect $N_2O$ emissions (i.e. through subsequent denitrification of $NO_3^-$ lost in leaching and runoff) in our budget. Offsite nitrous oxide emissions associated with leaching and runoff have been identified as strong sources [*Chen et al.*, 2016], especially in agricultural regions [*Griffis et al.*, 2013; *Turner et al.*, 2015]. If perennial crops can consistently reduce $NO_3^-$ leaching [*Ochsner et al.*, 2010], a necessary precursor for aquatic $N_2O$ production [*Turner et al.*, 2016a], it is conceivable that groundwater and riverine emissions would be mitigated by increased use of KC living mulch systems, although indirect emissions are highly uncertain and much additional research is needed.

Conclusions

Perennial cover crops offer many environmental benefits to agricultural systems. However, reduction of $N_2O$ emissions may not be one of them. We observed that even with a 43% reduced N application rate compared to a conventional corn-soybean system, the KC living mulch system increased direct $N_2O$ emissions. Our data suggest an important trade-off in the KC system whereby emissions prior to strip-tilling may be lowered due to N scavenging, but strong emissions driven by post-anthesis mineralization offset this benefit. Lastly, because differences in corn grain yield were not significant, it

is possible that the N application rate could be reduced further to minimize $N_2O$ emissions.

## Acknowledgements

**Figure 4.1.** Daily area-scaled N$_2$O fluxes (symbols) and cumulative emissions (lines) for (A) 2013 and (B) 2014 averaged ($n = 4$) by treatment. Missing data due to instrument downtime were not gap filled. Cumulative emissions represent the sum of treatment daily averaged fluxes throughout the measurement period. Dotted vertical lines and numbers correspond with emission intervals described in Table 4.1.

| Year | | Prior to Field Activity 1 | Tillage, Planting 2 | Mowing 3 | Side-Dressing 4 | Spraying 5 | Fertigation 6 | Post Anthesis 7 | Cumulative |
|---|---|---|---|---|---|---|---|---|---|
| 2013 | DOY Range | 114-151 $n = 37$ | 152-164 $n = 11$ | 165-170 $n = 6$ | 171-175 $n = 2$ | 176-199 $n = 23$ | 200-226 $n = 27$ | 227-316 $n = 90$ | 114-316 $n = 196$ |
| | Kura Clover Treatment (mg N m$^{-2}$) | 37.8 | 26.2 | 9.4 | 7.1 | 51 | 30.6 | 64.4 | 226.5 |
| | Conventional Treatment (mg N m$^{-2}$) | 47.1 | 10 | 6.4 | 4.8 | 26.2 | 10.2 | 26.6 | 131.3 |
| | Treatment Difference (mg N m$^{-2}$) | -9.3 $p = 0.15$ | 16.2 $p < 0.01$ | 3 $p = 0.4$ | 2.3 $p = 0.02$ | 24.8 $p < 0.01$ | 20.4 $p < 0.01$ | 37.8 $p < 0.01$ | 95.2 $p < 0.01$ |
| 2014 | DOY Range | 99-150 $n = 32$ | 151-162 $n = 9$ | 163-174 $n = 9$ | N/A | 175-226 $n = 52$ | N/A | 227-279 $n = 49$ | 99-279 $n = 151$ |
| | Kura Clover Treatment (mg N m$^{-2}$) | 27.7 | 15.5 | 6.4 | | 32.9 | | 78.8 | 161.3 |
| | Conventional Treatment (mg N m$^{-2}$) | 39.7 | 4.3 | 4 | | 12.7 | | 12.1 | 72.8 |
| | Treatment Difference (mg N m$^{-2}$) | -12 $p = 0.3$ | 11.2 $p < 0.01$ | 2.4 $p = 0.08$ | | 20.2 $p < 0.01$ | | 66.7 $p < 0.01$ | 88.5 $p < 0.01$ |

**Table 4.1.**  The cumulative emissions and results from statistical analyses from each activity period during the two sample years.  The numbered intervals correspond to Figure 4.1.  Sample size (*n*) excludes instrument downtime.  The total emissions during a measurement interval are reported while the difference between treatments (kura clover – corn-soybean) has been given.  Significance was determined using paired *t*-tests were performed on the log-transformed emissions over the listed DOY range.

# Chapter 5

# A geostatistical approach to identify and mitigate agricultural nitrous oxide emission hotspots

Peter A. Turner, Timothy J. Griffis, David J. Mulla, John M. Baker, and Rodney T. Venterea (2016), *Science of the Total Environment*, (572), 442-449,

## Highlights

1. Geospatial analyses resolved $N_2O$ emissions at fine spatial scales

2. Hotspots emitted $N_2O$ at rates more than 2-fold greater than non-hotspot locations

3. Targeted management of $N_2O$ hotspots could reduce emissions by 17%

## Overview

Anthropogenic emissions of nitrous oxide ($N_2O$), a trace gas with severe environmental costs, are greatest from agricultural soils amended with nitrogen (N) fertilizer. However, accurate $N_2O$ emission estimates at fine spatial scales are made difficult by their high variability, which represents a critical challenge for the management of $N_2O$ emissions. Here, static chamber measurements ($n = 60$) and soil samples ($n = 129$) were collected at approximately weekly intervals ($n = 6$) for 42-d immediately following the application of N in a southern Minnesota cornfield (15.6-ha), typical of the systems prevalent throughout the U.S. Corn Belt. These data were integrated into a geostatistical model that resolved $N_2O$ emissions at a high spatial resolution (1-m). Field-scale $N_2O$ emissions exhibited a high degree of spatial variability, and were partitioned into three classes of emission strength: hotspots, intermediate, and coldspots. Rates of emission from hotspots were 2-fold greater than non-hotspot locations. Consequently, 36% of the field-scale emissions could be attributed to hotspots, despite representing only 21% of the total field area. Variations in elevation caused hotspots to develop in predictable locations, which were prone to

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nutrient and moisture accumulation caused by terrain focusing. Because these features

are relatively static, our data and analyses indicate that targeted management of hotspots

could efficiently reduce field-scale emissions by as much 17%, a significant benefit

considering the deleterious effects of atmospheric $N_2O$.

## Introduction

Nitrous oxide ($N_2O$) is a potent greenhouse gas [*Hartmann et al.*, 2013] and the

leading cause of stratospheric ozone loss [*Ravishankara et al.*, 2009]. In response to its

deleterious environmental effects, efforts to mitigate agricultural emissions, which

account for nearly 75% of the national anthropogenic source [*US Department of State*,

2014], are in development. Such efforts often focus on N management improvements

(e.g., optimizing the source, depth, and timing of fertilizer) at the field or farm scale.

Yet, the findings from these mitigation strategies have been highly variable [*Venterea et

al.*, 2016], in part because episodic and spatially variable emissions hinder accurate

budget estimates [*Velthof et al.*, 2000; *Mathieu et al.*, 2006]. For instance, field-scale

$N_2O$ emission measurements with chambers can yield a coefficient of variation (CV) as

high as 500% [*Folorunso and Rolston*, 1984; *van den Pol-van Dasselaar et al.*, 1998],

suggesting that our ability to accurately determine the outcome of mitigation practices is

cause for concern. At fine sub-field spatial scales (<1 $m^2$ to 1000 $m^2$), $N_2O$ "hotspots"

appear to be disproportionately strong sources [*Parkin*, 1987; *van den Heuvel et al.*,

2009], yet their influence over cumulative field-scale emissions remains uncertain

because high-resolution data are rarely available. For farmers to manage $N_2O$ emissions

effectively, subfield-scale emission estimates are necessary to identify potential hotspots and to benchmark their effects on field-scale mitigation practices.

Light detection and ranging (LiDAR) digital elevation models (DEMs) are powerful tools that can help guide precision agriculture and conservation strategies [*Galzki et al.*, 2011; *Wan et al.*, 2014]. When coupled with geospatial techniques, this emerging technology helps generate high-resolution maps of agriculturally relevant information such as the presence of hydric soils [*Fink and Drohan*, 2016], moisture content [*Moore et al.*, 1993; *Murphy et al.*, 2009], and soil nitrogen status [*Weintraub et al.*, 2014] that allow farmers to focus extra attention and resources on critical areas. Furthermore, complex processes like methane emissions [*Sundqvist et al.*, 2015] have been characterized using DEMs, suggesting that this technology can better resolve the field-scale spatial distribution of $N_2O$ emissions.

Indeed, differences in topography and landscape position have a strong influence on $N_2O$ emissions [*Ball et al.*, 1997; *Ambus*, 1998] because terrain gradients redistribute moisture and nutrients that are necessary for the production of $N_2O$. Consequently, $N_2O$ emission frequency distributions are typically positively skewed by a few strong sources [*Parkin*, 1987; *Velthof et al.*, 2000] observed at topographically low positions [*Ambus*, 1998]. Here, terrain focusing enables the development of hotspots by concentrating organic matter, moisture, and nitrate ($NO_3^-$) into localized, but potentially predictable areas. Taken together, these soil characteristics can support disproportionately high rates of denitrification [*Groffman et al.*, 2009] that we posit are capable of sustaining high $N_2O$ emissions. However, field-scale emission distribution maps remain coarse, since an

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unrealistic number of static chambers are required to resolve the high variability, implying poor constraints on hotspots.

With the aid of DEMs and geospatial analyses, denitrification hotspots can be isolated and mapped by pinpointing locations with the highest probability of moisture and $NO_3^-$ accumulation [*Anderson et al.*, 2015].  We propose that a similar approach can resolve the distribution of $N_2O$ emissions at a high spatial resolution that will guide targeted mitigation practices.  Here, we examine the spatial distribution of $N_2O$ fluxes and cumulative emissions in a strip-tilled cornfield to address three questions: 1) can DEMs help predict where $N_2O$ hotspots will develop on the landscape; 2) how significant are hotspots in the cumulative field-scale budget; and 3) how can DEMs be used to guide N management and $N_2O$ mitigation?

## Materials and Methods

## Site Description and Experimental Design

The tile-drained, corn-soybean rotation research field (15.6-ha) was located on a private farm 11-km south of Northfield, Minnesota (44°21'37.2"N, 93°12'14.8"W).  The predominant underlying soil is a Prinsburg silty clay loam (Typic Endoaquolls, USDA Classification) overlying a loam.  Measurements were made during the corn (*Zea mays*, L.) phase in 2014 on DOY 126, 134, 150, 156, 161, and 168.  The field was strip-tilled prior to planting and fertilized with 32% urea ammonium sulfate (UAS) on DOY 125 at a rate of 140 kg N ha$^{-1}$.

A 3-m micrometeorological tower was installed on the west side of the field to measure air temperature (VP-4; Decagon Devices, Pullman, WA, USA). Observations were recorded with a data logger at 5-min intervals and averaged hourly (Model EM50; Decagon Devices, Pullman, WA, USA).

All soil and chamber sample locations were georeferenced using a GPS device (GeoXH; Trimble, Sunnyvale, CA, USA) connected to a Mi-Fi mobile hotspot (model 2200; Verizon Wireless, Wallingford, CT, USA) that boosted the horizontal accuracy to 0.1 m. Spatial data were analyzed using ArcMap (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA).

To capture the effects of terrain on $N_2O$ emissions and to ensure potential hotspots were included in the measurement campaign, a Wetland Probability Index (WPI) map was created (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA) to guide the experimental design. The WPI is a regression function of four factors: the presence of hydric soils, slope, profile curvature, and a compound topographic index (CTI) that is a function of flow accumulation and slope. The WPI provides a relative metric to describe the likelihood that water will pond at a specific location and has been used to identify areas for efficient wetland reclamation [*Wan et al.*, 2014]. The WPI was chosen rather than the widely used soil wetness index (SWI), because the WPI incorporates drainage (hydric soils), a recognized shortcoming of the idealized SWI [*Murphy et al.*, 2009]. In the context of $N_2O$ production, field locations with wetland terrain characteristics are likely to accumulate moisture and nutrients and are thus candidates for hotspot formation. These areas are likely to experience more frequent and prolonged periods of soil

saturation than upland areas, in part because of low slopes and elevation. Using high-resolution (1-m) DEM data (Minnesota Geospatial Information Office) and soil survey information, each position on the landscape was assigned a relative WPI value of 0 to 1 [*Wan et al.*, 2014].

Since the natural movement of soil moisture is not confined to the explicit 1-m WPI grid, the highest spatial resolution is not necessarily appropriate for direct comparison with a dependent variable [*Sørensen and Seibert*, 2007]. For instance, contour cropping, crop residues, buffer strips and microtopography can affect the movement of moisture. To minimize these uncertainties, we have reduced the WPI resolution to 10-m [*Zhang and Montgomery*, 1994; *Anderson et al.*, 2015] for direct comparison of $N_2O$ emission measurements and surface characteristics. All other analyses used the high-resolution WPI data set.

Because terrain differences can influence emissions, a stratified sampling design based on WPI was used to characterize emission heterogeneity. Groups ($n = 6$) of chambers ($n = 10$) were installed in the field across a range of WPI values on each of the sample dates. Measurements were taken at approximately weekly intervals for 42-d immediately after fertilization (DOY 125). Previous experiments in this field indicate that $N_2O$ fluxes are highest in the 20 to 50-d following fertilization [*Fassbinder et al.*, 2013; *Baker et al.*, 2014]. Beyond this time frame, $N_2O$ fluxes decline [*Baker et al.*, 2014; *Turner et al.*, 2016b] and as a result, the cumulative emission budget is most sensitive to loss during this brief period.

Nitrous Oxide Measurements

Soil $N_2O$ fluxes were measured manually with non-flow-through non-steady-state chambers with a design that has been used extensively in agricultural systems [*Maharjan and Venterea*, 2014; *Maharjan et al.*, 2014; *Venterea and Coulter*, 2015]. Briefly, each chamber consisted of a stainless steel base inserted 0.05-m into the soil and a removable top (0.50 m x 0.29 m x 0.086 m). Weather stripping and spring clamps attached to opposing sides sealed the chamber headspace from ambient mixing. Each chamber top was vented and covered with an insulated, reflective material. Measurements were taken after at least 48-hr following chamber installation to avoid the potential influence of soil disturbance on the flux.

Gas samples were taken from between 0900 and 1500 local time at 0, 15, 30, and 45 minute intervals using a 12-mL polypropylene syringe inserted through a butyl rubber septum on the chamber lid. An ambient air sample was taken immediately after chamber closure. Samples were immediately transferred into glass vials sealed with butyl rubber septa and analyzed within one week using a headspace autosampler (Teledyne Tekmar; Mason, OH, USA) connected to a gas chromatograph (model 5990; Agilent/Hewlett-Packard, Santa Clara, CA, USA) equipped with an electron capture detector. Helium was used as the carrier gas in the GC analyses and the system was calibrated with analytical standards (Scott Specialty Gases, MI) [*Bavin et al.*, 2009]. Concentrations from the GC were converted into mass per volume units, assuming ideal gas relations and a known air temperature while sampling.

The slope of the chamber headspace gas concentration was determined using either a linear regression or a quadratic model depending on the curvilinearity of the slope [*Parkin et al.*, 2012; *Venterea*, 2013]. The linear slope was calculated using the SLOPE function (Excel v.2013; Microsoft, Redmond, WA) and the quadratic slope was estimated using the LINEST function at time zero. The quadratic model accounts for suppression of the concentration gradient in response to chamber closure, but is not always necessary. A linear slope was chosen if the second derivative of the quadratic equation was greater than zero [*Maharjan et al.*, 2014]. Soil fluxes were calculated using:

$$F = \frac{S*V}{A}$$ 
Equation 5.1

where: $S$ is the slope, $V$ is the chamber volume ($0.02\text{-m}^3$), and $A$ ($0.14\text{-m}^2$) is the chamber footprint. Cumulative $N_2O$ emissions were calculated using trapezoidal integration that assumes linearity between sampling periods.

## Soil Analyses

Within 24-hours of gas sampling, soil samples ($n = 129$) to a depth of 0.15-m were taken from a georeferenced 35-m grid using a hand corer. Soil samples were weighed within two hours. After drying at 105º C, gravimetric water content ($\theta$) was determined. Using a 2 M KCl extraction, soil $NO_3^-$ concentration was also determined [*Maharjan and Venterea*, 2014]. Extracts were filtered (Whatman no. 1) and $NO_3^-$ was quantified using a flow-through injection analyzer (Lachat, Loveland, CO, USA). The $NO_3^-$ intensity ($NO_{3\,int}^-$) was calculated using trapezoidal integration [*Venterea et al.*,

2011; *Maharjan and Venterea*, 2014], which assumes a linear slope between sample dates. Conceptually, $NO_3^-{}_{int}$ represents the cumulative exposure of soil microbes to $NO_3^-$. The $\theta$ intensity ($\theta_{int}$) was calculated similarly. Stepwise regression models were used to identify any terrain indices that were significantly correlated with soil chemical variables.

Geostatistical Analyses

Interpolations of high-resolution $N_2O$ flux and cumulative emission data were performed with ordinary cokriging (OC) in ArcMap (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA). Ordinary cokriging is a geostatistical approach that uses more frequently sampled secondary variables to improve prediction of the primary variable [*Vauclin et al.*, 1983]. This method is useful when the primary attribute is costly or logistically more difficult to sample than other correlated variables.

Mean $N_2O$ fluxes and cumulative emissions were interpolated at a resolution of 1-m with OC using an omnidirectional "stable" model. Soil $NO_3^-$ and $\theta$ were used as secondary variables in this OC model. The sill (variance), nugget (estimate of independent or micro-scale errors), and range (maximum distance of autocorrelation) of each model were estimated from the semivariogram. The model parameters were optimized for estimation of the range value and neighborhood weights were based on distance. Cross validation was accomplished iteratively by comparing the observation to the OC model predicted value. All inputs were log transformed prior to OC to meet the assumption of normality.

A Getis-Ord Gi* statistical test identified spatial clustering of high (hotspots) and low (coldspots) emissions at a 95% significance threshold [*Ord and Getis*, 2010]. The field was partitioned into three emission classes based on their respective $z$-score significance using ArcMap (ArcGIS v.10.2; ESRI Inc., Redlands, CA, USA). Locations with statistically significant high and low $z$-scores are referred to as emission hotspots and coldspots, respectively. All other values, i.e. those with insignificant ($p > 0.05$) $z$-scores, are considered "intermediate" locations. A Kruskal-Wallis significance test ($\alpha = 0.05$) was used to determine if there was a WPI difference among emission classes.

## Results and Discussion

### Meteorology and Soil Characteristics

Over the course of our measurement campaign, this field received 116.8 mm of precipitation and experienced a mean air temperature of 16.4ºC. Across all sampling dates, the mean (range) soil $NO_3^-$ concentration and $\theta$ content were 20.5 (0-107) mg $NO_3^-$ $kg^{-1}$ and 25% (12-50), respectively (Figure 5.1). Reported $NO_3^-$ concentration and $\theta$ content frequency distributions were positively skewed on each sample date (data not shown), indicating the potential for nutrient processing hotspots. Following fertilization on DOY 125, the daily mean soil $NO_3^-$ concentrations increased until DOY 157, after which they started declining, likely as a result of a combination of leaching, denitrification, and crop uptake.

Analyses indicated that the WPI (10-m) was significantly ($p < 0.05$) correlated with $\theta_{int}$ and $NO_{3\ int}^-$ observations ($r^2 = 0.6$ and $r^2 = 0.14$, respectively) (Figure 5.2).

These relationships provide evidence of terrain focusing, implicit in the WPI calculation (e.g., elevation, slope). Indeed, measurements of $\theta_{int}$ were significantly ($p < 0.05$) and negatively correlated with both elevation ($r^2 = 0.6$) and slope ($r^2 = 0.4$). Observations of $NO_3^-{}_{int}$ were not as tightly coupled to elevation ($r^2 = 0.09$) or slope ($r^2 = 0.05$) as $\theta_{int}$, probably because of the complex N cycling dynamics (i.e. including both production and consumption of $NO_3^-$) present in soils. Overall, the samples with the highest $\theta_{int}$ and $NO_3^-{}_{int}$ were observed in locations with the lowest slope and elevation (Figure 5.2), suggesting that the soil factors necessary to sustain high denitrification fluxes can become concentrated in predictable areas. This finding provides further support that remote sensing techniques can offer important insights into field-scale N processing dynamics by identifying locations that have an elevated likelihood of moisture and nutrient accumulation [*Weintraub et al.*, 2014; *Anderson et al.*, 2015].

N$_2$O Emissions
Temporal Dynamics

Across all chambers and sampling dates, the mean (range) N$_2$O flux was 1.7 (-1 – 32) mg N$_2$O-N m$^{-2}$ d$^{-1}$. The magnitude of N$_2$O fluxes ranged from 0.7 mg N$_2$O-N m$^{-2}$ d$^{-1}$ on DOY 126, within 24-hrs of fertilization, to a peak emission of 4.3 mg N$_2$O-N m$^{-2}$ d$^{-1}$ on DOY 157, and decreased to a value of 1.8 mg N$_2$O-N m$^{-2}$ d$^{-1}$ on DOY 168 (Figure 5.1). Over the sample period, the average N$_2$O flux was positively correlated ($r^2 = 0.06$; $p < 0.05$) to WPI (10-m), indicative of a terrain signal. Indeed, elevation ($r^2 = 0.12$; $p < 0.01$) and slope ($r^2 = 0.04$; $p = 0.06$) correlated with average N$_2$O fluxes (Figure 5.3)

These hourly mean flux density observations are comparable in strength to a previous study that used 6 automated chambers to estimate the annual $N_2O$ budget at this field site during the 2010 corn phase [*Fassbinder et al.*, 2013]. Those investigators determined that $N_2O$ emissions were elevated for 20 to 50 days after fertilization, but then losses declined precipitously and the average hourly standard deviation fell 14-fold, suggesting relatively low temporal measurement uncertainty beyond this brief period [*Fassbinder et al.*, 2013].

Spatial Dynamics

Trapezoidal integration of chamber data indicated that the mean (SD) cumulative $N_2O$ emission was 69 (61) mg $N_2O$-N m$^{-2}$ during the 42-d sampling period. We calculated a field-scale CV of 88% from the cumulative chamber data, which is lower than some investigations [*Folorunso and Rolston*, 1984; *Ambus and Christensen*, 1995; *Ball et al.*, 1997; *Jones et al.*, 2011; *Molodovskaya et al.*, 2011] and significantly higher than others [*Christensen et al.*, 1996]. The reason for our comparatively low CV may have been because our sample size ($n = 60$) was relatively large compared to those previous studies and better captured the spatial heterogeneity. Contrary to our hypothesis, there was not a significant relationship ($r^2 = 0.03$; $p = 0.1$), between the WPI (10-m) and cumulative $N_2O$ emissions (Figure 5.3). The low $r^2$ was probably the result of other factors that influence emissions but were not explicitly included in our model, e.g., pH, gas diffusivity, and sources of $N_2O$ other than denitrification including nitrification [*Kool et al.*, 2011; *Venterea et al.*, 2015]. Similarly, slope ($r^2 = 0.04$; $p =$

0.08) was not a significant correlate with $N_2O$ emissions either (Figure 5.3). However, elevation ($r^2 = 0.09$; $p < 0.05$) exhibited a negative, although weak relation to $N_2O$ emissions (Figure 5.3), indicating that topographic position can affect $N_2O$ production.

Based on *a priori* hypotheses, $\theta_{int}$ and $NO_3^-{}_{int}$ were included as secondary OC variables to improve the average $N_2O$ flux and cumulative emission model prediction ($n$ = 156,190). Cross-validation of cumulative emissions determined that an omnidirectional stable model was appropriate. Stable model semivariograms indicate that the sill, nugget, and range of the average $N_2O$ flux were 0.59 mg $N_2O$-N m$^{-2}$ d$^{-2}$, 0.37 mg $N_2O$-N m$^{-2}$ d$^{-2}$, and 244-m, respectively, while the sill, nugget, and range of the cumulative emissions were 0.7 mg $N_2O$-N$^2$ m$^{-2}$, 0.43 mg $N_2O$-N$^2$ m$^{-2}$, and 320-m, respectively (data not shown). As a measure of variance, the sill provides a field-scale estimate of spatial uncertainty, while the nugget is an estimate of either measurement uncertainty or microscale variation [*Yanai et al.*, 2003]. Here, a large nugget effect suggests large uncertainty at fine-scales. Observations taken from points separated by a distance greater than the range are no longer spatially autocorrelated, a point identified in the semivariogram where variance becomes asymptotic (i.e. the sill).

During the measurement period, the field emitted on average (SD) 1.4 (0.6) mg $N_2O$-N m$^{-2}$ d$^{-1}$, with a 43% CV, more than half that of the original chamber data (Figure 5.4). Cumulatively, the OC model predicted that 8.7 kg $N_2O$-N were emitted over the 42-d measurement (Figure 5.3). This translates to a field-scale mean (SD) cumulative flux of 55.4 (22) mg $N_2O$-N m$^{-2}$. The emission distribution was positively skewed, indicating that the data set was likely affected by hotspots. Because soil samples were not taken at

each individual chamber, OC interpolations of $NO_3^-{}_{int}$ and $\theta_{int}$ at each chamber were extracted to assess their relationships with cumulative $N_2O$ emissions. These data show that cumulative $N_2O$ emissions were significantly ($p < 0.01$) correlated with $NO_3^-{}_{int}$ ($r^2 = 0.25$) and $\theta_{int}$ ($r^2 = 0.18$) predictions (Figure 5.5).

Using a Getis Ord Gi* statistical analysis, locations in this field were partitioned into three classes based on their emission strength within the context of neighboring values [*Ord and Getis*, 2010]. These analyses identified significant clustering of high and low $N_2O$ emissions, characteristic of hotspots and coldspots, respectively (Figure 5.6). The mean (SD) flux from hotspots, intermediate, and coldspot locations was 2.5 (0.4) mg $N_2O$-N m$^{-2}$ d$^{-1}$, 1.3 (0.3) mg $N_2O$-N m$^{-2}$ d$^{-1}$, and 0.8 (0.05) mg $N_2O$-N m$^{-2}$ d$^{-1}$, respectively. Cumulatively, 3.1 kg $N_2O$-N, 4.6 kg $N_2O$-N, and 0.9 kg $N_2O$-N were emitted from hotspots, intermediate, and coldspot locations, respectively.

These analyses indicate that a disproportionate share of the field-scale emission budget can be attributed to hotspot locations. Here, hotspots were responsible for 36% of the cumulative $N_2O$ emission budget despite occupying only 21% of the field, while coldspots emitted 11% of the cumulative budget from a comparable area (18%). The remaining $N_2O$ emissions (53%) were lost from intermediate locations, largely because 61% of the land surface fell under this emission class. However, the area of a field that qualifies as a hotspot could fluctuate based on meteorology – for instance, a particularly wet spring could increase the surface area of locations that experience prolonged and high moisture exposure. Kruskal-Wallis tests showed that the WPI observed in hotspot locations was greater than the WPI values typically found in the other emission classes,

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in part because these locations had low slopes and elevation. A Kruskal-Wallis test

revealed that hotspots had statistically different slopes (mean = 1.6%) and elevation

(mean = 327.8-m) than intermediate (mean = 3.3%; 331.4-m) or coldspot (mean = 3.7%;

331.1-m) locations (data not shown).

Consequently, the general locations of hotspots were largely static, likely because

of the strong relation with topographic indices, including elevation and slope. The

positive relations identified here indicate that topography, *via* its controls on nutrient and

moisture distributions, can help guide $N_2O$ management practices. Towards this end, the

disproportionate strength and stability of $N_2O$ hotspots indicates that targeted

management of these sources could efficiently reduce total emissions. For instance, if the

average hotspot flux density were reduced from 2.5 mg $N_2O$-N $m^{-2}$ $d^{-1}$ to 1.3 (0.3) mg

$N_2O$-N $m^{-2}$ $d^{-1}$, a magnitude that is more in step with intermediate areas, the mean field-

scale flux density over the entire measurement period could be reduced by up to 14%

(10-18). By reducing the cumulative hotspot emissions to 49 (10.4) mg $N_2O$-N $m^{-2}$, the

rate observed in intermediate areas, the field-scale budget could be reduced by as much

as 17% (12-22). The removal of hotspots through native wetland reclamation could

reduce emissions by as much as 36%. Given the strong radiative forcing and other side

effects of $N_2O$, these findings deserve serious consideration, especially if the distribution

of potential hotspots is similarly predictable throughout the U.S. Corn Belt.

From a management perspective, emission hotspots were generally collocated

with $NO_3^-{}_{int}$ hotspots. Consequently, variable rate nitrogen application (VRNA), a recent

advancement in precision agriculture, could prove an effective tool to address $N_2O$

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hotspots.  This technology translates crop reflectance readings into fine-scale fertilizer

decisions and has been shown to increase yield and income while providing promising N

uptake results [*Scharf et al.*, 2011].  Better soil N management overall will potentially

reduce $N_2O$ emissions; however, the one-size-fits-all approach to fertilizer application

may be a contributing factor to hotspots that VRNA can overcome.  For instance, because

low-lying areas accumulate surplus $NO_3^-$ from upland areas and may not require

additional N, VRNA can limit over application.  Further, easing the $NO_3^-$ surplus in

upland areas using fine-scale fertilizer decisions could help mitigate the effects of terrain

focusing.  Alternatively, the selective application of enhanced efficiency N fertilizers

(EENFs), which show promising $N_2O$ mitigation results [*Halvorson et al.*, 2014], to

hotspots *via* VRNA could minimize their strength.  However, extrapolating the effect

EENFs may have on hotspots here becomes difficult since EENF results are often

specific to soil type and climate.

These data also showed that $N_2O$ and $\theta_{int}$ hotspots were collocated, suggesting

that $N_2O$ hotspots are most likely to require subsurface drainage to ensure crop success.

If conservation wetlands or VRNA were capable of reducing $NO_3^-$ losses in tile drainage,

either by improving N uptake for target and non-target species (i.e., wetland plants) or by

reduced subsurface drainage overall, indirect emissions downstream could also be

mitigated [*Turner et al.*, 2016a].  A reduction of offsite nitrate losses, like those from

leaching and runoff, would be an important benefit because these can be

disproportionately strong sources of $N_2O$, especially in the Corn Belt [*Griffis et al.*, 2013;

*Turner et al.*, 2015; *Chen et al.*, 2016].  However, little is known about emissions from conservation wetlands or the ultimate $N_2O$ effect from VRNA.

Since our data set only includes six sample dates, these analyses may not include episodic emissions and therefore likely represent a conservative estimate.  To resolve this uncertainty, automated soil chambers are an effective means for taking high frequency measurements [*Baker et al.*, 2014; *Turner et al.*, 2016b].  However, sampling constraints (e.g., cost, tube length, and on-site power) tether chambers to a central point, limiting their ability to capture the spatial distribution of emissions observed here.  Therefore, the potential for terrain artifacts to bias measurements must be considered when selecting chamber placement.  For instance, past work in this field explored various $N_2O$ treatment effects using an automated chamber system [*Fassbinder et al.*, 2013; *Baker et al.*, 2014].  Although, those experiments were situated in a location that our analyses has classified as an intermediate strength emitter, they highlight the risks of automated chamber clusters in hotspot or coldspot regions.

## Conclusions

Our data and analyses have shown that LiDAR DEMs and geospatial techniques can be valuable tools to resolve hotspots and model fine-scale $N_2O$ emissions.  Here, hotspots were disproportionately strong sources, responsible for more than a third of the cumulative emissions.  Because hotspots are reliant on terrain focusing for nutrients and moisture, they are relatively static features.  Consequently, their regularity and

predictability should facilitate targeted management practices that could reduce field-scale emissions by as much as 17%.

## Acknowledgements

**Figure 5.1.** Boxplots of a) $NO_3^-$ concentration (mg $NO_3^-$ $kg^{-1}$), b) gravimetric moisture content (%), and c) $N_2O$ flux density (mg $N_2O$-N $m^{-2}$ $d^{-1}$). Red points designate outliers.

**Figure 5.2.** Plotted relationships between topographic indices and soil characteristics (*n* = 129). Top row). Mean soil $NO_3^-$ concentration (blue dots); mean gravimetric water content ($\theta$; green triangles). Bottom row). Integrated soil $NO_3^-$ ($NO_3^-{}_{int}$; blue dots); integrated gravimetric water content ($\theta_{int}$; green triangles).

**Figure 5.3.** Plotted relationships between mean N₂O fluxes (a, b, and c) and cumulative N₂O emissions (d, e, and f) over the measurement period against topographic indices ($n = 60$). Lines of linear best fit (red lines) for each graph are included.

**Figure 5.4.** The Wetland Probability Index (WPI) overlain with chamber measurements (blue circles) and soil samples (red diamonds). Results are presented from the $N_2O$ ordinary cokriging model, which interpolated mean flux density and cumulative emissions at a 1-m spatial resolution.

**Figure 5.5.** The relationship between cumulative $N_2O$ emissions and the soil characteristics, $NO_3^-{}_{int}$ and $\theta_{int}$. A linear line of best fit is included (red).

**Figure 5.6.** Results from the Getis Ord Gi* statistic that was used to identify the spatial distribution of hotspots and coldspots. Intermediate locations are transparent.

# Appendix

Results from the semivariogram and covariance models used to interpolate field-scale $N_2O$ distributions.

**Covariance**

| | Partial Sill | | | Nugget | Range |
|---|---|---|---|---|---|
| | Mean Flux | Mean Nitrate | Mean Moisture | | |
| Mean Flux | 0.22 | | | 0.37 | 157 |
| Mean Nitrate | 0.15 | 0.10 | | 0.14 | |
| Mean Moisture | 0.13 | 0.09 | 0.11 | 0.0001 | |

| | Partial Sill | | | Nugget | Range |
|---|---|---|---|---|---|
| | Cumulative Emissions | Nitrate Intensity | Moisture Intensity | | |
| Cumulative Emissions | 0.27 | | | 0.49 | 321 |
| Nitrate Intensity | 0.07 | 0.05 | | 0.19 | |
| Moisture Intensity | 0.08 | 0.05 | 0.08 | 0 | |

**Semivariogram**

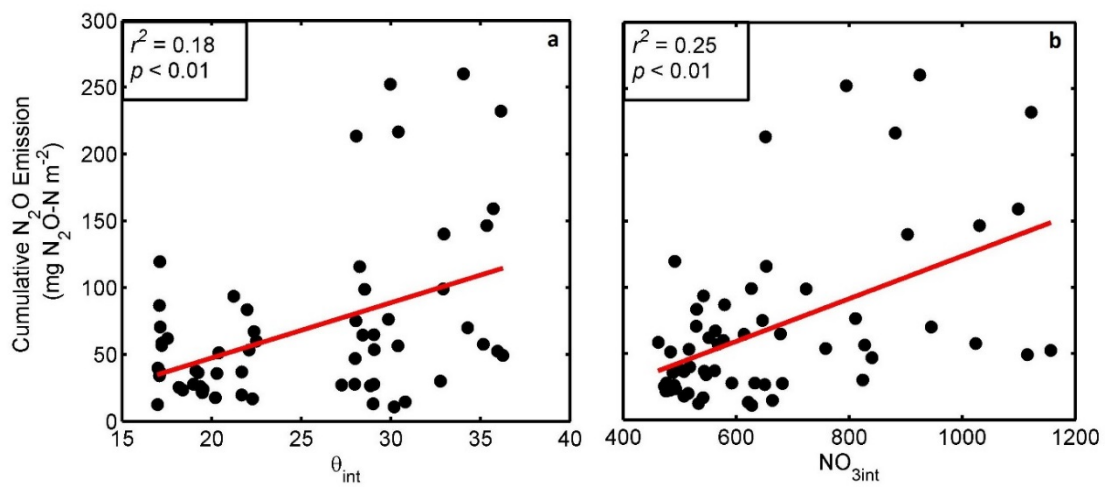| | Partial Sill | | | Nugget | Range |
|---|---|---|---|---|---|
| | Mean Flux | Mean Nitrate | Mean Moisture | | |
| Mean Flux | 0.22 | | | 0.37 | 244 |
| Mean Nitrate | 0.11 | 0.09 | | 0.16 | |
| Mean Moisture | 0.11 | 0.07 | 0.07 | 0.001 | |

| | Partial Sill | | | Nugget | Range |
|---|---|---|---|---|---|
| | Cumulative Emissions | Nitrate Intensity | Moisture Intensity | | |
| Cumulative Emissions | 0.27 | | | 0.43 | 320 |
| Nitrate Intensity | 0.73 | 0.05 | | 0.2 | |
| Moisture Intensity | 0.07 | 0.05 | 0.08 | 0 | |

# Chapter 6
# Conclusion

This study sought to: 1) quantify the strength of indirect $N_2O$ emissions from leaching and runoff and revise the EF ($EF_5$) accordingly; and, 2) identify the underlying mechanisms that control direct and indirect emissions in order to help guide $N_2O$ mitigation practices. The findings presented here provide a roadmap for policy makers and farm managers to address and proactively manage agriculturally linked $N_2O$ emissions.

Over the last decade, the indirect emission factor for rivers ($EF_{5r}$) has emerged as one of the most uncertain components included in bottom-up $N_2O$ emission inventories. This finding can be attributed, in large part, to the broad range of stream morphology types that directly affect the exchange efficiency at the atmosphere – water interface and the rate of nitrogen (N) processing. Yet, a framework that incorporates these differences across a stream network gradient has never been considered. In Chapter 2, static chamber measurements taken longitudinally from a stream network found that $N_2O$ fluxes decline exponentially with the Strahler stream order. When coupled with high-resolution stream network data sets, this exponential function was used to upscale $N_2O$ emissions, which indicated that the $EF_{5r}$ is underestimated by as much as 9-fold in a high-density agricultural region. As a result, bottom-up inventories could be as much as 40% greater than previously reported. Consequently, when our revised $EF_{5r}$ is incorporated, the difference between bottom-up and top-down inventories becomes insignificant. The findings presented in Chapter 2 suggest that either the piston velocity, N processing, or a combination of the two, declines with increasing stream size. From these data alone

however, the instream controls on $N_2O$ production remain unclear and must be identified in order to implement practices designed to mitigate indirect emissions.

Towards this end, Chapter 3 sought to improve understanding of the instream biochemical controls that promote $N_2O$ supersaturation because present $N_2O$ data sets provide limited contextual information. Using a novel gas equilibrator approach, the world's largest freshwater dissolved $N_2O$ data set and the first measurements from the Mississippi River are presented. These data indicate a strong, non-linear relation between dissolved $N_2O$ and $NO_3^-$, which suggests that the asymptotic behavior of $N_2O$ at high $NO_3^-$ concentrations is caused by environmental limitations on N processing. According to riverine model projections of $NO_3^-$ doubling, $N_2O$ emissions from the Upper Mississippi could increase by as much as 40%. However, emissions could be diminished if ancillary variables – including, turbidity were reduced. Therefore, these findings suggest that in addition to reducing $NO_3^-$ leaching and runoff, indirect emissions could be curtailed by reducing riverine sediment loading.

Direct emissions from soils are responsible for a significant fraction of $N_2O$ losses and thus, efforts to mitigate emissions from this source deserve serious attention. Practices designed to mitigate direct emissions often focus on traditional nitrogen management, allowing the farmer to play a greater role in climate change mitigation. Increased adoption of alternative management practices, including cover crops that minimize soil erosion and increase pest resilience while fixing N, have created a need to understand how these practices may affect $N_2O$ emissions. In Chapter 4, data are presented from the first study to measure $N_2O$ emissions from a kura clover living mulch

in a rotational corn – soybean system.  Analysis of high-resolution data obtained using automated chambers determined that in both the corn and the soybean years, emissions from the kura clover treatment were significantly greater than plots without kura clover. This response was caused by enhanced $N_2O$ emissions from the kura clover during periods of soil disturbance, plant stress, and post-anthesis.  These findings suggest that although kura clover does not offer a direct $N_2O$ benefit, indirect emissions might be reduced if $NO_3^-$ leaching and sediment losses were minimized.

The results from one-size-fits-all N management practices (e.g., optimizing the placement, source, and timing of fertilizer) designed to mitigate $N_2O$ losses by improving field-scale N use efficiency have been mixed.  These findings are promoted by the high spatial variability of $N_2O$ emissions, whereby upscaling exercises are beset with uncertainty.  Such variability results from differential soil properties, which cause some locations to produce $N_2O$ at disproportionately high rates (i.e. "hotspots") and others to have anomalously low production rates (i.e. "coldspots").  Consequently, many studies find that emission frequency distributions are positively skewed by hotspots, which are often discovered in low-lying areas.  In Chapter 5, $N_2O$ emissions at a high spatial resolution were resolved using geospatial analyses.  Analysis of these data detected hotspots and their relative importance in field-scale emission budgets was quantified. These findings showed that hotspots emitted as much as 38% of the field's $N_2O$ budget, despite occupying only a fraction (21%) of the field area.  As hypothesized, hotspots were concentrated in low-lying areas where terrain focusing ensured ample soil moisture and $NO_3^-$ to sustain high rates of denitrification.  Further, these data indicate that targeted

management of hotspot locations *via* variable rate nitrogen application or conservation

wetlands could substantially reduce direct emissions by as much as 17%.

## Future Research Directions

### "Legacy" Nitrogen

Mitigation of indirect emissions must also consider the importance of "legacy" N,

which has been accumulating in soils over decades of fertilizer application. In the

Mississippi River basin, legacy N export models suggest a 35-yr biogeochemical lag

[*Van Meter et al.*, 2016] before riverine $NO_3^-$ concentrations are affected by N

management practices. Historical data from Pool 8 of the Upper Mississippi River

(UMR) provided by the United States Geological Survey (USGS) appears to support that

hypothesis. There, dissolved inorganic nitrogen (DIN) concentrations have not changed

over the 1991-2013 period ($p = 0.5$) despite the dramatic expansion of the Conservation

Reserve Program throughout the watershed. Because Chapter 3 suggests that $N_2O$ is

limited in the absence of suspended sediments (lowered nitrification potential), reducing

soil erosion could offer an alternative option to mitigate indirect emissions until N

management practices offset legacy N. Yet, since long-term $N_2O$ measurements in rivers

are non-existent, the effects that conservation policies have had on aquatic $N_2O$ emissions

remains uncertain.

### Machine Learning Applications

Across the U.S., a water quality network deployed by the USGS has created a

long-term, publicly available data set of water chemistry attributes. Using the ensemble

regression model created in Chapter 3 as a training data set, a variety of research

directions could be pursued – including, tightening constraints on riverine $N_2O$ emission

inventories, assessing policy initiatives by hindcasting $N_2O$ based on historical data, and

identifying national aquatic emission trends.

## Agricultural Drainage

To sustain the high headwater fluxes described in Chapter 2, a strong water –

atmosphere gradient must be maintained by either strong *in-situ* $N_2O$ production or large

direct agricultural $N_2O$ inputs from subsurface tile drainage.  Because Chapter 3 has

shown that dissolved $N_2O$ plateaus at high $NO_3^-$ concentrations, strong emissions from

headwaters streams may represent a terrestrial signal from tile drainage.  These systems

act as direct conduits of $NO_3^-$ and $N_2O$ laden leachate to headwater streams, but direct

measurements of drainage water are sparse.  As a result, data are needed to disentangle

$N_2O$ that is produced *in-situ* and the terrestrially produced $N_2O$ delivered *via* tile

drainage.  Further, a recent meta-analysis suggests that the emission factor for $N_2O$ from

groundwater should be lowered by nearly an order of magnitude [*Sawamoto*, 2005], yet

measurements from the U.S. Corn Belt or a dense agricultural region were not included in

this data set.  Because a large fraction of the agricultural landscape is tile drained,

emissions from this component could be a large, yet remain a poorly understood source.

## Moving Forward

At present, a silver-bullet, broad-scale solution that can reduce $N_2O$ emissions

without negatively affecting food security does not exist.  However, the data presented

here can develop a roadmap for policy makers and farmers to address and proactively manage agriculturally linked $N_2O$ emissions. A combinatory approach, equivalent to climate stabilization wedges [*Pacala and Socolow*, 2008] levied at the watershed-scale to curtail the N cascade into non-target ecosystems [*Galloway et al.*, 2003] would be an effective starting point.

From Chapter 2, the relationship between $N_2O$ flux and stream order implies that indirect emissions can be mitigated most efficiently by targeting low-order, headwater streams. Indeed, $NO_3^-$ runoff conservation practices would provide beneficial water and air quality benefits. However, the non-linear $N_2O:NO_3^-$ relationship shown in Chapter 3 suggests that such practices would have a minimal effect on $N_2O$ in the $NO_3^-$ laden headwater systems prevalent in the U.S. Corn Belt [*Wall et al.*, 2013]. Alternatively, measures that reduce both $NO_3^-$ and sediment runoff, the latter of which was identified in Chapter 3 as an important driver of riverine $N_2O$, would likely limit *in-situ* $N_2O$ production. Cover crops are capable of reducing both $NO_3^-$ and sediment runoff, and although Chapter 4 did not quantify indirect emissions, it is likely that the broader distribution of cover crops would have a beneficial effect on indirect emissions. Further, as detailed in Chapter 5, farmers can begin to play a more proactive role in $N_2O$ management by expanding the use of fine-scale N application, a technique that can increase farm profits, providing a veritable win-win for farmers and air quality. Cumulatively, these practices could help reduce direct and indirect $N_2O$ emissions and guide effective policies.

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