NITROUS OXIDE EMISSION FROM RIPARIAN BUFFERS IN

AGRICULTURAL LANDSCAPES OF INDIANA

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ABSTRACT

Katelin Rose Fisher

NITROUS OXIDE EMISSION FROM RIPARIAN BUFFERS IN AGRICULTURAL

LANDSCAPES OF INDIANA

Riparian buffers have well documented capacity to remove nitrate (NO_3^-) from runoff and subsurface flow paths, but information on field-scale N_2O emission from these buffers is lacking. This study monitored N_2O fluxes at two agricultural riparian buffers in the White River watershed (Indiana) from December 2009 to May 2011 to assess the impact of landscape and hydrogeomorphologic factors on emission. Soil chemical and biochemical properties were measured and environmental variables (soil temperature and moisture) were monitored in an attempt to identify key drivers of N_2O emission. The study sites included a mature riparian forest (WR) and a riparian grass buffer (LWD); adjacent corn fields were also monitored for land-use comparison. With the exception of net N mineralization, most soil properties (particle size, bulk density, pH, denitrification potential, organic carbon, C:N) showed little correlation with N_2O emission. Analysis of variance (ANOVA) identified season, land-use (riparian buffer vs. crop field), and site geomorphology as major drivers of N_2O emission. At both study sites, N_2O emission showed strong seasonal variability; the largest emission peaks in the riparian buffers (up to 1,300 % increase) and crop fields (up to 3,500 % increase) occurred in late spring/early summer as a result of flooding, elevated soil moisture and N-fertilization. Nitrous oxide emission was found to be significantly higher in crop fields than in riparian buffers at both LWD (mean: 1.72 and 0.18 mg N_2O-N m^{-2} d^{-1}) and WR (mean: 0.72 and 1.26 mg

N$_2$O-N m^{-2} d^{-1}, respectively). Significant difference (p=0.02) in N$_2$O emission between the riparian buffers was detected, and this effect was attributed to site geomorphology and the greater potential for flooding at the WR site (no flooding occurred at LWD). More than previously expected, the study results demonstrate that N$_2$O emission in riparian buffers is largely driven by landscape geomorphology and land-stream connection (flood potential).

Pierre-André Jacinthe, Ph.D., Chair

TABLE OF CONTENTS

DISCUSSION

CURRICULUM VITAE

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

WR   White River site

LWD   Leary Weber Ditch site

N_2O Nitrous oxide

DEA   Denitrification enzyme activity

SOC   Soluble organic carbon

MBC   Microbial biomass carbon

TC   Total carbon

DOC   Dissolved organic carbon

C:N   Carbon to nitrogen ratio

IPCC Intergovernmental Panel on Climate Change

INTRODUCTION

Statement of the problem

In modern agricultural systems, large amounts of synthetic fertilizer are applied to crop fields in order to maintain soil fertility and productivity. These inputs, especially nitrogen (N) fertilizer, are expected to continue to grow in light of increased demand, both in the US and abroad, for food, animal feed and ethanol production (U.S. EIA, 2008). However, agricultural ecosystems are notoriously leaky with leaching and runoff loss accounting for up to 20-30% of N applied (Owens et al., 1995; Klocke et al., 1999). Therefore, there is legitimate concern that intensification of agricultural production could result in greater nitrate (NO_3^-) export from cultivated fields into surface water systems.

Located at the interface between upland and streams, riparian buffers provide a natural filter for a wide range of nutrients and agricultural pollutants, especially nitrate (Schipper et al., 1993). Within a riparian buffer, soil microbial processes like denitrification offer a mode of N-transformation by which dissolved nitrogen (N) compounds in cropland runoff can be converted into gaseous nitrogen compounds. Since denitrification has the potential to terminate as nitrous oxide (N_2O), a major greenhouse gas and ozone depleting gas (IPCC, 2006), it becomes critical to understand riparian soil characteristics that favor N_2O emission.

Riparian zones in the agricultural region of the US Midwest provide particularly interesting venues to assess for these settings as N_2O sources. First, both overland and subsurface pathways contribute to N inputs in the low-gradient landscapes that characterize the region's riparian buffers. These landscape attributes lead to reduced flow velocity and increased residence time, thus allowing for longer "filtering time" and

more effective N transformation before the discharge of nitrate-enriched runoff onto adjacent streams. This function is often offered as one of the primary justifications for the preservation and restoration of riparian buffers (Fennessy and Cronk, 1997). Secondly, the US Midwest is characterized by intensive corn (*Zea mays, L*) production systems subject to large-scale annual application of nitrogen fertilizer (150-200 kg N ha^{-1} yr^{-1}). This agricultural land-use presents an environment where substantial loads of N can be transported to riparian zones. While the denitrification potential in riparian soils has been widely investigated in the laboratory, field-scale measurements of N_2O emissions in these ecosystems are sorely lacking (Groffman et al., 1998; Mosier et al., 1998). This investigation is an effort fill in this information gap and to identify soil properties and environmental factors controlling N_2O emission from these high nitrate-loaded and often water-saturated environments.

Continued increase in N_2O concentration in the atmosphere has been linked to the accelerated greenhouse effect and global climate change (IPCC, 2006). Depending on land-use and management, soils can be major sources and sinks of nitrous oxide (N_2O). The contribution of terrestrial ecosystems to atmospheric N_2O has been the focus of numerous studies in recent decades. These studies examined the effect of land-use (forest, grassland, cropland; Ambus, 1998; Vilain et al., 2010), management and climate (Dowrick, 1999; Flechard et al., 2007) on N_2O emission. Vilain et al. (2010) investigated the effect of slope position and land use on N_2O emissions. While the effect of tillage practices and fertilizer application on N_2O emission from agricultural fields was the focus of numerous studies (Eichner, 1990; Jacinthe and Dick, 1997; Yanai et al., 2003), there have been far fewer assessments of N_2O emission form riparian buffers. Hefting et al.

(2003) evaluated N_2O emission in chronically-loaded riparian zones in the Netherlands and supported a significant effect of land-use (forest vs. grassland) on emission. McLain and Martens (2006) measured lower N_2O fluxes in semi-arid riparian zones in Arizona but also noted an effect of vegetation type. To our knowledge, only two published studies (Kim et al. 2009; Jacinthe et al. 2012) have focused on agricultural riparian systems in the US Midwest.

Available data indicate that agricultural land-use and fertilizer application contribute at least 67% of total anthropogenic N_2O emission in the US (U.S. EPA, 2009). However, N_2O emission inventories (eg, IPCC, EPA) have generally failed to discretely estimate the contribution of riparian zones in agricultural watersheds. Research on nitrogen cycling in riparian ecosystems indicates that these landscape elements can be hotspots for N_2O emissions, especially if denitrification is incomplete (Ambus, 1998; Groffman et al., 1998; Hefting et al., 2003). In the US Midwest where large amounts nitrogen fertilizers are applied to hundreds of square miles of croplands annually, N_2O emissions may be substantial. In agricultural watersheds where ample NO_3^- is available for microbial transformation, it is important to identify the soil drivers responsible for N_2O emissions not only in the cropped area but also in the riparian zones that periodically receive cropland runoff. Since riparian buffer restoration has become increasingly popular for their nutrient-removal ability, there is a need to understand N_2O emission dynamics and to quantify the contribution of these landscape hotspots to watershed-scale N_2O emission inventories.

Nitrate retention and mitigation in riparian buffers

In agricultural watersheds, fertilized croplands represent the dominant source of mineral nitrogen entering the buffer zones via several pathways including subsurface, groundwater and runoff flow (Groffman et al., 1998). Riparian buffer zones are biogeochemically and hydrologically unique ecosystems (Triska et al., 1993) that serve as a filter between terrestrial upland and open-channel waters. In many cases, riparian zones offer a low-gradient landscape where the velocity of incoming water can be considerably reduced resulting in a temporary water-detention area and providing a greater opportunity for biochemical transformations or immobilization (microbial and plant uptake) of dissolved nutrients (Osbourne and Kovacic, 1993; Hill 1996; Fennessy and Cronk, 1997). This function is of particular importance to the removal of dissolved nitrate before it reaches an open water channel (Triska et al., 1993; Vought et al., 1995; Burt et al., 1999).

If massive amounts of nitrate made its way to surface waters, a host of environmental and public health concerns could arise such as eutrophication and methemoglobinemia. Eutrophication of aquatic systems results in enhanced microbial respiration depleting the dissolved oxygen supply. These low oxygen conditions drastically degrade water quality and negatively impact the integrity of aquatic habitats (Carpenter et al., 1998). A public health concern regarding ingestion of nitrate loaded water can result in methemoglobinemia in infants, commonly known as "blue baby syndrome". Blue baby syndrome is a condition in which the body transforms nitrate into nitrite blocking the oxygen carrying capacity of blood hemoglobin (Johnson et al., 1987). These concerns alone provide enough support for restoring and preserving riparian buffer

4

strips, especially in agricultural watersheds where nitrate availability is often in excess.
While the necessity of riparian buffer ecosystems for dissolved nitrate load reduction
remains undisputed, attention must be paid as to how nitrogen transformation in these
ecosystems could affect atmospheric quality in terms of nitrous oxide (N_2O) emission.
Research is needed to identify environmental factors and soil conditions that promote the
emission of nitrous oxide. This knowledge can then be incorporated into future plans for
riparian zone restoration and management to minimize these undesirable emissions.

Riparian zones naturally mitigate nitrate loads by modes of plant uptake,
microbial immobilization and dilution (Hill, 1996); however, denitrification is the most
efficient mitigation process as it provides for the complete conversion of dissolved NO_3^-
into gaseous end-products (Hefting et al., 2006).

Denitrification is a process that is mediated by heterotrophic microbes that reduce
dissolved nitrate into N gases via this sequence of reactions (Smith et al., 2003):

$$NO_3^- \text{ (aq)} \rightarrow NO_2^- \text{ (aq)} \rightarrow NO \text{ (g)} \rightarrow N_2O \text{ (g)} \rightarrow N_2 \text{ (g)}$$

The extent and rate at which these reactions occur depend on a number of factors
including oxygen, nitrate and organic carbon availability (Tiedje, 1988). The process,
therefore, can be enhanced given an optimal combination of these factors.

Soil characteristics and conditions affecting N_2O emission via denitrification

Understanding the controlling factors of denitrification is not synonymous with
understanding the factors that control N_2O emission into the atmosphere. That is to say,
only a portion of the N_2O produced in soils ends up in the atmosphere (Letey et al.,1980);
ideally the denitrification process can continue to elemental nitrogen (N_2) which

composes approximately 78% of the lower atmosphere (Girard, 2005). Though N_2 may

be the environmentally ideal end-product of denitrification, the combination of

environmental soil conditions that are most conducive to its production are not well

understood (Letey et al., 1980; Jacinthe et al., 2000). Soil moisture, oxygen, nitrate, and

soil organic carbon (SOC) availability and pH have been identified as the dominant

factors that influence the composition of denitrification end-products and control their

emission into the atmosphere.

i.   *O_2 availability*

The effect of oxygen availability on N_2O fluxes is strongly linked to soil moisture

and texture factors that determine gaseous diffusion constraints within the soil profile.

A frequently saturated soil environment is one of the many attributes that make

riparian buffers ideal for N-transformation by denitrification. Assuming that ample

nitrate is available in runoff waters delivered to riparian soils, an anaerobic environment

is necessary to initiate denitrification (Weitz et al., 2001). The frequency of flooding

events and fluctuations in water table depths play critical roles in denitrification by

influencing oxygen availability in the soil atmosphere (Jacinthe et al., 2000). Various

water table depths determine the depth of the saturated zone within the soil column, thus

the higher the water table the greater anaerobic soil environment. If soil becomes

completely saturated, air is expelled out of the pores and residual oxygen is quickly

exhausted by resident microbes. Soil saturation restricts the diffusion of oxygen into soil

pores and the soil progressively develops into an anaerobic, reducing environment

(Hillel, 1998). Similarly, denitrification rates and N_2O emissions from soil tend to

increase with increasing water-filled pore space (WFPS) (Keller and Reiners, 1994; Smith et al. 1998; Dobbie and Smith 2001).

Soil texture also affects water movement and gas diffusion, and thus relate to emission of N_2O. Soils with higher porosity and hydraulic conductivity generally promote higher diffusion rates; therefore coarser soils tend to correspond to better drained and better aerated soils. In contrast, gases diffuse at much slower rates through liquids and smaller soil pores (Hillel, 1998), therefore increasing residence time of gaseous molecules in the soil. A review of soil N_2O emissions performed by Stehfest and Bouwman (2006) showed that finer-textured soils lead to significantly higher N_2O emissions in comparison to coarse and medium textured soils. Further, Hefting et al. (2004) found that higher denitrification rates occurred in fine textured sites after rainfall events. Since finer textured soils have smaller pores they tend to give rise to a capillary zone in organic soil. Because of their capacity to retain moisture lighter textured soils may be more conducive to producing and maintaining denitrifying conditions longer than in better drained coarser soil (Bouwman et al., 1993).

Diffusion also plays a role in the conversion of N_2O into N_2; the longer it takes N_2O to diffuse to the atmosphere, the more likely denitrifying bacteria will transform it into N_2 before reaching the atmosphere (Davidson, 1991; Smith et al., 1998; Hefting et al., 2004).

ii.   *Nitrate availability*

Once oxygen is depleted within the soil and an anaerobic environment is formed within the soil column, soil microbes begin to use nitrate instead of oxygen as the

electron acceptor in microbial metabolism (Hedin et al., 1998); this is the basis of denitrification.

In landscapes down gradient from fertilized croplands, mineral nitrogen availability is generally higher than in other landscapes. Weitz et al. (2001) found that mineral nitrogen availability and soil moisture were the most important factors controlling N_2O emission variability. However, Smith et al. (1998) showed under laboratory conditions that mineral nitrogen application had little to no effect on N_2O emissions until the soil was wetted, while Pfenning and McMahon (1996) found that denitrification potential was not limited by nitrate concentrations. These studies suggest that while nitrate availability is crucial to denitrification, soil moisture plays a larger role in N_2O emissions.

iii.   *Organic carbon availability*

Soil organic carbon (SOC), particularly dissolved organic carbon, also acts as a regulator of denitrification and emission of N_2O from soils. During denitrification, organic carbon acts as an electron donor for microbial metabolic processes (Hedin et al., 1998). In this way, organic carbon availability can be a limiting factor in denitrification and thus N_2O emission in a riparian ecosystem.

A study by Pfenning and McMahon (1996) showed that N_2O production rates increased in response to increasing organic carbon concentrations in riverbed sediments. The study also reported higher N_2O production rates occurred in the presence of organic matter from surface sediments rather than with organic matter in groundwater (Pfenning and McMahon, 1996). In addition, Stehfest and Bouwman (2006) concluded that the N_2O/N_2 ratios in denitrification products increased with SOC content. That study

concluded that denitrifying microbes showed a preference for the transformation of nitrate to nitrous oxide rather than nitrous oxide to dinitrogen in the presence of an ample supply organic carbon to denitrifiers (Stehfest and Bouwman, 2006). Burford and Bremner (1975) also suggested that, where an abundant supply of nitrate and SOC exists, microbes preferentially transform nitrate to N_2O instead of the conversion of N_2O to N_2.

iv.   *Soil temperature and pH*

Soil temperature also plays a role in N_2O emission of soils. Pfenning and McMahon (1996) found that lowering incubation temperatures of nitrate-rich riverbed sediments from 22 to 4 $^{\circ}$C resulted in a 77 % decrease in N_2O production rates. These findings are consistent with a previous study by Hanson et al. (1994) suggesting that denitrification rates were affected by annual temperature changes. Additionally, Dobbie and Smith (2001) showed that identical soil cores amended with the same amounts of nitrate and water showed an appreciable increase in N_2O emissions with increased soil temperature. However, Goossens et al. (2001) found that 7-76 % of the total annual N_2O emitted occurred during the winter months (October-February) and consequently suggested that annual N_2O emission budgets should not overlook colder winter months as this could result in underestimation of annual emissions.

Additionally, N_2O emissions can be affected by soil pH. According to Stehfest and Bouwman (2006), higher N_2O emissions were correlated with lower soil pH. Although the exact relationship has not been fully elucidated, it has been hypothesized that low soil pH (4.9-6) enhances denitrifying capabilities of soil microbial communities (Simek et al., 2002). In contrast, study where soil pH was adjusted to pH values of 3.9,

5.9, and 7.6, Yamulki et al. (1997) concluded that average N_2O emissions decreased significantly with decreasing pH.

Research questions and hypotheses

Question 1:

How do N_2O fluxes in riparian buffers compare to those in adjacent crop fields? Can differences in N_2O fluxes be attributed to differences in soil characteristics and nutrient availability between cropland and riparian buffers? Additionally, how do climatic factors affect the variability of N_2O emissions in these two ecosystems? In other words, do N_2O fluxes in these adjacent ecosystems show similar temporal variation and show similar patterns in response to these weather events?

Hypothesis 1:

Numerous studies (Goossens et al., 2001; Hefting et al., 2003; Jacinthe and Lal, 2004; Hefting et al., 2004) have shown that in non-intensively managed terrestrial systems the highest N_2O emissions tend to occur in response to wet weather events (freeze-thaw and flooding). Therefore, given their landscape position and susceptibility to flooding, it is hypothesized that seasonal variation in N_2O fluxes will be higher in riparian buffers compared to adjacent crop fields. The position of the water table could further contribute to the development of conditions favorable to denitrification in the riparian zone. In addition to being flood-prone and wetter environments, it is also speculated that higher organic carbon contents will further support higher N_2O emissions in riparian zones compared to adjacent croplands.

Question 2:

Riparian zones within the same watershed may differ in terms of land-use, geomorphology, flooding duration, and the grain size of sediments deposited during flooding. Consequently, major differences in soil properties may exist among different riparian environments in a watershed. How do these differences in soil properties affect N_2O emissions?

Hypothesis 2:

The channel-riparian relationship determines flood potential, ponding duration and soil moisture conditions in riparian zones. In addition, the nature of sediments deposited during flooding may also dictate pedogenetic processes and riparian soil properties. If the channel-riparian relationship is such that the riparian zone is frequently flooded, it may be hypothesized that such a riparian area will exhibit higher N_2O emissions compared to a less frequently flooded riparian zones. Deposition of coarse materials (sand, gravel) may lead to the formation of riparian soils that are naturally well-drained, and therefore have a lower capacity to retain high moisture levels and maintain denitrifying environments for long periods. In contrast, soils that are finer and compacted may maintain a higher soil moisture level for a longer period allowing denitrification and N_2O emission to persist. Therefore, both the frequency of flooding and soil moisture regime may determine the ability of riparian soils to sustain a denitrifying environment after a wet weather event. It is hypothesized that riparian soil characteristics will determine annual N_2O emission from various riparian ecosystems within a watershed.

Project objectives

The overall objective of this study is to investigate the properties of riparian soils affecting seasonal N_2O fluxes. In addition, this research effort will compare N_2O emissions (seasonal and annual) from riparian zones and adjacent crop fields, and examine relationships between N_2O emission, environmental conditions (moisture and temperatures) and soil properties.

Project significance

Current research interest on riparian zones has primarily been motivated by water quality concerns. However, an equally important and relevant concern has not received adequate attention. The water quality benefits of riparian landscapes may negatively affect atmospheric N_2O concentrations, and so far, this connection is not well documented. Despite the growing interest in the biogeochemical N cycling (sources and sinks) in a wide range of ecosystems, data remains limited concerning N_2O fluxes in riparian zones. In the most recent version (IPCC, 2006) of the methodologies to construct N_2O budget in agricultural landscapes, the Intergovernmental Panel on Climate Change (IPCC) distinguished between "direct emissions" and "indirect emissions" of N_2O from managed soils. Direct emissions constitute N_2O emitted in the cultivated field while "indirect emissions" are produced from associated land where transported NO_3^- (via leaching and runoff) can be transformed into N_2O. The relative proportion of nitrogen loads converted into N_2O in the riparian area is termed an "indirect emission factor". Indirect emission factors between 0.05-2.5 % have been proposed to estimate nitrous oxide emission from riparian landscapes affected by agriculture (IPCC, 2006).

It is important to recognize that the data collected to support the assignment of these IPCC emission factors were derived from research conducted on open water streams and estuaries and may not account for the N_2O emission potential present in riparian areas. Thus, wide adoption of currently proposed indirect emission factors (IPCC, 2006) might lead to drastic underestimations of riparian zone contribution to total N_2O emission in agricultural landscapes. If riparian zones exposed to high loads of nitrogen do in fact produce higher than estimated N_2O emissions, the question of whether we are sacrificing air quality for water quality becomes highly relevant to riparian restoration efforts in agricultural watersheds.

MATERIALS AND METHODS

Description of study sites

This study was conducted at two riparian buffers and adjacent crop fields in central Indiana. At both sites the riparian buffer is located down-slope from intensively managed agricultural fields under corn-soybean (*Glycea max, L*) rotation. The sites present contrasting physical and geomorphological characteristics (drainage properties, channel geomorphology and land-use). The first site (39^0 29' 39.49" N, 86^0 25' 2.39" W; Morgan County) is a riparian forest south of Indianapolis (hereafter referred to as White River, WR) and the second site is located east of Indianapolis (39^0 51' 20.34"N, 85^0 50' 24.68"W; Hancock County) consisting of a mixture of grasses and shrubs (hereafter referred to as Leary Weber Ditch, LWD). These riparian sites are drastically different in terms of vegetation cover, soil drainage, and geomorphology of the adjacent channel; these factors should affect soil texture, organic carbon availability and soil moisture conditions, and ultimately N_2O emission. As hypothesized, these contrasts could result in significant difference in N_2O fluxes.

The White River site (WR) is a riparian forest bordering a 4th order segment of the White River. At this deciduous riparian forest, vegetation consists of sugar maple (*Acer rubrum*), silver maple (*Acer saccharinum*), beech (*Fagus sylvatica* L.), sycamore (*Platanus occidentalis*), oak (*Quercus bicolor*) and ash (*Fraxinus pennsylvanica*). The riparian area is approximately 150 m wide strip of land between the river channel and the cultivated field at its northern edge. Field observations and regional surficial geology maps indicate that soils at this site derive from alluvium deposits associated with flooding events of the White River and last glaciation. The overall coarser (silt to sand) alluvial

soils that dominate this site are the products of the White River geomorphology and flooding events since the last glacial maximum. This site is estimated to have approximately 2 m of silt loam soil atop a 50 cm layer of compacted gravel. This layer represents the lower boundary of the effective water table. As a floodplain of the White River, this site is highly susceptible to floods, which often occur after early spring snowmelt and major rain events in late spring and early summer. The entire site can be under up to 4 m of floodwater for extended periods of time during the most extreme of these events. Soils are well-drained predominantly classified as Genesee silt loam (fine-loamy mesic fluventic Eutrudepts) and Stonelick sandy loam (USDA-NCRS Web Soil Survey). Upland land-use is primarily corn (*Zea mays*) and soybean (*Glycine max*) rotation; however, in both the 2009 and 2010 growing seasons when N_2O fluxes were monitored for this study, the upland crop field at WR was in corn. This site is estimated to have approximately 2 m of silt loam soil atop a 50 cm compacted gravel layer. This low permeability layer represents the lower water table boundary. As a floodplain of the White River, this site is highly susceptible to floods, which often occur after early spring snowmelt and major rain events in late spring and early summer. The entire site can be under up to 4 m of floodwater for extended periods of time during the most extreme of these events.

The Leary Weber Ditch site (LWD) is a grassland-shrub riparian zone approximately 25 m wide on both sides of an agricultural ditch flowing west to east within the reach of the study site. To prevent flooding of adjacent crop fields in this flat landscape, the ditch has periodically been dredged, straightened and artificially deepened. As a result of these alterations, the riparian zone is not subject to active sediment

deposition from flooding events as might be expected with a non-modified channel. This site is dominated by fine-textured and poorly-drained soils mostly classified as Brookston loam (fine-loamy mesic typic Argiaquolls). Soils at this site develop above a compacted glacial till layer at a depth of approximately 2 m below the surface (SCS, 1978). A tile drainage network, located approximately 1 m above this till layer, flows underneath the crop field and riparian area, and discharge into the Leary Weber ditch. At the LWD site, the adjacent crop fields are also in soybean-corn rotation. During this study the north side of the ditch was in soybean while corn was planted on the south side of the ditch. Before planting corn in the spring of 2010, 121.5 kg N ha^{-1} of urea ammonium-nitrate (UAN) was applied to the south field.

Monitoring of N_2O emission

Nitrous oxide emission was monitored from December 2009 to May 2011. At the White River site, N_2O emission and soil properties were measured along three transects with two transects in the riparian zone, and one transect in the crop field. In the riparian area, transects were delineated so as to include high (ridge) and low (swale) topography, and extended from the field edge to the river channel edge. A schematic layout of the WR site is shown in Fig. 1. Along each of the riparian zone transects 5 static chambers were installed and remained in place for the duration of the study. The chambers installed in the crop field were removed during harvest and fertilizer application. Next to the chamber near the middle of the first transect (chambers 1-5), soil probes (HOBO Micro Station Logger with 12-bit Temperature Smart Sensor S-TMB-M006 and Soil

Moisture Smart Sensor S-SMA-M005) were installed for continuous measurement of soil moisture and temperature at 20 cm below the surface.

Likewise at the LWD site, static chambers and soil moisture and temperature probes (also at 20cm depth) were deployed in both the crop field and riparian zone. To maintain consistency throughout the study with the field crop type, the crop field transect remained on the south field to follow the corn-rotation; for the 2010 growing season the north riparian buffer reflected emissions adjacent to soybean cultivation. Given the flat topography and uniform landscape at LWD, chambers were installed along a predetermined grid from field to ditch edge (Fig. 2). Chambers installed in the crop fields were removed as needed to accommodate agricultural field operations including fertilizer application, seeding and fall harvest.

Trace gas sampling and analysis

Nitrous oxide gas samples were collected in the field at both sites on a monthly to bi-monthly basis between December 2009 and May 2011. Sampling frequency was be adjusted with occurrence of wet weather events and site accessibility (frozen or heavily flood chambers limited accessibility). Deployed static chambers consisted of 30 cm inner-diameter PVC cylinders securely inserted 8-10 cm into the ground with an above ground headspace average height of 12-15 cm. The bottom edge of the chamber was beveled to facilitate ground insertion. During sampling, chambers were covered with PVC lids secured on the base with bungee cords and metal hooks. The lid was fitted with a gasket at its underside edge to make an air-tight seal, and butyl rubber septa at its center to form a sampling port.
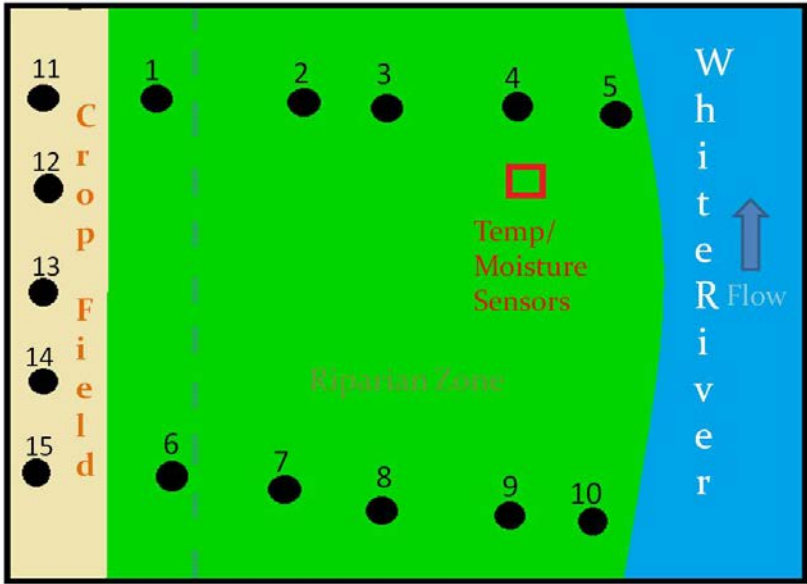
Fig. 1. A schematic layout of the WR site showing the location of the static chambers (numbered dots) and soil moisture and temperature sensors (labeled square). The arrow indicates the general channel flow direction (approximately north-south).
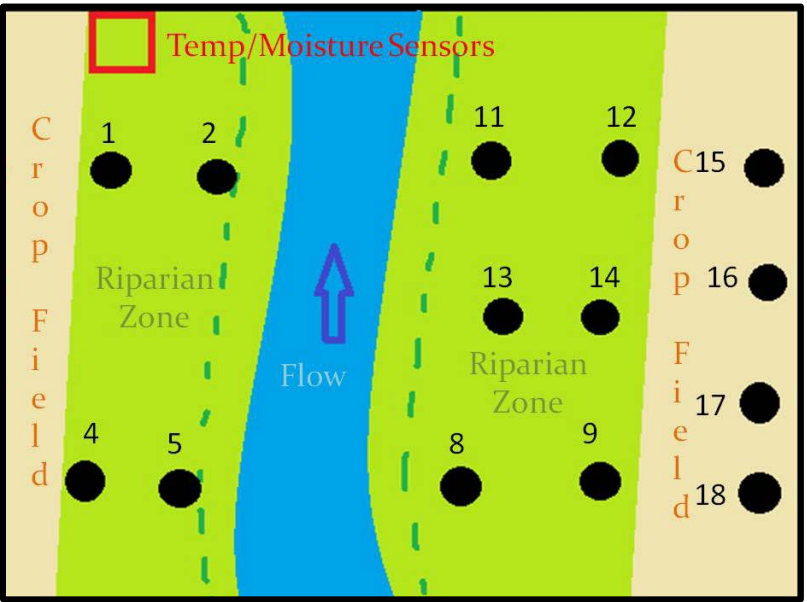
Fig. 2. A schematic layout of the LWD site showing the approximate location of the static chambers (numbered dots), and soil moisture and temperature sensors (labeled square). The arrow indicates the general channel flow direction (approximately west-east).

Chamber headspace gas was sampled at 20-30 min intervals for one hour to determine gas concentration. Gas samples (~20 ml) were stored in 10 ml evacuated glass vials fitted with butyl rubber septa and kept away from heavy light exposure until analyzed.

Gas samples were analyzed using a CP-3800 gas chromatograph (Varian, Palo Alto, CA), in conjunction with a Combipal headspace auto-sampler (CTC Analytics, Zurich, Switzerland). The GC is equipped with an electron capture detector (300 $^\circ$C) and two stationary phase Porapak Q columns (90-cm long pre-column and 180-cm long analytical column). The GC was calibrated with standard gases obtained from Alltech (Deerfield, IL). Nitrous oxide fluxes were computed using the following calculation:

$$F = \frac{dC}{dt}\frac{V}{A} k$$

Where: dC/dt: rate of change of N_2O concentration in chamber headspace (mg N_2O-N m^{-3} min^{-1}); V: chamber volume (m^3); A: area of soil circumscribed by chamber (m^2); k: time conversion factor (1440 min d^{-1})

Additionally, cumulative N_2O emitted during the study was computed for each sampling point by integration between sampling occasions using the trapezoidal rule. Area under the curve computation was carried out using SigmaPlot 11.0.

Soil sample collection and analysis

Soil samples were collected in October 2009 next to each static chamber at each site to determine soil properties. Soil samples were collected as close as possible to the chamber but not within the chambers. These samples were composite soil samples collected at depths of 0-20 cm at each chamber location to represent an overall characterization of the most microbially-active soil layer. Intact soil cores were also

extracted to determine surface bulk density and total porosity. The intact soil cores were

then dried in an oven at 105 °C for 48 hrs to obtain total mass of dry soil within the core.

Subsequently, soil bulk density is determined using the following equation:

$$\rho_s = \frac{M_s}{V_c}$$

Where: ρ_s = soil bulk density (g cm^{-3}); M_s = dry soil mass (g); V_c = core volume (cm^3)

Using soil bulk density the total porosity of the soil can be determined using the

following equation:

$$\varphi = 1 - (\rho_s/\rho_p)$$

Where: φ = total soil porosity; ρ_s = soil bulk density (g cm^{-3}); ρ_p = soil particle density
(2.65 g cm^{-3});

Each composite soil sample was split into a moist and dry fraction. The moist

fraction was used for assessment of biochemical properties whereas the dry fraction was

used to determine physical and mineral properties. Soil analysis will focus on properties

that are most likely to influence N$_2$O fluxes and denitrification. All results were reported

on a dry soil mass basis in which the soil was dried at 105 °C for 48 h. All tests were run

in duplicate.

The biochemical factors analyzed were nitrogen mineralization rates (net

nitrification), soil microbial biomass, denitrification enzyme activity (DEA) and

dissolved organic carbon (water extractable carbon).

Nitrogen mineralization rates were determined using an amended laboratory

method described by Jacinthe et al. (2002). First, inorganic nitrogen is extracted from

fresh, field moist soil (sieved 2 mm) in 1 M KCl solution, filtered (Whatman 42) and

analyzed for mineral nitrogen concentrations ($t_{1\ conc}$). Then, 10 g of field moist soil (2 mm) was incubated at 25 °C for 15 days. After incubation, mineral nitrogen was extracted again following the procedure described above (t_{2conc}). Net N-mineralization rate was then calculated by dividing the change in mineral N concentration (t_{2conc} - $t_{1\ conc}$) by the time of incubation (15 days). This mineralization rate can be viewed as the net nitrification activity occurring within the soil.

Soil microbial biomass was determined using the substrate-induced respiration procedure, which employs the stimulation of microbial respiration by glucose amendment and assumes that the subsequent respiration activity is proportional to the size of the microbial biomass in the soil (Anderson and Domsch, 1978). First, 20 g of fresh, field moist soil (sieved 2 mm) was amended with a glucose-talc mixture (1:4) and placed inside an air-tight jar fitted with a sampling port. To obtain initial values (t_{1CO2}), a jar with only glucose-talc was also incubated. After a 2 h incubation period (22 ^{0}C), the jar headspace is sampled (~20 ml air) and analyzed for CO_2 concentration by gas chromatography (t_{2CO2}). The rate of CO_2 production (t_{2CO2} - t_{1CO2} divided by incubation time) was used to calculate the soil microbial biomass.

Denitrification enzyme activity (DEA) was performed to determine the total denitrification potential of the soil by using the acetylene (C_2H_2) inhibition method. This technique was adapted from Smith and Tiedje (1979) with the exception that chloramphenicol was be used. First, 5 mL of deionized water and 5 mL of a potassium nitrate solution (1.43 g L^{-1}) was added to 10 g field moist soil (sieved 2 mm) in a 160 mL serum bottle. The bottle was then crimp-sealed and vigorously shaken to create a slurry, then evacuated and flushed 3 times with a stream of N_2 gas to expel oxygen from the

bottle. The bottle was brought to atmospheric pressure and 15 mL of C_2H_2 was added to obtain a final C_2H_2 partial pressure of ~10 kPa. After a 2 h incubation (22 °C) period, 15 ml of bottle headspace was extracted and analyzed for N_2O by gas chromatography (t_{2N2O}). To obtain an initial N_2O value (t_{1N2O}), a bottle containing only DI water and potassium nitrate was included. The rate of N_2O production (t_{2N2O} - t_{1N2O} divided by incubation time) was used to calculate denitrification potential.

Dissolved organic carbon was determined as described in Burford and Bremner (1975). Dissolved organic carbon was extracted at laboratory temperature (22 °C) from soil suspension (20 mL deionized water added to 10 g field moist soil). The suspension was shaken for 1 h and centrifuged (6,000 rpm for 5 minutes). The supernatant was then filtered through 0.45 µm nylon filters (Sartorius Biolab) and analyzed for TOC using an Elementar Vario TOC/TNb Cube Analyzer (Mt. Laurel, NJ).

Other soil characteristics analyzed were soil organic carbon, pH and texture. Soil organic carbon was determined using a dry combustion method. Soil was dried (105 °C, 48 h) and finely ground and sieved (150 µm). Soil sub-samples (8-15 mg in tin capsule) were combusted at approximately 900 °C (Elementar Vario TOC/TNb Cube Analyzer) to determine C and N content. Determination of soil pH involved the addition of deionized water to dry soil sample (sieved 2mm), shaking for 30 minutes and values obtained using a pH meter (Accumet model 25 pH/ion meter). Texture analysis was performed using the Bouyoucos (hydrometer) method (Bouyoucos, 1936). First, to burn off all organic matter (OM), 40 g dried (105^0C, 48h), sieved (2 mm) soil and was treated with 30% hydrogen peroxide (H_2O_2) and heated to dryness. Next, sodium hexametaphosphate (50 g L^{-1}) was added to the sample and shaken overnight for complete dispersion of soil materials.

Hydrometer readings were taken at 40 seconds (approximate settling time for sand) and 2 hours (silt settling time). The percentage of sand, silt and clay was then calculated from these readings.

An additional aspect to field sampling included monitoring the depth of the water table. Next to most of the static chambers located within the riparian area (with exception of chambers 13 and 14 at the LWD site, see Fig. 2), wells were dug to monitor water table depth. Groundwater samples were periodically taken to determine mineral nitrogen concentration and dissolved organic C. Dissolved oxygen, oxidation-reduction potential and water temperature were also measured during well sampling.

Although physical, chemical and biochemical characteristics were based on laboratory analysis, defining these properties aimed to aid in the effort to determine if and how variability of these properties affect *in situ* N_2O emission measurements. While literature supports soil moisture as the leading controller of denitrification and associated N_2O emission, an understanding of the combination of factors and how these soil factors differ between ecosystems (both between cropland and riparian zone and between differing riparian zones) hoped to bring insight into what soil conditions promote N_2O emissions in the field.

Statistical analysis

Analysis of variance (ANOVA) was carried out to assess the effect of geomorphology and land-use on N_2O fluxes. In this analysis, the response variable was N_2O flux and the class variables were geomorphology (glacial outwash at WR and till plain at LWD) and land-use (riparian buffer and cropland). Additionally, the effect of

sampling date was assessed using repeated-measured ANOVA with sampling occasion as the time-repeated factor (Little, 1989). For separation of means, t-tests were also conducted in order to compare overall N_2O fluxes between sites and land-use. Prior to ANOVA, the data was first tested for normality. If the data did exhibit a normal distribution, transformations (i.e. log, reciprocal, square root, exponential, or square law) were applied to normalize the data. If the data could not be normalized with one of the transformation methods listed above, the non-parametric equivalent test was used. A statistically significant difference confidence level of $p < 0.05$ was used for all tests.

Additionally, biochemical, chemical and physical soil properties, as well as environmental conditions (soil temperature, moisture, and water table depth) were included in regression analysis to investigate links between soil properties, environmental conditions and N_2O emission.

RESULTS

Environmental soil conditions

The two study sites exhibited different soil moisture and temperature regimes probably due to differing soil types and hydrogeomorphic settings (Figs. 3-4). The Leary Weber Ditch (LWD) site resides in the Tipton till plain dominated by poorly drained Brookston soils that require subsurface tile drainage for agriculture. In fact, our sampling area was located between two tile drains (40 m space between tiles) that discharge into LWD ditch. In contrast, soils at the WR site are well-drained Alfisols overlying glacial outwash and alluvium deposits. Additionally, the LWD site received higher rainfall amounts during the study than the White River (WR) site (Table 1). The combination of these factors contributes to the overall higher soil moisture at LWD than at WR (0.16 and 0.21 m^3m^{-3}, respectively; Fig. 5). On the other hand, soil temperature was comparable between the two sites remaining within 1-3 ºC during the sampling period (Fig. 5).

The study sites were also variably affected by flood events. While no indication of flooding was observed at LWD, the WR site was flooded at least 4-5 times during the study period with the most extensive flood occurring after major rainstorms in the spring/summer 2010 and spring 2011. During these events, flood waters reached up to 4 m above ground level within the riparian buffer, and it took up to 2-3 weeks (June 1, 2010) for the waters to fully recede. Though water table regimes at the sites were quite different, difference in surface soil moisture was more muted (Fig. 5). Soil moisture content tended to peak in late spring to early summer and generally dropped starting in late summer (Figs. 3 and 6). Additional climate comparisons are displayed in Table 1.
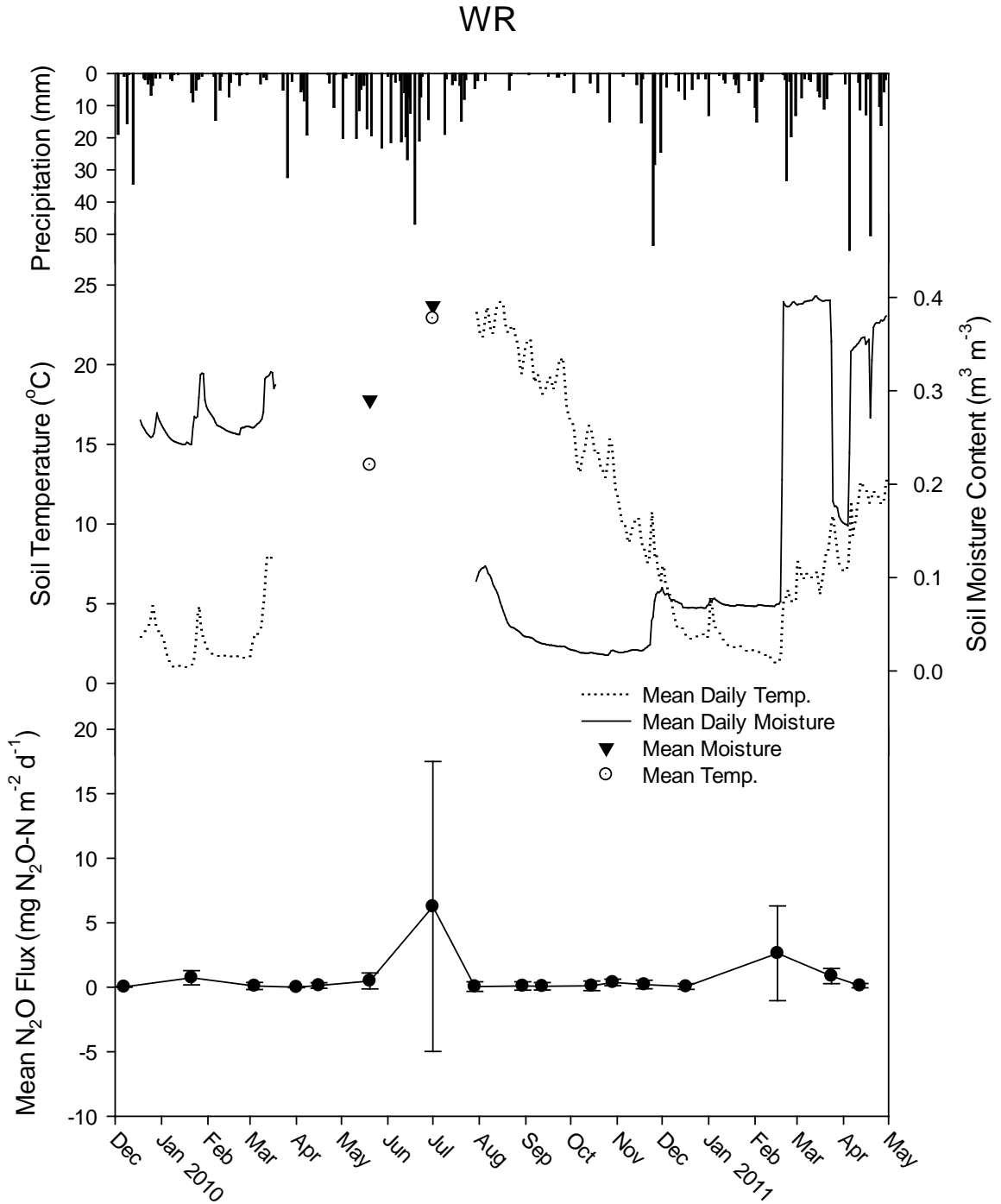
Fig. 3. Average daily flux of N$_2$O, precipitation, soil moisture, and soil temperature at the WR riparian forest. Each data point is the mean of 13 measurements. Error bar represents standard deviation of the mean. The gap in soil moisture and temperature data is due to soil probe and logger malfunction due to stagnant flood water. Sensors were installed at approximately 20 cm below the soil surface near WR chamber 4.
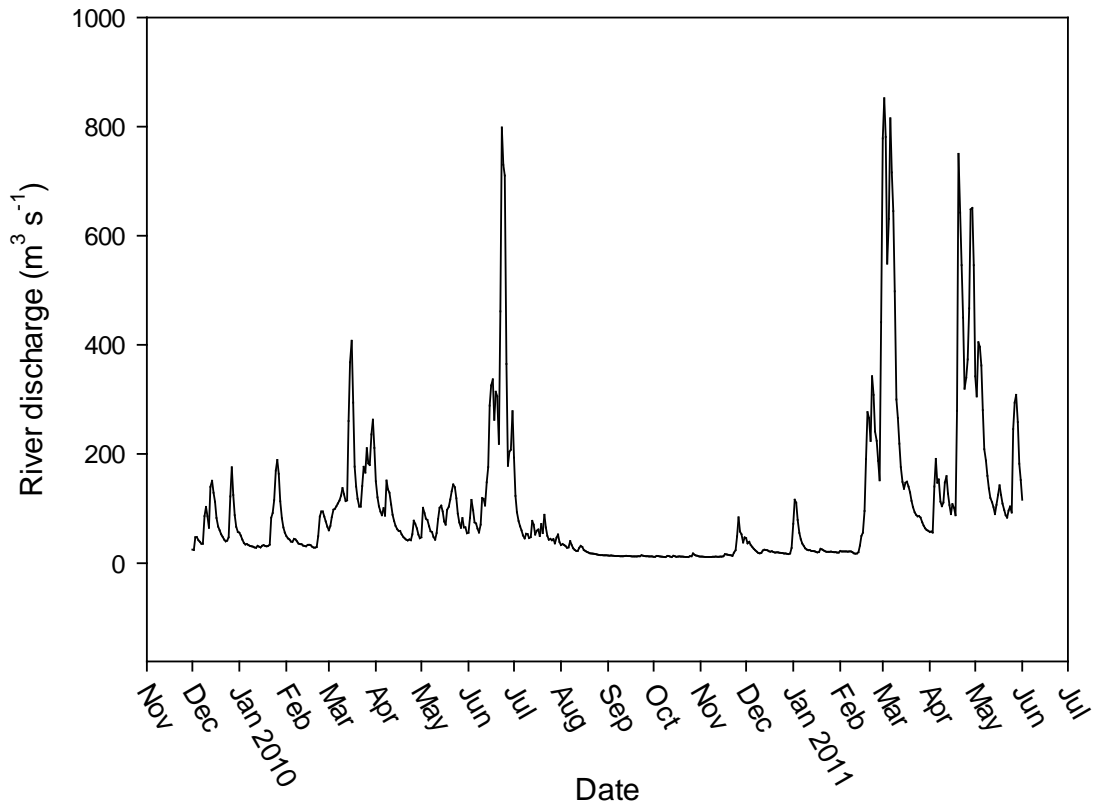
Fig. 4. White River discharge near the WR site during the sampling period December 2009 to May 2011.

Table 1. Air temperature and rainfall during the study period in comparison to long-term weather data for Central Indiana. Abbreviations: LWD = Leary Weber Ditch, WR = White River.

	Mean temperature (°C)			Mean rainfall (mm)		
Season	Indiana†	WR‡	LWD‡	Indiana	WR	LWD
Winter	0.06	-1.18	-1.46	206	88	141
Spring	15.9	16.4	16.3	318	380	396
Summer	21.2	22.6	23.5	286	112	296
Fall	6.32	6.32	6.75	244	181	199

† Mean annual data for 1971-2000 obtained from the Indiana State Climate Office (https://climate.agry.purdue.edu/climate/facts.asp)

‡ Mean annual data for the sampling period (December 2009 through May 2011) obtained from the National Oceanic and Atmospheric Association's National Climatic Data Center (http://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USC00125407/detail) (http://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USC00123527/detail)
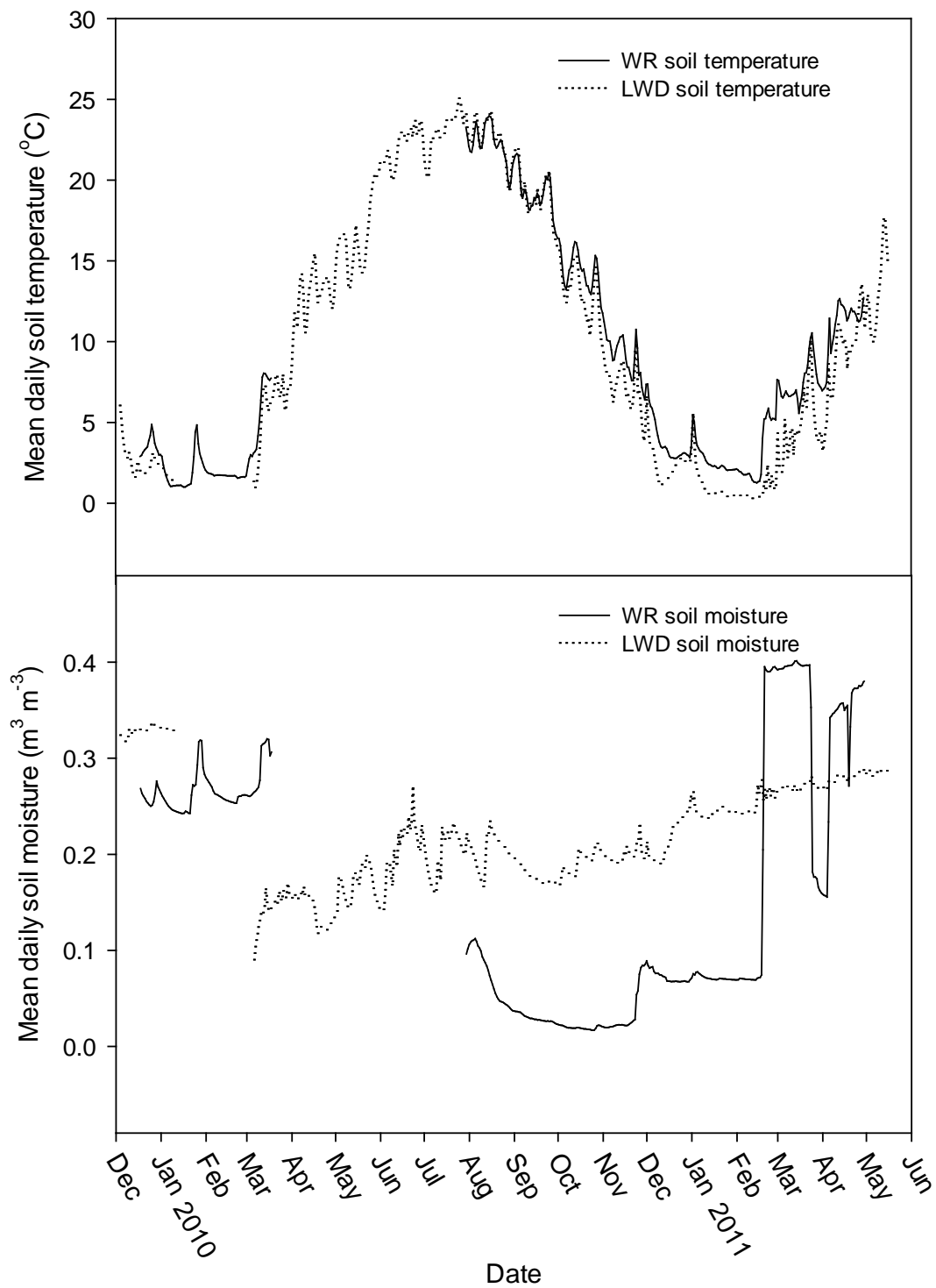
Fig. 5. Soil temperature and moisture (0-20 cm depth) at the study sites.
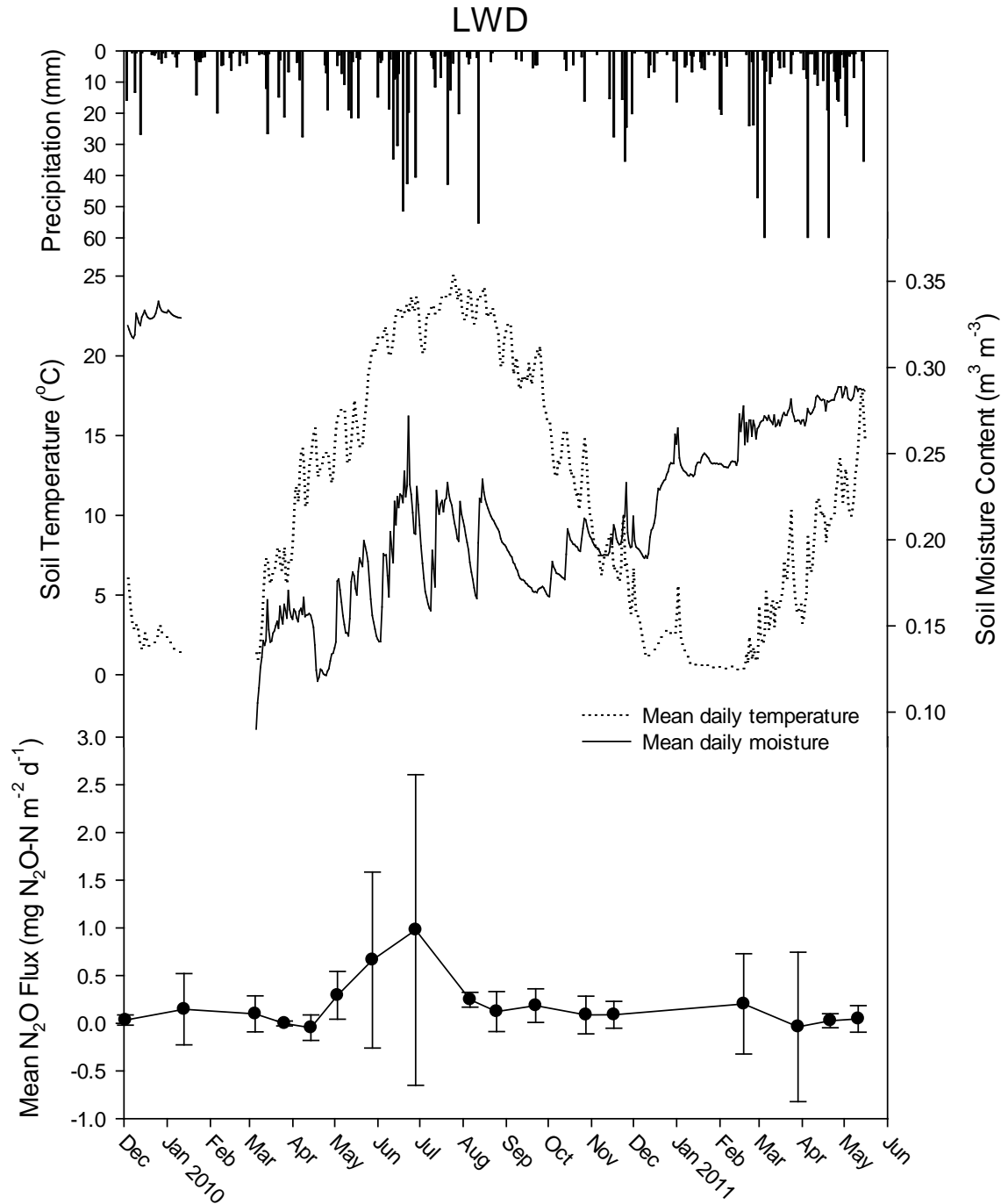
Fig. 6. Average daily flux of N$_2$O, precipitation, soil moisture, and soil temperature at the LWD riparian buffer. Each data point is the mean of 10 measurements. Error bar represents standard deviation of the mean. The gap in soil moisture and temperature data is due to rodent damage to soil probe and loggers. Sensors were installed 20 cm below the surface near LWD chamber 2.

Temporal variability of N₂O emissions

Nitrous oxide emissions were temporally variable regardless of site and land use (Figs. 3 and 6). Seasonal variability was most pronounced during the wettest period of the year (mid to late spring). At both riparian sites, seasonal peaks of N_2O emission were highest during periods of increased precipitation and increased soil moisture (coefficient of variation: ~150 % in July 2010, Figs. 3 and 6). These periods of increased N_2O flux often corresponded to seasonal peaks in soil temperature. These combinations of factors contributed to the statistical significance of sampling dates shown by ANOVA (Table 2).

Seasonal variation in N_2O flux at the WR riparian site reflected to a large extent the temporal pattern observed at LWD, but there were some important differences. The highest (mean: 6.26 mg N_2O-N m^{-2} d^{-1}) and the most variable N_2O flux (coefficient of variation: 250%) at the WR riparian site was recorded in spring/summer 2010 (Fig. 3). This peak flux also corresponded with a period of prolonged precipitation, and increased soil moisture and soil temperature (Fig. 3). This riparian area was flooded for several days with flood water levels ~2.5 m above ground during and following maximum White River discharge (Fig. 4). The gap in soil temperature and moisture data (May-July 2010) was due to flood-related damage to the sensors; hand samples were taken during sampling events to compensate for loss of sensor data. Another, but smaller, peak of N_2O emission was observed at WR during the spring-thaw event of February 2011 (mean flux: 2.63 mg N_2O-N m^{-2} d^{-1}). Soil moisture increased abruptly due to the melting of snow/ice when soil temperatures increased to above 5 °C.

In addition to weather-related factors, farming activities may have indirectly affected N_2O emission in riparian buffers. At the LWD riparian buffer, a period of

increased N_2O emission (0.29-0.98 mg N_2O-N m^{-2} d^{-1}) was observed during April-June

2010 (Fig. 6) probably due to off-site migration of urea fertilizer applied to the corn crop

grown in the cultivated field that year. However, in May 2011 a similar rise in N_2O

emission was not observed although spring soil moisture and temperature were similar in

both years (Fig. 5). The weak N_2O emission (0.03 mg N_2O-N m^{-2} d^{-1}) was most likely

due to the fact that soybean crop was planted in 2011 and therefore N-fertilizer was not

applied to the crop field.

Table 2. Two-way ANOVA of N_2O flux

Class Variables	df	SS	MS	F	P
		Response Variable: Riparian N_2O Flux			
Site	1	25.58	25.58	5.57	0.019
Date #	14	246.55	17.61	3.84	<0.001
Site x Date	14	145.84	10.42	2.27	0.006

df = degrees of freedom
SS = sum of squares
MS = mean square
F = f- test value
P = significance level

Land-use effects on N_2O emission

At WR, significant differences between land-use (crop field vs. riparian zone)

with respect to N_2O flux were observed in May 2010 (p=0.008), September 2010

(p=0.027), October 2010 (p=0.046) and February 2011 (p=0.008). An interesting pattern

was observed from May to July 2010. After an early May 2010 urea fertilizer application to the crop field, measured N_2O emission was significantly larger in the crop field (10.63 mg N_2O-N m^{-2} d^{-1}) than the adjacent riparian zone (0.48 mg N_2O-N m^{-2} d^{-1}; Fig. 3). This pattern was reversed at the next sampling occasion in July 2010 after two weeks of sustained flooding during which the riparian zone was inaccessible for sampling due to high flood waters. Although a statistically significant effect of land-use was not detected due to numerous outliers, N_2O flux was noticeably more intense in the riparian zone than within the crop field (Fig. 7). Another significant difference in land-use was observed during the February 2011 spring-thaw during which mean flux was significantly higher in the riparian zone (2.63 mg N_2O-N m^{-2} d^{-1}) than in the crop field (0.24 mg N_2O-N m^{-2} d^{-1}).

In contrast, LWD displays a much different behavior in N_2O fluxes between riparian zone and crop field. Overall, the crop field at LWD was a stronger N_2O emitter than either LWD or WR riparian zones (Table 3). Crop field N_2O fluxes were significantly higher than riparian fluxes in May 2010 (p=0.013), February 2011 (p=0.006), April 2011 (p=0.006) and May 2011 (p=0.014). The largest N_2O fluxes from the crop field occurred in February 2011 at the first true thaw of the spring at which point surface soil temperatures began to rise above freezing (Fig. 6). During this February 2011 thaw, the LWD crop field exhibited a significantly higher N_2O emission than the riparian buffer (Fig. 8). This trend was the opposite of what was observed at WR with much greater emission from the forested buffer than from the crop field (Fig. 7). This opposing behavior was also apparent in the June/July 2010 sampling occasion during which crop field emission exceeded riparian buffer emission at LWD whereas at WR the forested riparian buffer was a stronger N_2O emitter than the crop field during that

sampling period (Figs. 4 and 6). The other large N_2O fluxes were associated with increased soil moisture and temperature in late spring and early summer after N-fertilizer application (Fig. 6).

Cumulative N_2O emission from the crop fields averaged 6.37 and 7.82 kg N_2O-N ha^{-1} at LWD and WR, respectively. This annual emission corresponds to 5-6.4 % of the N fertilizer applied. Cumulative N_2O emission (Table 3) from the WR riparian forest (4.32 kg N_2O-N ha^{-1}) was significantly higher than emission from the LWD buffer (1.03 kg N_2O-N ha^{-1}). At the WR site, the amount of N_2O emitted from the riparian buffer during the late spring/early summer flooding of 2010 (mean flux: 6.24 mg N_2O-N m^{-2} d^{-1}; overall emission: 2.29 kg N_2O-N ha^{-1}) accounted for 51% of the total N_2O emitted during the 2-year study.

WR
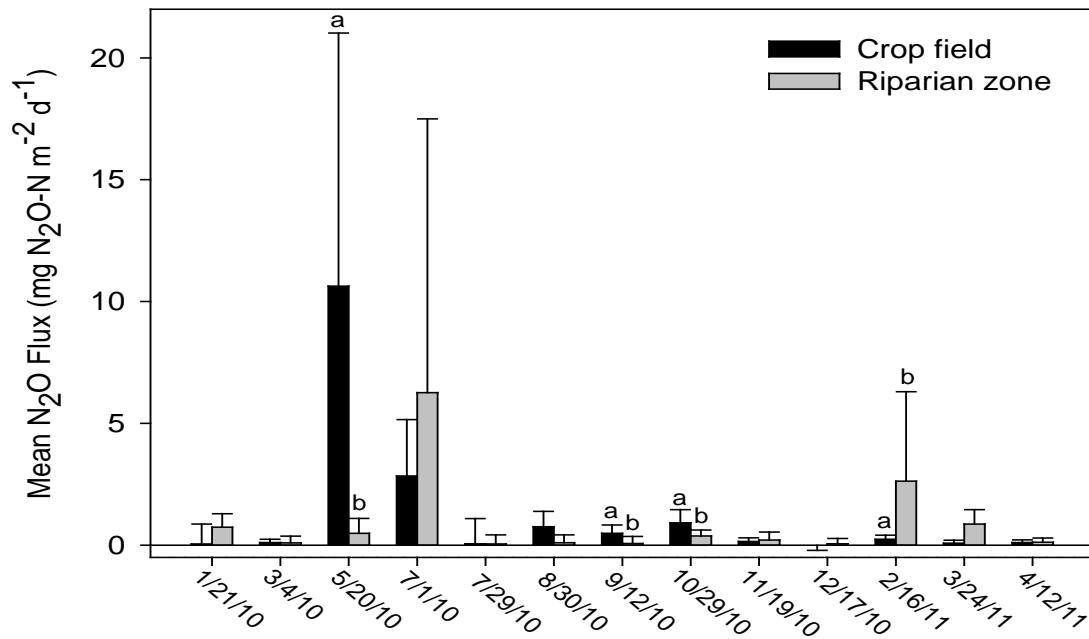
Fig. 7. Nitrous oxide emission from adjacent cropped field (corn) and forested riparian areas at the White River site. Error bar represent standard deviation of the mean (n = 13). Adjacent bars labeled with different letters denote statistically significant difference at P < 0.005.

Table 3. Average and cumulative N_2O emission by land-use at the study sites. Values are means ± standard deviation

		Riparian zone		Crop Field	
	Units	WR	LWD	WR	LWD
Mean N_2O flux	mg N_2O-N m^{-2} d^{-1}	2.03 ± 0.64*	0.43 ± 0.17	1.40 ± 1.17	1.67 ± 0.54
Cumulative N_2O†	kg N_2O-N ha^{-1}	4.32 ± 3.85	1.03 ± 0.93	7.82 ± 7.18	6.37 ± 1.85

†Cumulative amount between December
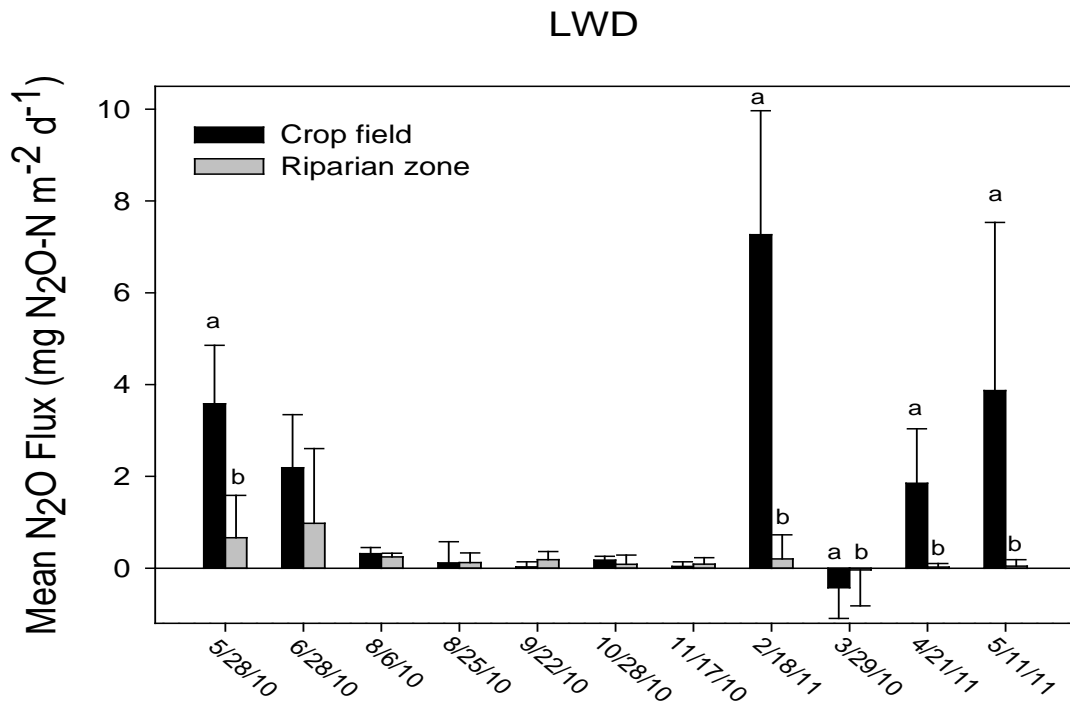
Fig. 8. Nitrous oxide emission from adjacent cropped field (corn) and grassed riparian areas at the Leary Weber Ditch site. Error bar represent standard deviation of the mean (n = 11). Adjacent bars labeled with different letters denote statistically significant difference at P < 0.005.

Relationships between soil properties and N_2O emission

Analysis of variance showed significant effect of land use and site for several of the soil properties considered in the study (Table 4). Although the sites were located in geomorphologically-distinct landscapes (glacial till plains for LWD and glacial outwash for WR), no significant difference in soil texture was found (Tables 4 and 5). While significant effect of land-use was found for several variables, these trends generally varied with site (as indicated by several significant site by land-use interactions, Table 5). The water-extractable DOC data may serve as a good illustration of that trend. While at the WR site the amount of extractable DOC was similar regardless of land use, at LWD nearly twice as much DOC was extracted from the grassy riparian buffer than from the cropland (Table 4). Regardless of study site, net nitrification was higher and C:N ratios lower in the crop field than in the riparian buffers. Conversely, SOC, total soil N, MBC and DEA were several-fold higher in the riparian zone compared to the crop field (Table 4). Contrary to expectations, higher values of these soil parameters did not translate into higher N_2O emission from the riparian buffers. During the study period, mean N_2O emission was 1.8-6 times higher in the cultivated fields than in the riparian areas. While cumulative mean N_2O emission was similar at the two cultivated sites, WR showed a much higher deviation around the mean emission compared to LWD. The riparian buffer emission also varied between sites, being 4 times higher at the WR compared to the LWD site (Table 3); however a significant site by land-use effect was not detected (Table 5). This unexpected insignificance has been attributed to high emission peaks during flooding being deemed as outliers and therefore do not occur frequently enough in the sample data to reflect overall site by land-use effects.

Table 4. Physical and biochemical properties of soils at the study sites in relation to land-use.

Soil property	Units	WR		LWD	
		Riparian zone	Crop field	Riparian zone	Crop field
pH	unitless	7.33 ± 0.09†	7.44 ± 0.07	6.90 ± 0.50	6.59 ± 0.16
Bulk density	g cm^{-3}	1.17±0.14	1.43±0.08	1.10 ± 0.14	1.34 ± 0.04
Sand	%	39.09 ± 5.7	47.19 ± 6.0	41.94 ± 4.4	42.01 ± 1.64
Silt	%	28.32 ± 5.7	23.32 ± 2.0	23.91 ± 4.4	25.87 ± 1.6
Clay	%	32.58 ± 6.2	29.48 ± 4.3	34.14 ± 3.7	32.11 ± 3.2
DOC‡	mg C kg^{-1} soil	15.79 ± 2.8	18.38 ± 4.2	25.67 ± 6.0	13.35 ± 2.4
Total carbon	%	3.67 ± 0.24	2.87 ± 0.31	4.12 ± 0.55	1.76 ± 0.37
C:N ratio	unitless	16.42 ± 1.29	14.80 ± 1.40	15.13 ± 2.11	8.98 ± 1.91
MBC	g C kg^{-1} soil	0.415 ± 0.08	0.325 ± 0.14	0.496 ± 0.72	0.165 ± 0.24
DEA	mg N$_2$O-N kg^{-1} soil d^{-1}	1.83 ± 1.1	0.403 ± 0.20	1.95 ± 1.0	0.328 ± 0.22
Net Nitrification	mg NO$_3$-N kg^{-1} soil d^{-1}	0.088 ± 0.12	0.124 ± 0.13	0.016 ± 0.02	0.059 ± 0.04

†Mean value ± standard deviation; n=10 for WR and LWD in riparian zones, n=5 for WR and n=4 for
     LWD in crop fields
DOC = dissolved or water-extractable organic carbon
MBC = microbial biomass carbon
DEA = denitrification enzyme activity

Table 5. Two-way ANOVA of soil properties

Class variables	df	Mean N$_2$O flux	Bulk density	pH	TC	C:N	DOC	MBC	DEA	Net nitrification	Sand	Silt	Clay
Site	1	NS	NS	***	*	***	NS	NS	NS	NS	NS	NS	NS
Land use	1	***	*	NS	****	****	**	**	**	NS	NS	NS	NS
Site x Land use	1	NS	*	NS	***	**	***	*	NS	NS	NS	NS	NS

* symbolizes the level of significance (NS= not significant) found by analysis of variance where * = p<0.05, ** = p<0.01 and *** = p<0.001.

40

While ANOVA revealed significant effects of site and land-use with respect to several soil properties, regression analysis showed that net N mineralization was the only soil property that significantly correlated with N_2O flux (Table 6 and Fig. 9). When regression analysis was conducted for each site separately much stronger correlations of MBC, DEA, SOC, C:N, and net N mineralization with N_2O flux were observed at LWD (Fig. 10). However, net N mineralization remained the only soil property significantly correlated with N_2O flux at the WR site (Fig. 11). Since MBC, DEA, SOC, C:N, and net N mineralization are indicators of N-cycling in soils, weak and insignificant correlations with N_2O flux were somewhat surprising.

Regression analysis was conducted to evaluate possible linkages between daily fluxes of N_2O and antecedent soil moisture and temperature (mean for the previous five days before a N_2O sampling occasion). While no trend was observed at WR (Fig. 12), data from the LWD site yielded a marginal (yet significant) correlation between soil temperature and N_2O flux (Fig. 13). Results of the correlation analysis (r^2 and significance level) between soil properties and N_2O flux at the study sites are reported in Table 7.

Links between 5-day antecedent water table depths and N_2O fluxes were examined, but the regression analysis yielded mixed results. At LWD, water table depth marginally but significantly correlated with mean N_2O flux (Fig. 14). However, at WR no such trend was observed (Fig. 15). Thus, relationships between water table depth and N_2O flux can be complex and site-dependent.

Table 6. Regression analysis of soil properties and N_2O flux at the study sites

Soil property	Coefficient of determination (R^2)	P-value
pH	0.0004	0.915
MBC	0.24	0.007
DEA	0.047	0.256
Net nitrification	0.615	<0.001
Total Carbon	0.330	0.001
C:N	0.127	0.570
DOC	0.125	0.060
Sand	0.001	0.865
Silt	0.002	0.836
Clay	0.007	0.672
Bulk density	0.093	0.107
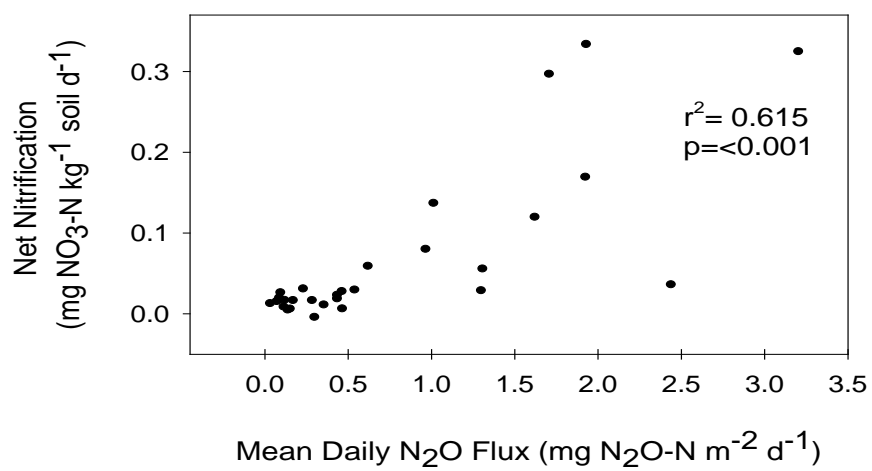
Fig. 9. Relationship between net N mineralization and mean N$_2$O fluxes at the study sites.

LWD
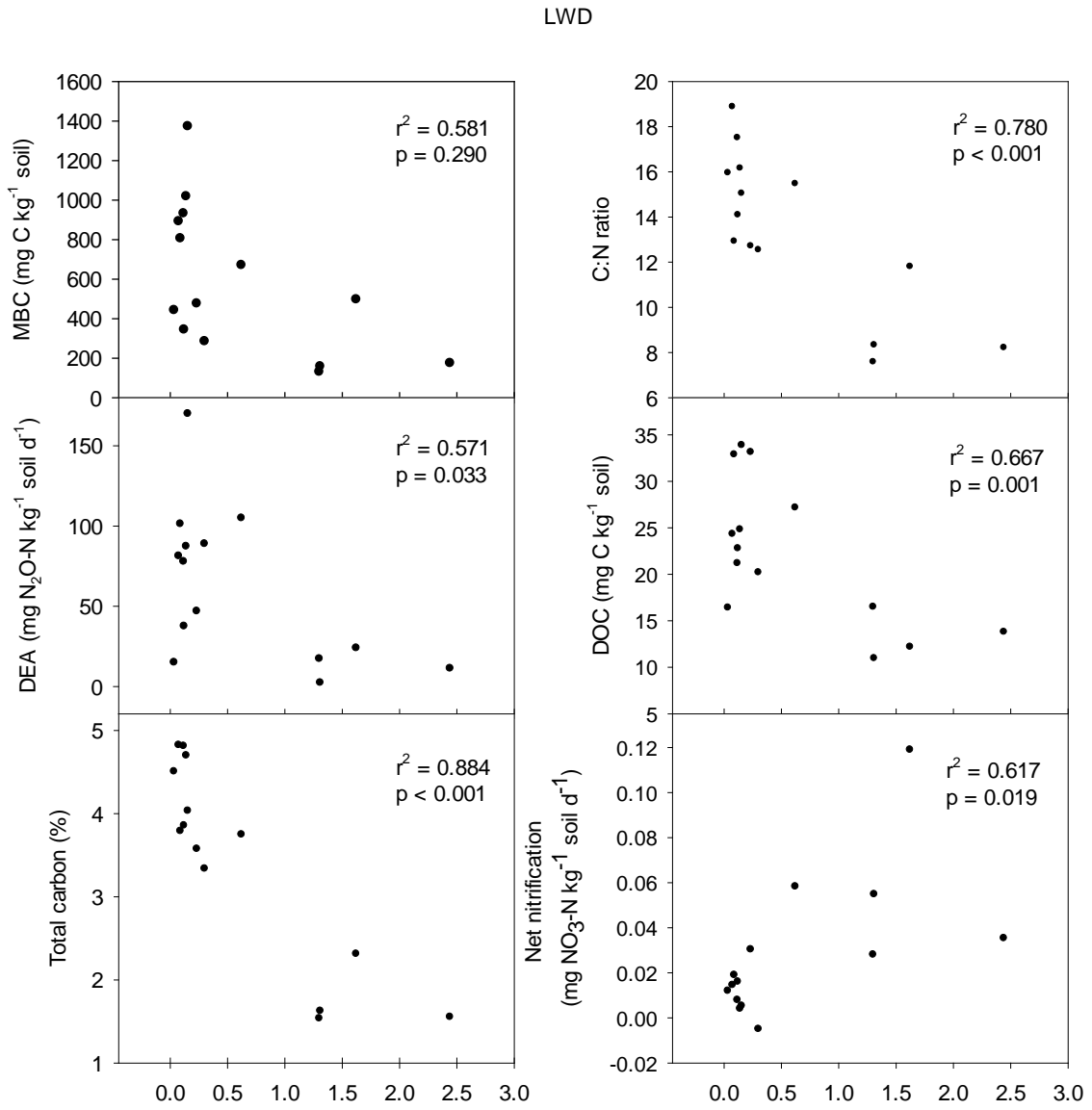
Fig. 10. Relationships between soil properties and N$_2$O flux at the LWD site.

WR
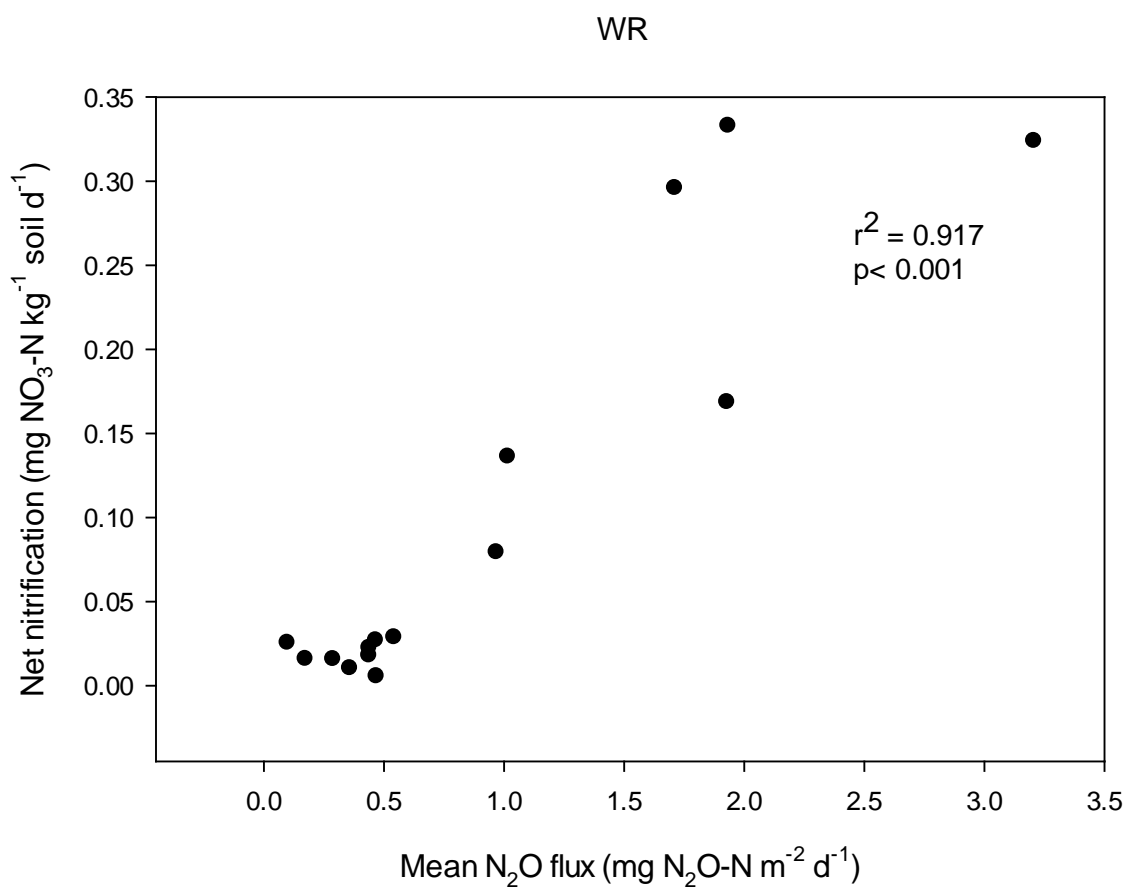
Fig. 11. Relationship between net N mineralization and N_2O flux at the WR site.

WR
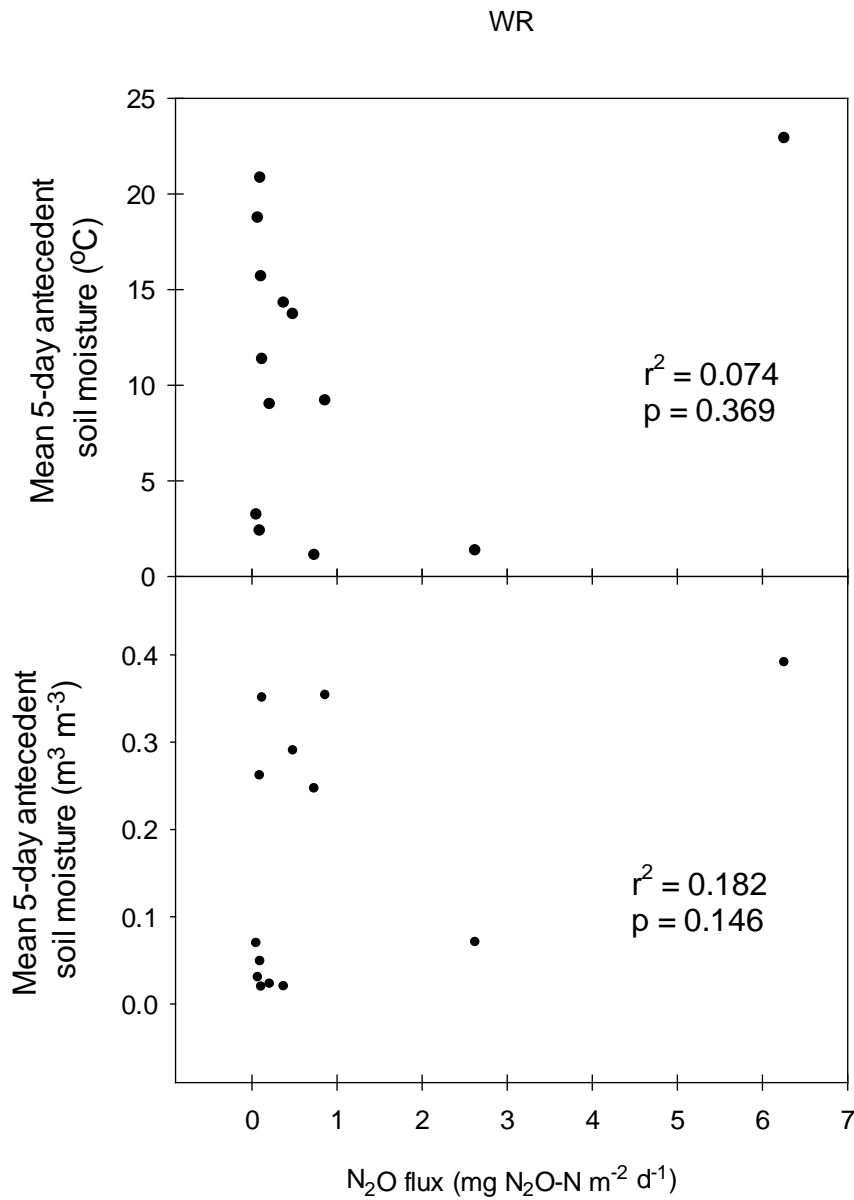
Fig. 12. Relationships between surface (0-20 cm) soil temperature (top panel) and moisture (bottom panel) and N_2O flux at the White River (WR) site.

LWD
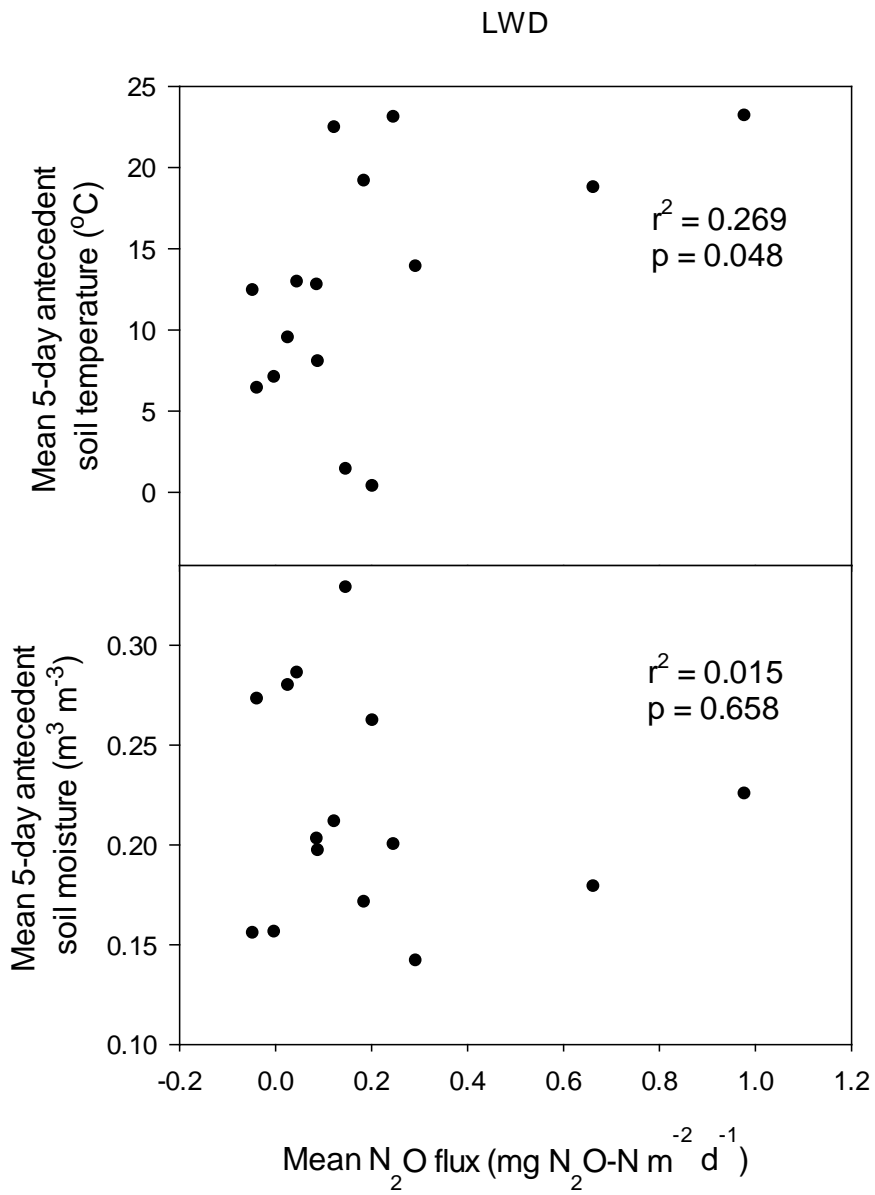
Fig. 13. Relationships between surface (0-20 cm) soil temperature (top panel) and moisture (bottom panel) and N_2O flux at the Leary Weber Ditch (LWD) site.

Table 7. Regression analysis of soil properties and N_2O fluxes at the White River site

	WR		LWD	
Soil property	Coefficient of determination (R^2)	P-value	Coefficient of determination (R^2)	P-value
pH	0.054	0.41	0.170	0.14
MBC	0.206	0.09	0.337	0.03
DEA	0.002	0.87	0.326	0.03
Net nitrification	0.840	<0.001	0.380	0.02
Total carbon	0.043	0.46	0.781	<0.001
C:N	0.017	0.65	0.608	0.001
DOC	0.066	0.35	0.445	0.01
Sand	0.002	0.86	0.00007	0.98
Silt	0.020	0.61	0.051	0.44
Clay	0.004	0.82	0.063	0.39
Bulk density	0.001	0.92	0.425	0.01

LWD

$r^2 = 0.236$
$p = 0.048$
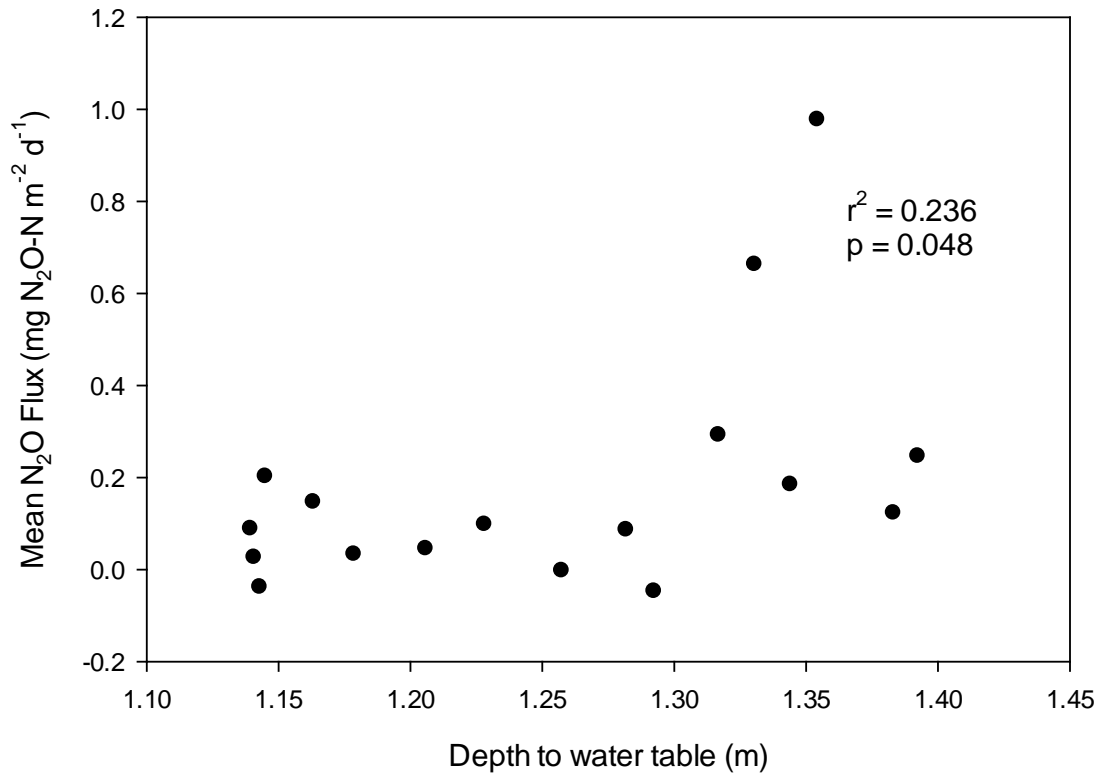
Fig. 14. Relationship between mean N_2O flux and 5-day antecedent mean water table depth at the LWD site.

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WR
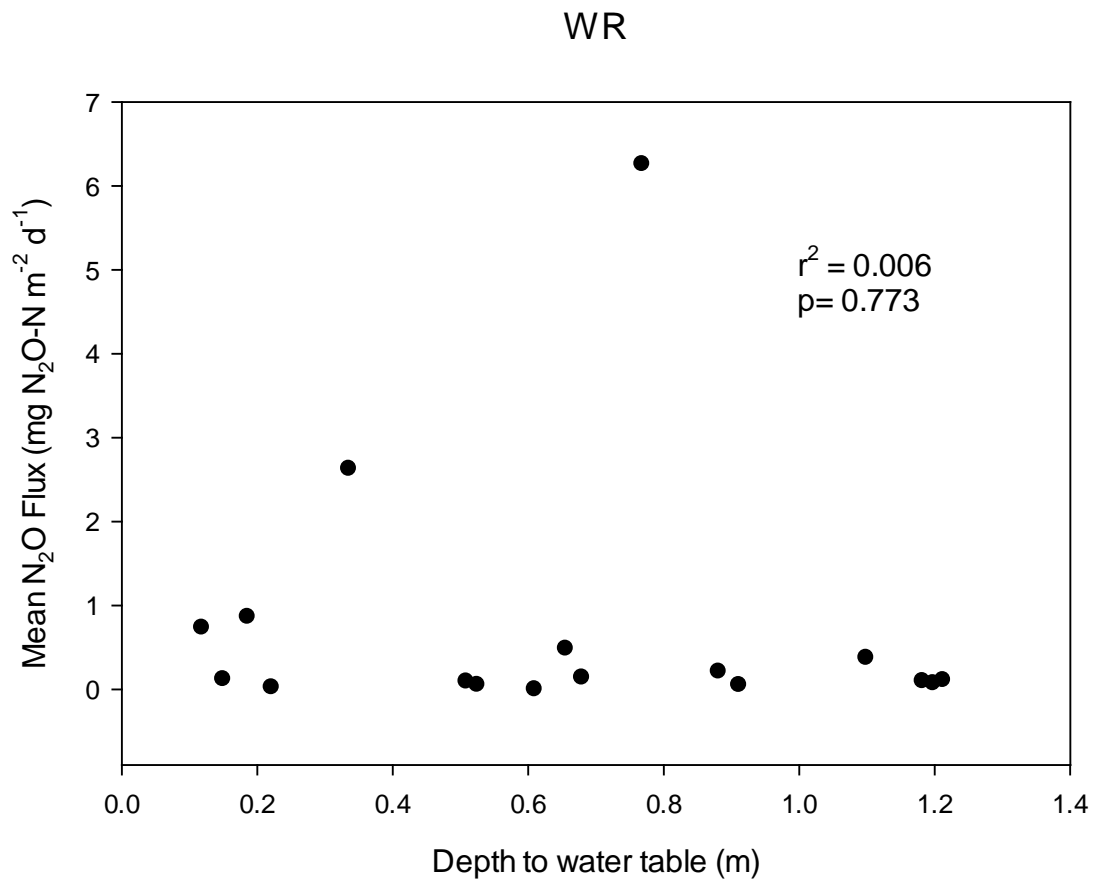
Fig. 15. Relationship between mean N$_2$O flux and 5-day antecedent mean water table depth at the WR site. Water table level was monitored with a water level logger installed near chamber 4 at WR.

Spatial variability of N₂O emissions in relation to landscape geomorphology

During the study period, the average daily N_2O emission was almost 5 times higher at the WR riparian zone than at LWD (Table 3). When the daily site average was deconstructed and analyzed by individual chambers, strong indication of spatial variability was found. At the WR site for example, two chambers (chambers 2 and 4) were identified as hotpots of N_2O production and have probably skewed the average N_2O emission to much higher rates (Fig.7). This may be related to the complex and variable geomorphology (swales, ridges, scoured surfaces and flood-induced debris deposition) of the WR site. Chambers 2 and 4 were located in depressions (Fig. 16) which, based on field observations, tended to hold water longer than surrounding areas after large rainfall events (like the sustained flooding of May/June 2010). After riparian floodwaters receded enough to sample on July 1, 2010, N_2O emission from chambers 2 and 4 (25.52 mg N_2O-N m^{-2} d^{-1} and 27.84 mg N_2O-N m^{-2} d^{-1}, respectively) far exceeded the average emission (1.62 mg N_2O-N m^{-2} d^{-1}) from the other 11 chambers deployed at the WR riparian forest (Fig. 17); in contrast, there was muted N_2O emission variation during dry summer conditions (Fig. 18). At the LWD site, however, riparian zone geomorphology was much more uniform (Fig. 19), and consequently the spatial variation in N_2O emission was much more moderate than at WR. Chamber 14 at LWD was the only sampling point that exhibited much higher mean N_2O emission than the other chambers, but the period of enhanced N_2O emission was limited to late May and June 2010, a noticeably wet period following crop field N application (Fig. 6).
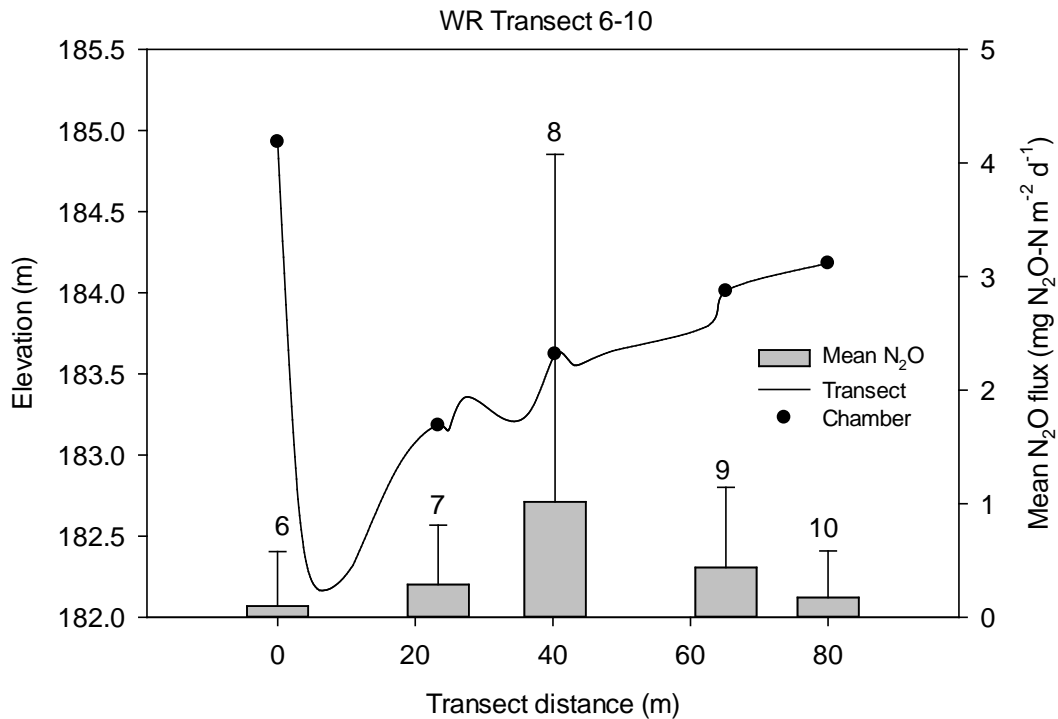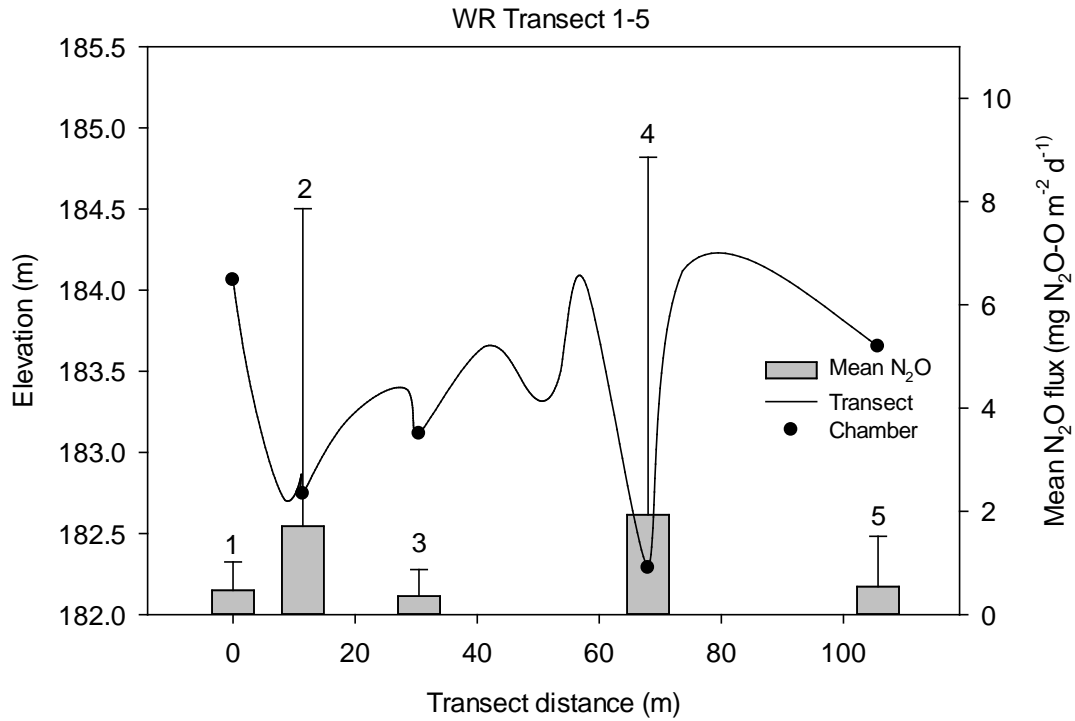
Fig. 16. Relative elevation of ground surface and study-wide mean N_2O flux along transects of sampling points at the WR riparian forest. Static chamber location and number is indicated by the filled circles. Vertical exaggeration is 0.0435.
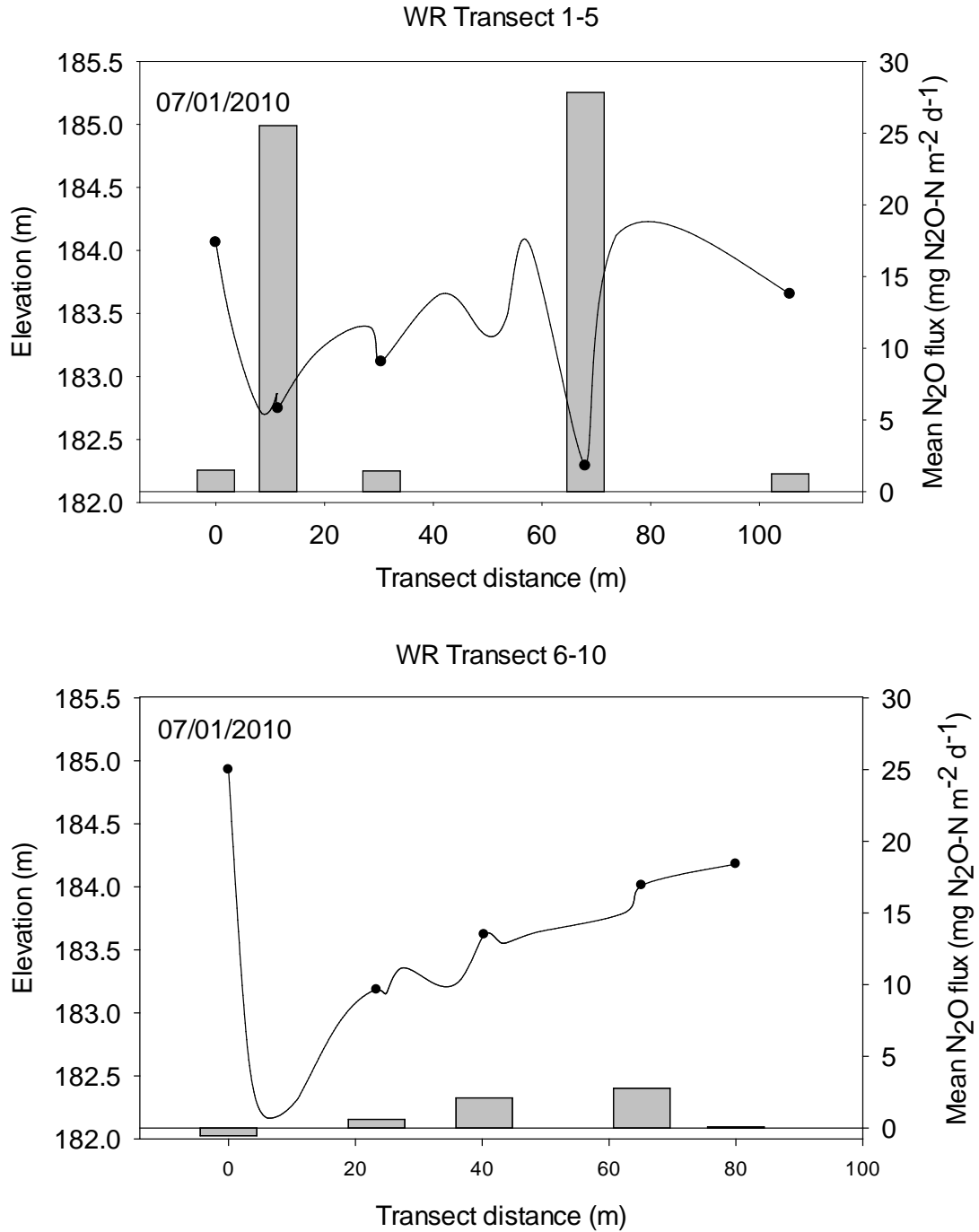
Fig. 17. Relative elevation of ground surface and N$_2$O fluxes across the WR riparian buffer after the prolonged flooding of June/July 2010. N$_2$O fluxes from chambers 2 and 4 (hot spots) were the largest rates recorded during the 2-year study.
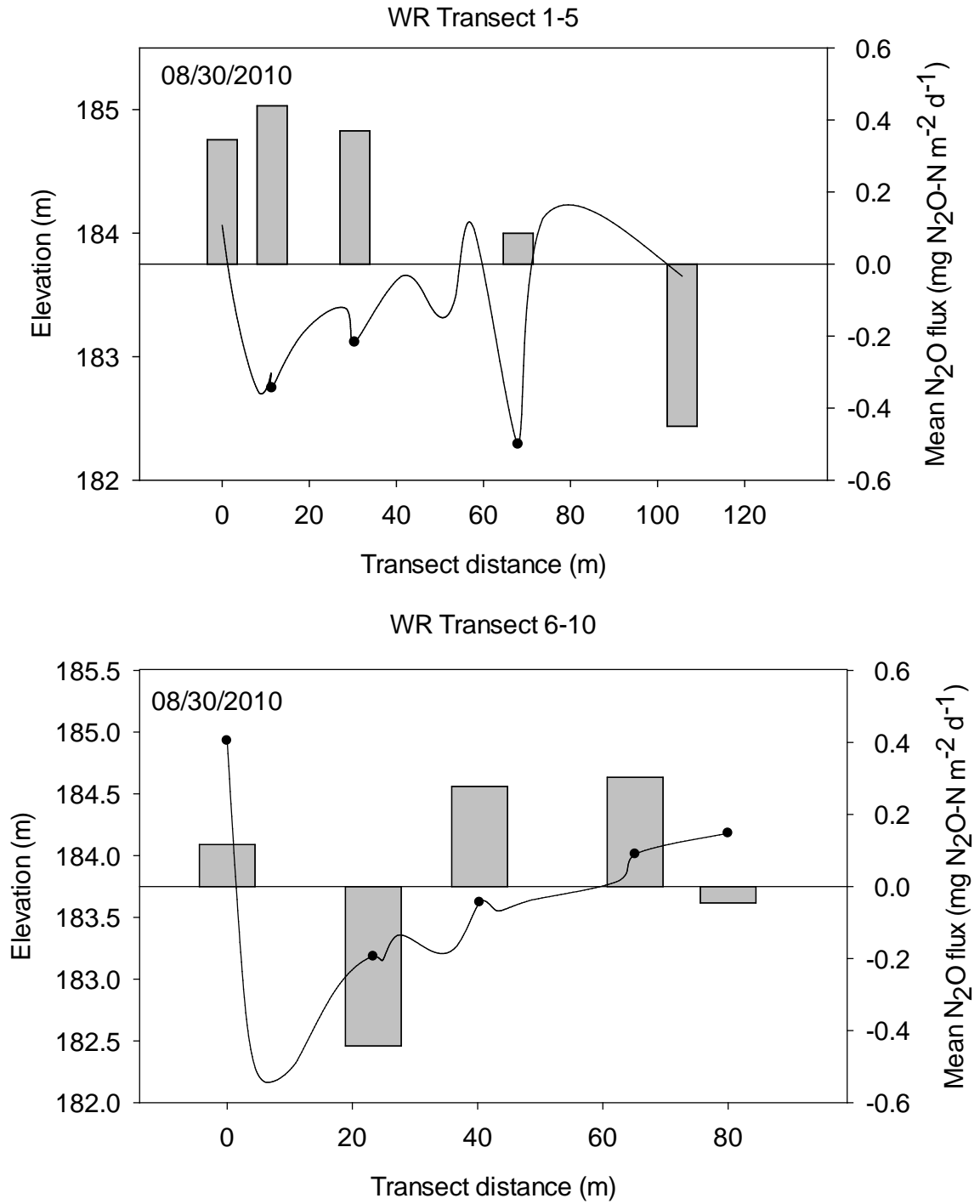
Fig. 18. Relative elevation of ground surface and N_2O fluxes across the WR riparian buffer during a late summer dry period.
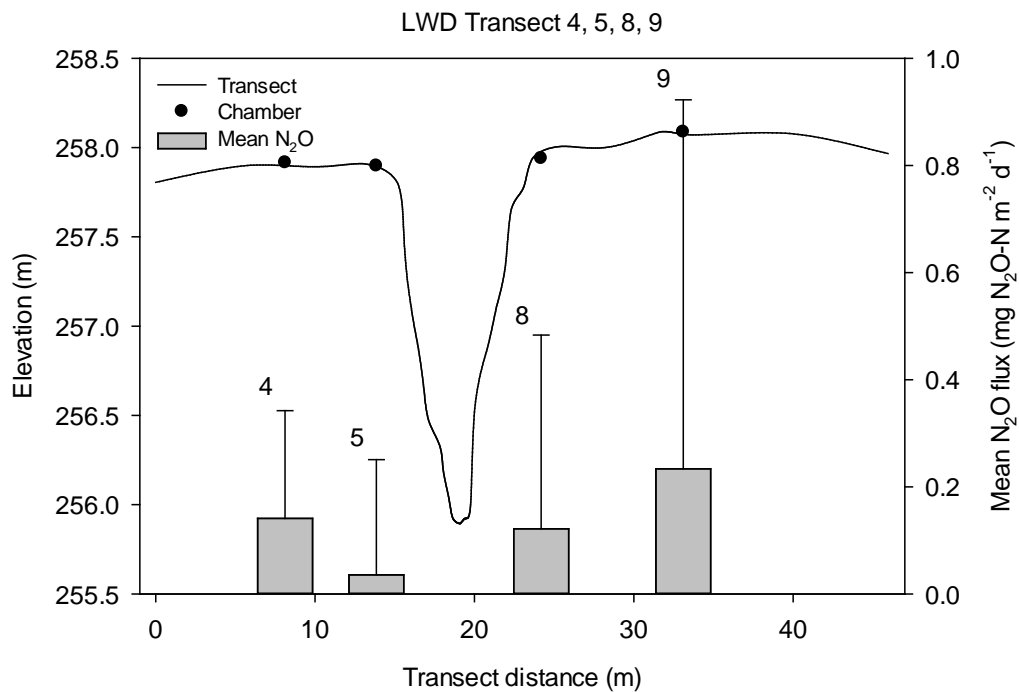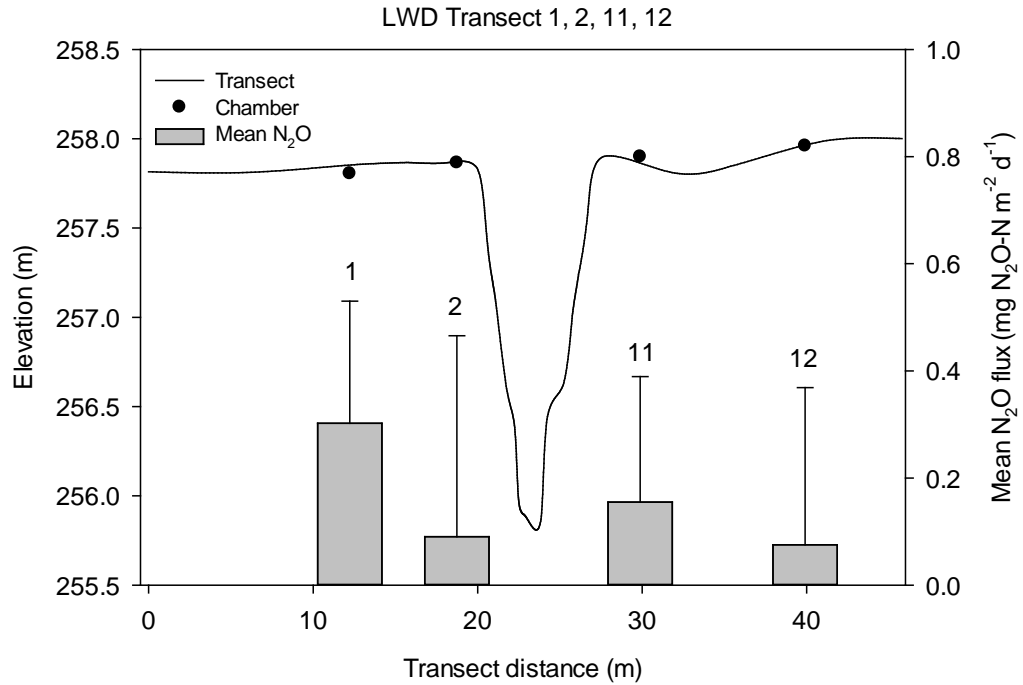
Fig. 19. Relative elevation of ground surface along transects of sampling points at the LWD riparian buffer. Static chamber location and number is indicated by the filled circles. The large central trough in each transect represents the ditch. Vertical exaggeration is 0.0478.

DISCUSSION

Riparian landscapes are characterized by dynamic water tables and, depending on landscape features, are periodically affected by flood events. In the US Midwest, riparian ecosystems can potentially receive significant amounts of mineral N from surrounding crop fields, and thus could be strong sources of N_2O in agricultural watersheds. This study, conducted in the White River watershed in Indiana, was initiated with the expectation that soil conditions would be more favorable to denitrification, and consequently N_2O fluxes would be larger in riparian buffers than in adjacent agricultural fields. The study also aimed to identify the factors controlling N_2O emission in these ecosystems. Results showed significant interactions between land-use (riparian buffer vs. crop field), geomorphology and climatic events on N_2O emission.

Land-use effects on N_2O emissions

To be considered a threat to air quality despite their water quality values, riparian buffers would have to exhibit significantly greater N_2O emission intensity in comparison to adjacent crop fields. Previous studies have reported mean daily N_2O emission from riparian zones ranging between -0.85 to 11.56 mg N_2O-N m^{-2} d^{-1} across various types of land-use and landscapes (Hefting et al., 2003; Dhondt et al., 2004; Kim et al., 2009; Jacinthe et al., 2012). Mean riparian N_2O fluxes measured in this study ranged between 0.002 and 6.26 mg N_2O-N m^{-2} d^{-1} at WR, and from -0.04 and 0.98 mg N_2O-N m^{-2} d^{-1} at LWD (Table 3). In the adjacent crop fields, N_2O fluxes ranged from -0.004 to 10.63 mg N_2O-N m^{-2} d^{-1} at WR and -0.42 to 7.26 mg N_2O-N m^{-2} d^{-1} at LWD. These values are not atypical of what has been previously reported (range: 0.40 - 4.60 mg N_2O-N m^{-2} d^{-1}) for

corn, soybean and wheat fields (Ambus and Christensen, 1995; Hernandez-Ramirez et al., 2009; Kim et al., 2009). This comparison indicates that, at WR, the riparian zone has the potential to emit N_2O at the same level as cultivated fields. Because frequently-flooded and chronically nitrate-loaded riparian areas similar to the WR buffers can emit N_2O at a level similar to adjacent croplands, one may justifiably be concerned about the air quality impact of riparian buffers as these buffers continue to be restored and installed next to streams and rivers. That would not be the case, however, for riparian buffers similar to the one investigated at LWD.

This study showed that, on average, the crop fields were higher emitters of N_2O than the riparian buffers (Table 4); however, the WR riparian buffer exhibited significantly higher N_2O emissions than the adjacent crop field after flooding events (Fig. 3). Kim et al. (2009) reported similar results in a comparison of cropland and riparian sites in Iowa. This is a surprising result given that soil properties (SOC, DOC, microbial biomass and denitrification potential) known to be favorable to N_2O production were higher in the riparian soils. Greater N_2O emission from the cultivated field at LWD was likely the result of high N availability due to mineral N-fertilizer application as indicated by the N_2O emission peak observed following spring N-fertilization in preparation for the corn crop. This observation is in accord with several past studies (Ambus and Christensen, 1995; Jacinthe and Dick, 1997; Skiba and Smith, 1999; Hernandez-Ramirez et al., 2009) that have reported enhancements in N_2O emission following N fertilizer application to corn. Studies have also shown that up to 80 % of the annual N_2O emission can occur during that short time period (Jacinthe and Dick, 1997; Dunesbury et al. 2008;

57

Hernandez-Ramirez et al., 2009). In the present study, 51% of annual emission occurred within the weeks immediately following N application.

In this study, spring fertilizer application may have also indirectly affected N_2O production in the riparian buffers. The data collected at the WR site in spring/summer 2010 support that interpretation. The timing of N_2O peak at the WR riparian buffers relative to that in the crop field suggests a possible downslope migration of fertilizer-N from the crop field to the riparian buffer. Following N application, N_2O emission was nearly 25 times higher in the crop field than in the riparian buffer on May 20, 2010 (Fig. 5). However, a few weeks later (July 1, 2010; Fig. 5), and during which the riparian buffer experienced extensive flooding (Fig. 5), a reversal in N_2O emission intensity by land-use was observed. On that sampling occasion, N_2O emission was 3 times higher in the riparian buffer than in the crop field. This temporal trend was likely due to the export of mineral N, either via runoff or subsurface leaching, from the crop field into the riparian zone. It should be noted that, besides the adjacent crop field, increased mineral N-availability in the riparian buffer during that period may have also been associated with the deposition of nutrients by flood waters from the White River.

Seasonal variability of N_2O emission

In this study, strong seasonality in N_2O emission was noted under both types of land-use. In the riparian buffers, seasonal variation in emission was driven by flood events and wet soil conditions. In the cultivated fields, the data suggest a marked effect of freeze-thaw phenomena. The effect of soil moisture on N_2O emission from riparian zone has been reported in previous studies (Dhondt et al., 2004; Ambus, 1998; Wagner-

Riddle et al., 1996; McLain and Martens, 2006; Kim et al., 2009; Jacinthe et al. 2012). In general, N_2O emission was much lower in semi-arid Arizona riparian buffer (0.1 to 1.21 mg N_2O-N m^{-2} d^{-1}; McLain and Martens, 2006) than reported in recent studies from the Midwest (Kim et al., 2009; Jacinthe et al., 2012) reflecting the effect of precipitation. These studies suggest that the wet spring and summer months that are characteristic of the US Midwest (humid continental climate) could yield higher N_2O emissions from riparian ecosystems. Jacinthe et al. (2012) found that frequently-flooded riparian zones in south-central Indiana emitted significantly higher amounts of N_2O than buffers that are occasionally-flooded. Post-flood emission up to 81 mg N_2O-N m^{-2} d^{-1} was reported (Jacinthe et al., 2012)-a level of emission three times the highest N_2O peak measured at WR after 3 weeks of sustained flooding. Since the floods investigated were short-lived and soils at their study sites were well-drained, these authors (Jacinthe et al., 2012) speculated that these conditions favor the onset of denitrification (short residence time of N_2O in coarse-textured soil) but not the conversion of N_2O to N_2. As a result, N_2O emission was extremely enhanced. This line of reasoning would suggest that N_2O emission will progressively decrease with longer flood duration. It is also consistent with the relatively lower post-flood N_2O emission observed in the present study. Thus, the true N_2O emission peaks associated with the spring 2010 flood event may have been missed.

Nitrous oxide emission peaks were also found to be significant at both LWD and WR during spring-thaw. In Central Iowa riparian buffers, Kim et al. (2009) estimated that freeze-thaw events contributed 70 % of annual emission (wet periods accounting for only 11% of annual N_2O emission). During the February 2011 spring thaw at the WR site,

59

N_2O emission from the riparian forest was more than 10 times higher than in the adjacent crop field (Fig. 6). On that sampling date, it was observed that soil in the cultivated field was still frozen (at least 3 cm below surface) while the riparian soil was completely thawed. The earlier thaw of the riparian forest may be due to ground insulation by dead plant residues preventing substantial soil freezing in the forested buffer (McKinney, 1929; Pikul et al., 1986). Ground insulation in the crop field is likely to be insignificant due to crop residue incorporation during fall tillage. At the LWD site, however, N_2O emission induced by spring-thaw was detected, not in the riparian zone, but in the crop field. It should be noted that, at LWD, the surface soil layer was completely thawed in both the riparian zone and the crop field at the time of sampling (approximately 2.5 °C; Fig. 3). Therefore, the LWD sampling schedule may have only captured the tail end of the freeze-thaw event. This seems likely because sampling at LWD occurred later than at WR and the ground, therefore, may have had more time to thaw. Further, in contrast to the WR site where the riparian forest shadow may have retarded soil thawing in the cultivated field (northeast of forested buffer), the LWD site may have received more solar radiation due to its orientation and the absence of a forest cover.

Vigorous N_2O bursts during freeze-thaw cycles have been reported in previous studies (Goodroad and Keeney, 1984; Cates and Keeney, 1987; Christensen and Teidje, 1990; Burton and Beauchamp, 1994; Jacinthe and Lal, 2003). Müller et al. (2002) found that thawing contributed more than 70 % of the total annual N_2O loss from grassland soils in Germany. Kaiser et al. (1998) found that N_2O peaks during freeze-thaw accounted for 50 % of annual N_2O emission from arable lands, and attributed these results, not to rising soil temperatures, but to increased mineralization of the biomass of

microbes killed by sub-freezing temperatures. Furthermore, Wagner-Riddle et al. (2007) found that, in general, soils that are not well insulated by snow and plant residues exhibits higher N_2O peaks during soil thaw. These past studies indicate that seasonal thaw events can be hot moments of N_2O emission in a variety of terrestrial ecosystems. However, emission associated with these events may have not been fully captured by the bi-weekly sampling schedule adopted in the present study. Future investigations should take note of this limitation.

Effects of geomorphology and drainage on N_2O emission

Because soil type and landscape attributes are different at the WR and LWD sites, it was expected that these differences would be reflected in soil properties and N_2O fluxes. For the most part, biochemical soil properties showed differences due to land-use, but limited effect of site on these parameters was detected (Table 4). The pattern and magnitude of N_2O flux at the study sites was found to be primarily dictated by landscape variability and geomorphology at each site. Flooding frequency, as controlled by landscape morphology and human modifications of stream channel, plays a dominant role in determining the difference in N_2O flux between the riparian buffers at WR and LWD. As mentioned earlier, Jacinthe et al. (2012) reported a relationship between flood frequency and N_2O emission intensity - compared to rarely-flooded buffers, riparian forests most susceptible to flooding were larger N_2O emitters, both during flood and non-flood periods. During the present study (2009-2011), the riparian zone at WR experienced intense flooding (as high as 2-4 m above ground) during the spring and early

61

summer months. In contrast, water level at LWD always remained below bank full

during these times, and consequently this riparian buffer was not subject to flood events.

Furthermore, the present study also demonstrates an indirect effect of flooding on

N_2O emission through increased heterogeneity of riparian landscapes. Located on the

inside bend of a meander of the White River, the WR riparian landscape has been

sculpted by the migrating river. The riparian landscape is characterized by a series of

ridges and swales. Depressions (swales) within the site tended to be associated with the

highest N_2O emission rates measured during the study (Fig. 12). Vilain et al. (2010)

investigated the effect of slope position on N_2O emission, and found that toe-slope

positions produced 4-5 times more N_2O annually than side-slope. This trend was linked,

not to the availability of substrates, but primarily to increased water-filled pore space

(Vilain et al., 2010). Ambus and Christensen (1995) also observed higher N_2O emission

from low-lying areas than from upper landscape positions. It was evident in this study

that the depressions were N_2O emission hotspots during floods and may have skewed the

overall mean riparian N_2O fluxes at WR (Fig. 15). Because the LWD riparian buffer was

not affected by flooding and the landscape was fairly uniform, this help explained the

substantially lower (4-5 times lower) riparian emission at LWD compared to WR.

Besides a lack of topographical heterogeneity, the LWD site is located in a tile-

drained landscape. Although nitrate export from croplands may be substantial (David et

al., 1997), most of this nitrate is probably transported through underground tile drains and

may completely bypass the riparian buffer on its way to drainage ditches (Vought et al.,

1994). Thus, in tile-drained riparian buffers such as LWD, lower N_2O emission can be

attributed to low mineral N availability and limited interaction of NO_3-containing water with the riparian buffer due to tile drainage.

Implications of the study

This study attempted to identify the environmental, soil and landscape characteristics that drive field-scale N_2O emissions in riparian zones. Results have elucidated the effects of season and geomorphology on N_2O emission from riparian zones in agricultural landscapes. In the literature, N_2O fluxes are reportedly controlled primarily by soil moisture, nitrate availability and soil temperature (Skiba et al., 1998; Van Cleemput, 1998; Heincke and Kaupenjohann, 1999). While these factors are widely accepted as controlling variables of denitrification, it remains difficult to understand how these factors combine in the environment and how these combinations translate into variable N_2O emission intensity (Hefting et al., 2003). Further, because of the differences in physical characteristics between the riparian zones investigated, it is also unclear as to which factor is the most important controller of N_2O emission. While several factors may have played a role, the study results suggest a clear effect of season within this hierarchy of factors controlling N_2O emission.

Results of the study have also identified hydrogeomorphology as a determining driver of the magnitude and variability of N_2O emission from these buffers. Biological and chemical soil properties played weaker supporting roles. Since hydro-geomorphological characteristics (flooding, drainage, topography and soil types) are accessible in public databases (U.S. Geological Survey, USDA Natural Resource Conservation Service, USDA Soil Conservation Service), an implication of this research

is that regional N_2O emission from agricultural riparian buffers in the US Midwest can be modeled and estimated using these landscape parameters. These databases could provide the landscape parameters needed to generate watershed- and regional-scale N_2O emission budgets for riparian areas of the US Midwest by extrapolating emission rates to riparian buffers where landscape attributes have been characterized. Additionally, as we begin to better under why some buffers are seasonal hotspots of N_2O emission, it might possible to incorporate this knowledge into the design and restoration of buffers that favor a more complete denitrification (termination in N_2) on intercepted nitrate.

This study results suggests that application of the IPCC (2007) methodology to agricultural riparian zones in the US Midwest would result in underestimation of N_2O emission. According to the "indirect" N_2O emission factors proposed by the IPCC (2007), between 0.005 and 2 % of fertilizer N applied to cropland could result in N_2O emission in adjacent riparian buffers. Based on these factors and the application of 121.5 kg N ha^{-1} yr^{-1} N to the crop fields during the present study, emission from for riparian zones should be in the range of 0.002-0.78 kg N yr^{-1}. While the IPCC method marginally estimates (based on upper range estimations) N_2O emission from the LWD buffer (0.93 kg N_2O-N ha^{-1}, Table 3), annual emission measured at the WR riparian buffer (3.62 kg N_2O-N ha^{-1}, Table 3) was severely underestimated. However, when applied to the crop fields, the IPCC methodology suggests N_2O emission in the range of 8.12-9.16 kg N yr^{-1}. These estimates are reasonable and represent very well the N_2O emission measured at the WR and LWD crop fields (7.82 and 6.37 kg N_2O-N yr^{-1}, respectively). It is likely that the IPCC methodology to estimate emissions from crop fields is more robust, probably because it is based on a more comprehensive literature and research data. This reasoning

would also suggest that more empirical data is required to build a better model for estimating N_2O emissions from agricultural riparian buffers. The work presented in this thesis is a step toward that goal. The currently proposed indirect emission factors (IPCC, 2007) do not take into account landscape features. As this study results have clearly demonstrated, successful modeling attempts of N_2O emission in riparian buffers must incorporate hydrology and geomorphology, and modifications of these attributes by human intervention (tile drainage, channelization, dredging).

Limitations of the study

In this study, as with any gas sampling study of similar nature, the accuracy of N_2O emission estimates may have been affected by failure of sampling protocol to fully account for heterogeneity of soil properties and landscape attributes. The addition of more sampling chambers across these landscapes in conjunction with higher sampling frequency would always aid in providing higher resolution data for estimation of landscape scale N_2O emission. Additionally, it would have been useful to have had continuous soil moisture and temperature sensors in the crop fields (although these sensors would have to be removed during regular farming operations). Also, installing monitoring wells coupled with gas sampling chambers in riparian zone would have further elucidated the effects of water table dynamics on N_2O emission in riparian zones in comparison to crop fields. However, for a number of practical constraints, this was not possible.

Flooding events have a highly significant effect on both the temporal variability and the amount of N_2O emitted from riparian buffers. Efforts must be made to better

capture these events in future studies. When sites are not accessible, it might be possible to sample flood waters and derive N_2O emission from measurements of dissolved N_2O concentrations. Likewise, "floating-chambers" can be deployed for direct measurement of N_2O emission from flooded riparian buffers. After the recession of floodwaters, sampling with static chambers can be resumed. The combination of these monitoring approaches would help generate more refined and more temporally-resolved data for a better understanding of N_2O emission dynamics during these hot-moments.

CONCLUSION

Because of their capacity to sustain high rates of denitrification, riparian buffers can be sites of intense of N transformation, and thus could mitigate the export of mineral N from agricultural landscapes. Since this transformation often results in the emission of N_2O, improvement in water quality can have a negative impact on air quality. In contrast to past studies, regression models incorporating soil properties (denitrification potential, organic carbon, C:N, particle size, bulk density, pH) showed limited capacity to predict N_2O emission at the riparian sites included in the present investigation. The present study showed that the likelihood of riparian buffers to become hotspots of N_2O emission depends largely on flooding potential and land-stream linkage. Low-lying riparian areas that were subject to frequent flooding emitted up to 1,700 % more N_2O than non-flooded adjacent areas, especially during the weeks after fertilizer application to crop fields. Considering the limitations noted above, further research is needed to confirm these results and their range of applicability. These studies must include landscapes of similar attributes as well as riparian systems outside of the US Midwest. Ultimately, these efforts will lead to more data, better methodologies, and more robust models to assess the contribution of riparian buffers to N_2O budgets in agricultural watersheds across a range of eco-regions.

APPENDICES

Appendix A. Nitrous oxide flux at White River site (WR).

Site	Date	Chamber ID	N$_2$O flux (mg N$_2$O-N m^{-2} d^{-1})
WR	12/7/2009	1	0.012
WR	12/7/2009	2	0.018
WR	12/7/2009	3	0.021
WR	12/7/2009	4	-0.009
WR	12/7/2009	5	0.000
WR	12/7/2009	6	0.065
WR	12/7/2009	7	0.047
WR	12/7/2009	8	0.012
WR	12/7/2009	9	0.049
WR	12/7/2009	10	0.033
WR	1/21/2010	1	1.212
WR	1/21/2010	2	1.570
WR	1/21/2010	3	1.129
WR	1/21/2010	4	0.949
WR	1/21/2010	5	1.218
WR	1/21/2010	6	-0.158
WR	1/21/2010	7	0.516
WR	1/21/2010	8	0.243
WR	1/21/2010	9	0.320
WR	1/21/2010	10	0.348
WR	1/21/2010	11	0.959
WR	1/21/2010	12	-1.022
WR	1/21/2010	13	-0.004
WR	1/21/2010	14	0.256
WR	3/4/2010	1	-0.072
WR	3/4/2010	2	0.078
WR	3/4/2010	3	-0.143
WR	3/4/2010	4	-0.200
WR	3/4/2010	5	0.194
WR	3/4/2010	6	-0.326
WR	3/4/2010	7	0.542
WR	3/4/2010	8	0.207
WR	3/4/2010	9	0.388
WR	3/4/2010	10	0.280
WR	3/4/2010	11	0.132
WR	3/4/2010	12	0.004
WR	3/4/2010	13	0.292
WR	3/4/2010	14	-0.002

WR	4/1/2010	1	-0.003
WR	4/1/2010	2	0.009
WR	4/1/2010	3	0.039
WR	4/1/2010	5	0.012
WR	4/1/2010	6	0.021
WR	4/1/2010	7	0.021
WR	4/1/2010	8	-0.096
WR	4/1/2010	9	0.004
WR	4/1/2010	10	0.017
WR	4/16/2010	1	0.188
WR	4/16/2010	2	0.041
WR	4/16/2010	3	0.041
WR	4/16/2010	4	0.164
WR	4/16/2010	5	0.423
WR	4/16/2010	6	0.290
WR	4/16/2010	7	0.127
WR	4/16/2010	8	0.416
WR	4/16/2010	9	0.011
WR	4/16/2010	10	-0.311
WR	5/20/2010	1	1.598
WR	5/20/2010	2	0.914
WR	5/20/2010	3	0.153
WR	5/20/2010	4	-0.808
WR	5/20/2010	5	0.607
WR	5/20/2010	6	0.512
WR	5/20/2010	7	0.462
WR	5/20/2010	8	0.820
WR	5/20/2010	9	0.311
WR	5/20/2010	10	0.286
WR	5/20/2010	11	15.824
WR	5/20/2010	12	0.791
WR	5/20/2010	13	26.118
WR	5/20/2010	14	3.099
WR	5/20/2010	15	7.337
WR	7/1/2010	1	1.502
WR	7/1/2010	2	25.518
WR	7/1/2010	3	1.443
WR	7/1/2010	4	27.839
WR	7/1/2010	5	1.244
WR	7/1/2010	6	-0.536
WR	7/1/2010	7	0.606
WR	7/1/2010	8	2.112
WR	7/1/2010	9	2.778
WR	7/1/2010	10	0.078
WR	7/1/2010	11	5.512

WR	7/1/2010	13	1.528
WR	7/1/2010	15	1.486
WR	7/29/2010	1	0.477
WR	7/29/2010	2	0.133
WR	7/29/2010	3	0.694
WR	7/29/2010	4	0.098
WR	7/29/2010	5	0.022
WR	7/29/2010	6	-0.671
WR	7/29/2010	7	0.008
WR	7/29/2010	8	0.330
WR	7/29/2010	9	0.477
WR	7/29/2010	10	0.144
WR	7/29/2010	11	-1.134
WR	7/29/2010	14	0.513
WR	7/29/2010	15	0.781
WR	8/30/2010	1	0.345
WR	8/30/2010	2	0.439
WR	8/30/2010	3	0.370
WR	8/30/2010	4	0.085
WR	8/30/2010	5	-0.451
WR	8/30/2010	6	0.116
WR	8/30/2010	7	-0.443
WR	8/30/2010	8	0.278
WR	8/30/2010	9	0.303
WR	8/30/2010	10	-0.045
WR	8/30/2010	11	1.160
WR	8/30/2010	13	1.397
WR	8/30/2010	14	0.056
WR	8/30/2010	15	0.420
WR	9/12/2010	1	-0.293
WR	9/12/2010	2	0.147
WR	9/12/2010	3	0.096
WR	9/12/2010	4	0.035
WR	9/12/2010	5	0.186
WR	9/12/2010	6	0.431
WR	9/12/2010	7	0.461
WR	9/12/2010	8	-0.339
WR	9/12/2010	9	0.247
WR	9/12/2010	10	-0.253
WR	9/12/2010	11	0.590
WR	9/12/2010	12	0.966
WR	9/12/2010	13	0.567
WR	9/12/2010	14	0.124
WR	9/12/2010	15	0.186
WR	10/15/2010	1	0.425

WR	10/15/2010	2	0.045
WR	10/15/2010	3	-0.245
WR	10/15/2010	4	0.055
WR	10/15/2010	5	1.036
WR	10/15/2010	6	0.126
WR	10/15/2010	7	-0.141
WR	10/15/2010	8	-0.063
WR	10/15/2010	9	-0.065
WR	10/15/2010	10	-0.060
WR	10/29/2010	1	0.601
WR	10/29/2010	2	0.008
WR	10/29/2010	4	-0.024
WR	10/29/2010	5	0.400
WR	10/29/2010	6	0.250
WR	10/29/2010	7	0.402
WR	10/29/2010	8	0.579
WR	10/29/2010	9	0.634
WR	10/29/2010	10	0.530
WR	10/29/2010	11	1.301
WR	10/29/2010	12	1.506
WR	10/29/2010	13	0.913
WR	10/29/2010	14	0.751
WR	10/29/2010	15	0.119
WR	11/19/2010	1	1.035
WR	11/19/2010	2	0.099
WR	11/19/2010	3	0.222
WR	11/19/2010	4	0.119
WR	11/19/2010	5	0.274
WR	11/19/2010	6	-0.153
WR	11/19/2010	7	0.360
WR	11/19/2010	8	0.166
WR	11/19/2010	9	0.083
WR	11/19/2010	10	-0.094
WR	11/19/2010	11	0.156
WR	11/19/2010	14	0.299
WR	11/19/2010	15	-0.004
WR	12/17/2010	1	0.092
WR	12/17/2010	2	-0.131
WR	12/17/2010	3	0.025
WR	12/17/2010	4	0.633
WR	12/17/2010	5	-0.036
WR	12/17/2010	6	-0.005
WR	12/17/2010	7	0.063
WR	12/17/2010	8	-0.031
WR	12/17/2010	9	0.109

WR	12/17/2010	10	-0.182
WR	12/17/2010	11	0.069
WR	12/17/2010	14	-0.244
WR	12/17/2010	15	0.161
WR	2/16/2011	1	0.321
WR	2/16/2011	2	0.367
WR	2/16/2011	3	1.124
WR	2/16/2011	4	1.430
WR	2/16/2011	5	3.869
WR	2/16/2011	6	1.518
WR	2/16/2011	7	1.973
WR	2/16/2011	8	12.695
WR	2/16/2011	9	1.526
WR	2/16/2011	10	1.450
WR	2/16/2011	11	0.471
WR	2/16/2011	12	0.208
WR	2/16/2011	13	0.346
WR	2/16/2011	14	0.102
WR	2/16/2011	15	0.073
WR	3/24/2011	1	0.253
WR	3/24/2011	2	-0.071
WR	3/24/2011	3	0.780
WR	3/24/2011	4	0.476
WR	3/24/2011	5	0.079
WR	3/24/2011	6	0.075
WR	3/24/2011	7	-0.129
WR	3/24/2011	8	-0.100
WR	3/24/2011	9	0.089
WR	3/24/2011	10	0.203
WR	3/24/2011	11	0.082
WR	3/24/2011	12	0.886
WR	3/24/2011	13	0.682
WR	3/24/2011	14	0.498
WR	3/24/2011	15	0.029
WR	4/12/2011	1	0.272
WR	4/12/2011	2	-0.101
WR	4/12/2011	3	-0.019
WR	4/12/2011	4	0.085
WR	4/12/2011	5	0.135
WR	4/12/2011	6	0.107
WR	4/12/2011	7	0.009
WR	4/12/2011	8	0.042
WR	4/12/2011	9	0.173
WR	4/12/2011	10	0.516
WR	4/12/2011	11	-0.058

WR	4/12/2011	12	0.166
WR	4/12/2011	13	0.230
WR	4/12/2011	14	0.141
WR	4/12/2011	15	0.066

Appendix B. Nitrous oxide flux at Leary Weber Ditch site (LWD).

Site	Date	Chamber ID	N$_2$O flux (mg N$_2$O-N m^{-2} d^{-1})
LWD	12/2/2009	1	0.054
LWD	12/2/2009	2	0.074
LWD	12/2/2009	4	0.034
LWD	12/2/2009	5	-0.003
LWD	12/2/2009	8	0.004
LWD	12/2/2009	9	0.155
LWD	12/2/2009	11	0.017
LWD	12/2/2009	12	-0.036
LWD	12/2/2009	13	-0.005
LWD	12/2/2009	14	0.041
LWD	1/13/2010	1	0.327
LWD	1/13/2010	2	0.082
LWD	1/13/2010	4	0.106
LWD	1/13/2010	5	0.455
LWD	1/13/2010	8	-0.032
LWD	1/13/2010	9	0.760
LWD	1/13/2010	11	0.199
LWD	1/13/2010	12	-0.696
LWD	1/13/2010	13	0.162
LWD	1/13/2010	14	0.108
LWD	3/5/2010	1	0.144
LWD	3/5/2010	2	-0.131
LWD	3/5/2010	4	0.070
LWD	3/5/2010	5	0.202
LWD	3/5/2010	8	-0.043
LWD	3/5/2010	9	0.254
LWD	3/5/2010	11	0.286
LWD	3/5/2010	12	0.329
LWD	3/5/2010	13	-0.251
LWD	3/5/2010	14	0.125
LWD	3/26/2010	1	0.039
LWD	3/26/2010	2	-0.005
LWD	3/26/2010	4	0.005
LWD	3/26/2010	5	0.019
LWD	3/26/2010	8	-0.006
LWD	3/26/2010	9	0.004
LWD	3/26/2010	11	-0.042
LWD	3/26/2010	12	-0.045
LWD	3/26/2010	13	0.003
LWD	3/26/2010	14	0.006

LWD	4/14/2010	1	-0.025
LWD	4/14/2010	2	0.017
LWD	4/14/2010	4	0.004
LWD	4/14/2010	5	-0.030
LWD	4/14/2010	8	-0.019
LWD	4/14/2010	9	-0.155
LWD	4/14/2010	11	0.072
LWD	4/14/2010	12	0.007
LWD	4/14/2010	13	0.047
LWD	4/14/2010	14	-0.386
LWD	5/3/2010	1	0.811
LWD	5/3/2010	2	0.249
LWD	5/3/2010	4	0.035
LWD	5/3/2010	5	0.012
LWD	5/3/2010	8	0.387
LWD	5/3/2010	9	0.083
LWD	5/3/2010	11	0.094
LWD	5/3/2010	12	0.477
LWD	5/3/2010	13	0.440
LWD	5/3/2010	14	0.339
LWD	5/28/2010	1	0.549
LWD	5/28/2010	2	0.587
LWD	5/28/2010	4	0.182
LWD	5/28/2010	5	0.421
LWD	5/28/2010	8	-0.133
LWD	5/28/2010	9	0.342
LWD	5/28/2010	11	0.522
LWD	5/28/2010	12	0.574
LWD	5/28/2010	13	0.373
LWD	5/28/2010	14	3.211
LWD	5/28/2010	15	2.881
LWD	5/28/2010	16	2.361
LWD	5/28/2010	17	5.255
LWD	5/28/2010	18	3.838
LWD	6/28/2010	1	0.243
LWD	6/28/2010	2	0.867
LWD	6/28/2010	4	0.747
LWD	6/28/2010	5	-0.469
LWD	6/28/2010	8	1.140
LWD	6/28/2010	9	1.319
LWD	6/28/2010	11	0.782
LWD	6/28/2010	12	0.073
LWD	6/28/2010	13	-0.226
LWD	6/28/2010	14	5.302
LWD	6/28/2010	15	3.482

LWD	6/28/2010	16	1.989
LWD	6/28/2010	17	2.561
LWD	6/28/2010	18	0.715
LWD	8/6/2010	1	0.289
LWD	8/6/2010	2	0.204
LWD	8/6/2010	4	0.334
LWD	8/6/2010	5	0.141
LWD	8/6/2010	8	0.283
LWD	8/6/2010	9	0.315
LWD	8/6/2010	11	0.300
LWD	8/6/2010	12	0.188
LWD	8/6/2010	13	0.115
LWD	8/6/2010	14	0.299
LWD	8/6/2010	15	0.275
LWD	8/6/2010	16	0.412
LWD	8/6/2010	17	0.432
LWD	8/6/2010	18	0.139
LWD	8/25/2010	1	0.200
LWD	8/25/2010	2	0.207
LWD	8/25/2010	4	0.344
LWD	8/25/2010	5	0.139
LWD	8/25/2010	8	-0.345
LWD	8/25/2010	9	0.292
LWD	8/25/2010	11	0.233
LWD	8/25/2010	12	0.029
LWD	8/25/2010	13	-0.105
LWD	8/25/2010	14	0.237
LWD	8/25/2010	15	-0.565
LWD	8/25/2010	16	0.252
LWD	8/25/2010	17	0.369
LWD	8/25/2010	18	0.413
LWD	9/22/2010	1	0.537
LWD	9/22/2010	2	0.091
LWD	9/22/2010	4	0.183
LWD	9/22/2010	5	0.016
LWD	9/22/2010	8	-0.059
LWD	9/22/2010	9	0.230
LWD	9/22/2010	11	0.152
LWD	9/22/2010	12	0.415
LWD	9/22/2010	13	0.144
LWD	9/22/2010	14	0.140
LWD	9/22/2010	15	-0.056
LWD	9/22/2010	16	0.173
LWD	9/22/2010	17	-0.058
LWD	9/22/2010	18	0.054

LWD	10/28/2010	1	0.308
LWD	10/28/2010	2	0.284
LWD	10/28/2010	4	0.161
LWD	10/28/2010	5	0.175
LWD	10/28/2010	8	-0.257
LWD	10/28/2010	9	0.028
LWD	10/28/2010	11	0.268
LWD	10/28/2010	12	0.141
LWD	10/28/2010	13	-0.183
LWD	10/28/2010	14	-0.059
LWD	10/28/2010	15	0.158
LWD	10/28/2010	16	0.153
LWD	10/28/2010	17	0.294
LWD	10/28/2010	18	0.100
LWD	11/17/2010	1	0.100
LWD	11/17/2010	2	0.128
LWD	11/17/2010	4	0.018
LWD	11/17/2010	5	-0.155
LWD	11/17/2010	8	0.147
LWD	11/17/2010	9	0.325
LWD	11/17/2010	11	-0.059
LWD	11/17/2010	12	0.191
LWD	11/17/2010	13	0.203
LWD	11/17/2010	14	-0.009
LWD	11/17/2010	15	-0.102
LWD	11/17/2010	16	0.059
LWD	11/17/2010	17	0.132
LWD	11/17/2010	18	0.071
LWD	2/18/2011	1	0.587
LWD	2/18/2011	2	-0.215
LWD	2/18/2011	4	0.163
LWD	2/18/2011	5	-0.037
LWD	2/18/2011	8	0.113
LWD	2/18/2011	9	1.552
LWD	2/18/2011	11	-0.046
LWD	2/18/2011	12	0.042
LWD	2/18/2011	13	0.085
LWD	2/18/2011	14	-0.215
LWD	2/18/2011	15	10.947
LWD	2/18/2011	16	6.923
LWD	2/18/2011	17	6.742
LWD	2/18/2011	18	4.451
LWD	3/29/2011	1	0.314
LWD	3/29/2011	2	-0.895
LWD	3/29/2011	4	0.016

LWD	3/29/2011	5	-0.110
LWD	3/29/2011	8	0.653
LWD	3/29/2011	9	-1.654
LWD	3/29/2011	11	-0.112
LWD	3/29/2011	12	-0.244
LWD	3/29/2011	13	0.704
LWD	3/29/2011	14	0.949
LWD	3/29/2011	15	-1.342
LWD	3/29/2011	16	0.224
LWD	3/29/2011	17	-0.154
LWD	3/29/2011	18	-0.435
LWD	4/21/2011	1	0.135
LWD	4/21/2011	2	-0.050
LWD	4/21/2011	4	-0.035
LWD	4/21/2011	5	-0.025
LWD	4/21/2011	8	0.050
LWD	4/21/2011	9	0.011
LWD	4/21/2011	11	0.101
LWD	4/21/2011	12	0.021
LWD	4/21/2011	13	0.126
LWD	4/21/2011	14	-0.069
LWD	4/21/2011	15	1.450
LWD	4/21/2011	16	0.562
LWD	4/21/2011	17	3.395
LWD	4/21/2011	18	1.997
LWD	5/11/2011	1	0.365
LWD	5/11/2011	2	-0.176
LWD	5/11/2011	4	-0.043
LWD	5/11/2011	5	0.019
LWD	5/11/2011	8	0.017
LWD	5/11/2011	9	0.133
LWD	5/11/2011	11	-0.001
LWD	5/11/2011	12	0.070
LWD	5/11/2011	13	-0.005
LWD	5/11/2011	14	0.074
LWD	5/11/2011	15	0.733
LWD	5/11/2011	17	7.895
LWD	5/11/2011	18	2.983

Appendix C. Soil properties at the White River site (WR).

Chamber	Total N$_2$O (kg N$_2$O-N ha)	Mean N$_2$O flux (mg N$_2$O-N m^{-2} d^{-1})	Bulk density (g cm^{-3})	pH	MBC (mg C kg^{-1} soil)	Net nitrification (mg NO$_3$-N kg^{-1} soil d^{-1})	DEA (mg N$_2$O-N kg^{-1} soil d^{-1})	SOC (mg C kg^{-1} soil)	TC (%)	TN (%)	Clay (%)	Silt (%)	Sand (%)
1	17.93	0.46	1.28	7.20	457.86	0.01	24.88	12.74	3.60	0.24	27.68	28.21	44.11
2	72.95	1.71	0.94	7.32	417.50	0.30	106.64	17.39	3.76	0.22	37.61	25.88	36.51
3	14.30	0.35	1.18	7.22	566.49	0.01	93.99	14.15	3.84	0.21	37.75	28.15	34.10
4	77.62	1.93	1.11	7.32	432.42	0.33	162.54	13.38	3.88	0.23	40.20	31.52	28.28
5	25.25	0.54	1.23	7.39	415.94	0.03	84.41	13.81	3.84	0.23	37.73	15.63	46.64
6	4.39	0.09	1.37	7.52	406.60	0.03	110.77	13.34	3.25	0.21	22.71	30.16	47.13
7	13.73	0.28	1.02	7.31	424.76	0.02	28.03	15.30	3.22	0.22	35.20	36.14	28.66
8	54.06	1.01	1.16	7.26	382.49	0.14	39.85	17.61	3.71	0.24	31.50	34.58	33.92
9	18.16	0.43	1.11	7.40	432.46	0.02	42.08	19.51	3.85	0.23	31.52	28.54	39.94
10	7.13	0.17	1.31	7.32	219.16	0.02	69.43	20.69	3.70	0.21	23.96	24.39	51.65
11	88.19	1.92	1.45	7.43	351.21	0.17	18.99	14.72	3.03	0.18	25.19	22.97	51.84
12	19.95	0.43	1.36	7.47	256.03	0.02	2.49	14.24	2.61	0.19	27.69	20.60	51.71
13	129.11	3.20	1.33	7.52	131.01	0.32	23.14	21.45	2.74	0.20	27.67	23.06	49.27
14	21.21	0.46	1.52	7.48	479.08	0.03	26.58	17.54	2.79	0.18	36.39	26.11	37.50
15	18.36	0.96	1.50	7.33	410.63	0.08	127.04	23.93	3.17	0.21	30.47	23.89	45.64

79

Appendix D. Soil properties at the Leary Weber Ditch site (LWD).

Chamber	Total N$_2$O (kg N$_2$O-N ha)	Mean N$_2$O Emission (mg N$_2$O-N m^{-2} d^{-1})	Bulk density (g cm^{-3})	pH	MBC (mg C kg^{-1} soil)	Net nitrification (mg NO$_3$- kg^{-1} soil d^{-1})	DEA (mg N$_2$O-N kg^{-1} soil d^{-1})	DOC (mg C kg^{-1} soil)	TC (%)	TN (%)	Clay (%)	Silt (%)	Sand (%)
1	11.12	0.30	1.31	7.03	284.47	0.00	88.82	20.18	3.34	0.27	32.65	20.98	46.37
2	3.18	0.09	1.05	7.16	804.94	0.02	101.28	32.87	3.79	0.29	37.68	23.98	38.34
4	5.59	0.14	1.27	7.10	1017.92	0.00	87.30	24.81	4.70	0.29	39.45	21.83	38.72
5	1.39	0.04	1.07	7.22	441.85	0.01	15.00	16.40	4.50	0.28	35.12	21.21	43.67
8	4.94	0.12	1.15	7.09	343.53	0.02	37.51	22.77	3.85	0.27	37.65	18.73	43.62
9	13.79	0.23	1.05	5.79	475.32	0.03	46.91	33.13	3.57	0.28	27.69	26.19	46.12
11	5.16	0.15	0.94	6.99	1372.79	0.01	169.91	33.87	4.03	0.27	36.48	18.46	45.05
12	1.15	0.08	0.85	7.15	891.88	0.01	81.26	24.31	4.82	0.26	30.23	28.97	40.80
13	4.46	0.12	1.24	7.27	931.66	0.01	77.77	21.17	4.81	0.27	32.73	31.64	35.63
14	22.19	0.62	1.04	6.19	669.76	0.06	104.93	27.15	3.75	0.24	31.76	27.14	41.10
15	60.49	1.62	1.40	6.68	496.72	0.12	23.96	12.18	2.31	0.20	35.37	24.05	40.59
16	42.31	1.31	1.33	6.76	157.47	0.05	2.34	10.96	1.62	0.20	32.66	25.86	41.48
17	48.45	2.44	1.34	6.57	173.73	0.04	11.20	13.80	1.55	0.19	32.73	25.69	41.58
18	28.98	1.30	1.30	6.37	130.26	0.03	17.23	16.48	1.54	0.20	27.71	27.91	44.38

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Conference presentations

Baker M., Jacinthe P.A., Vidon P., Panunto M., Fisher K., Liu X. 2012. Hydrogeomorphic classification of riparian ecosystems in Central Indiana. AWRA Specialty Conference, Riparian Ecosystems, June 25-27, 2012, Denver, CO.

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