Investigating influence of nitrogen dynamics and hydroperiod on GHG emissions in Great Lakes coastal wetlands using a simulation model

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Abstract

Wetlands impact global warming by regulating the exchange of greenhouse gases (GHGs), including carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) with the atmosphere. Few studies have investigated the interactive effects of different environmental factors in wetlands, such as water residence time and nutrient inflows, on GHG emissions. Here we investigated GHG emission in Great Lakes coastal wetlands across various hydrology, temperature, and N inflow regimes using a process-based simulation model MONDRIAN. We found the emission of CH_4, N_2O and sequestration of C (i.e. negative net ecosystem exchange, NEE) all increased with increasing water residence time and N inflow in our modeling results, primarily driven by increased plant productivity and N uptake, which indicated greater C and N cycling rates in the model. The summed global warming potential (GWP) (i.e. sum GWP of CH_4, N_2O, and NEE) of wetlands on 20-year and 100-year time horizons were both primarily driven by CH_4 emissions. Under most conditions, NEE reduced by removing atmosphere C in our results, meaning modeled wetlands were net sinks of carbon as wetland plants assimilated atmospheric CO_2 and plant litter became accreted in underlying anaerobic soil. Negative effects of NEE on GWP partially offset the GWP of CH_4 emissions. GWP of N_2O was negligible because the amount of N_2O emitted from these simulated wetlands was very small. Our results suggested that under a wide range of conditions, the summed GWP from Great Lakes coastal wetlands may be strongly controlled by the tradeoffs among CH_4 emission and CO_2 sequestration, both of which were driven by elevated levels of N inflow in our simulations. Water level scenarios also had an effect on GHG exchanges by moderating the transitions between aerobic and anaerobic conditions. Higher temperature promoted higher GWP but under the modest range of temperature increases we simulated, reflecting those expected in this region by midcentury, temperature effects were minimal compared with those of other factors. These results highlight the previously understated role of nutrients in modulating GWP in coastal wetlands and point out the importance of water residence time in wetlands N cycling.

Keywords: global warming, greenhouse gas, wetlands, nitrogen, GWP, methane, C sequestration, water levels

1. Introduction

Global climate warming is one of the most serious environmental problems. It is mostly driven by increasing emissions of greenhouse gases (GHGs) into the atmosphere. Wetlands play a large role in GHG emissions. The magnitude of GHG emissions from wetlands may be affected by climate change and human activities that have impacted coastal wetlands in numerous ways, including changes in hydrology and elevated inflow of nitrogen (IPCC, 2013). Carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) are three key greenhouse gases (hereafter GHG) contributing to the anthropogenic greenhouse effect and global warming (Forster et al., 2007, IPCC, 2013). Emissions of CH_4 and N_2O have more severe impacts than CO_2 because the global warming potentials (GWPs) of equal masses of CH_4 and N_2O are 34 and 298 times greater respectively, than the contribution of CO_2 to global warming over a 100-year time horizon (IPCC, 2013).

Wetlands cover 5–8% of the Earth's land surface and are highly productive, able to store large amounts of carbon (C) in inundated soils and plant tissues that represent 10% of the total terrestrial soil C pool (Davidson & Janssens, 2006; Mitsch & Gosselink, 2007; Mitsch & Gosselink, 2015). Flooded and anaerobic conditions in soils not only increase C storage capacity of wetlands, but also facilitate production of GHGs, including methane (CH_4) through methanogenesis and nitrous oxide (N_2O) through denitrification (Xu et al., 2008). Wetlands are the world's largest natural source of CH_4, contributing about a third (177-284 Tg CH_4 y^{-1}) of the total global CH_4 emissions (500-600 Tg CH_4 y^{-1}) (Dlugokencky et al., 2011; Bridgham et al., 2013; Melton et al., 2013; Kirschke et al., 2013). Wetland ecosystems can also function as either sources or sinks of CO_2 as rates of CO_2 respiration and plant uptake shift under various environmental conditions. For example, changes in flooding regimes or temperature-driven decomposition rates can shift the direction of CO_2 flux in these systems (Scheller et al., 2012).

GHG emissions, including CO_2 generated from respiration, are driven by oxygen availability meaning that wetlands, which experience fluctuating water levels and alternating aerobic and anaerobic soil conditions, may exhibit high variability of GHG emissions. In flooded soils, oxygen availability is restricted to the water column and a thin layer of surface soil. Thus the water level becomes the key factor controlling oxic and anoxic conditions (Dinsmore et al., 2009). Previous studies have demonstrated that lowering the water table increased net CO_2 emissions (Moore & Dalva,1993; Chimner & Cooper, 2003; Blodau et al., 2004, Yang et al., 2013). As the water table lowers, soils become more oxygen rich and soil CO_2 emission can be expected to increase because of accelerated organic matter decomposition (Webster et al., 2013). By determining the extent and frequency with which wetland soil horizons experience aerobic and anaerobic conditions, water level fluctuations may also exert a strong control on methanogenic and methanotrophic processes. Decreases in wetland water level typically result in decreased net methane production (Moore & Dalva,1993, Blodau & Moore, 2003; Dinsmore et al., 2009). Emissions of N_2O are also highly connected with the shift of aerobic and anaerobic conditions as controlled by water level. Lowering the water table depth leads to a net increase in N_2O emissions from wetlands (Aerts & Ludwig, 1997; Dinsmore et al., 2009). Hydrologic pulses influence the oxygen availability of wetlands soils and consequently decomposition and denitrification rates. Water levels that fluctuate seasonally, or on shorter time scales of days to weeks, can shift the presence and depth of soil aerobic and anaerobic zones on seasonal and shorter time scales. Water levels of Great Lakes coastal wetlands change with lake levels in varying degrees and show both constant and fluctuated patterns.

In addition to variable water levels, water residence time also vary by wetlands. Water residence time is important in nitrogen (hereafter N) cycling because if the residence time of the water is very short (meaning the wetland hydrology has a high flushing rate), most of these nutrients may not remain long in the system but be flushed out quickly. However, research on water residence time is limited because it is hard to measure in reality. Longer water residence time and higher N inflow promotes more denitrification and N removal in simulation studies (Sharp et al., *in revision*). In membrane bioreactor experiment, as the hydraulic residence time reduced from 5 to 2.5 days, the percentages of C as CH_4 and N as N_2O gas were significantly decreased (Nuansawan et al., 2016).

Nitrogen inflow is another modulator of wetland GHG emissions, but how important it is and how nitrogen regulates wetland GHG emissions and GWP is still unclear. Many studies have focused on hydrology and nitrogen loading in regard to GHG emissions but the effect of the interactions between water level and nitrogen deposition in wetlands is not completely understood. Nitrogen inflow affects CO_2 flux by increasing plant productivity, improving the chemical quality of litter (lower C/N ratio) and alleviating N constraints on microbial metabolism (Lebauer & Treseder, 2008). N also alters CH_4 emissions through impacts on microbes and plants because nitrate inhibits methanotrophic activity by lowering redox potentials (Le Mer & Roger, 2001; Liu & Greaver, 2009). Nitrogen availability affects wetland plant productivity and plant community composition, which influences CH_4 production, oxidation and transport (Bubier et al., 2007). In addition, N inflow increases N_2O emissions by supplying more available N as materials for nitrifying and denitrifying bacteria (Dalal et al., 2003; Lohila et al., 2010). Temperature significantly influences the decomposition, respiration and microorganisms and bacteria activities for nitrification and denitrification. An increase of N_2O and CO_2 emissions, but not CH_4 emissions were found with increasing temperature (Schaufler et al., 2010). However, methanogenesis is more sensitive to temperature (Inglett et al., 2012). Few studies have investigated the interactive effects of temperature with other environment conditions such as soil moisture (Huang et al., 2016) and nitrate (NO_3^-) (Stadmark & Leonardson, 2007).

Here we investigate the ranges and drivers of GHG emissions in coastal wetlands of the Great Lakes region, USA, across various hydrology, temperature, and N inflow regimes. We used a process-based simulation model of wetland community-ecosystem processes, the MONDRIAN model (Currie et al., 2014; Martina et al., 2016). We formulated and tested the following hypotheses. (1) Greater N inflow should cause greater C sequestration that would function as a trade-off with CH_4 and N_2O emissions. (2) Low water level should increase net CO_2 emissions but decrease CH_4 and N_2O emissions, since CO_2 emissions from organic matter decomposition are greater under aerobic conditions but CH_4 and N_2O production chiefly occur under anaerobic conditions. (3) Greater water residence time should increase all three GHG emissions (for a given level of N inflow and hydrologic fluctuation regime) since this allows more N to be retained in wetlands, promoting greater plant uptake, nitrification, denitrification and N_2O emissions. (4) Higher temperature should accelerate the emissions of CO_2, CH_4 and N_2O because it should increase NPP, thus increasing the size of the detrital pools and higher rates of organic matter decomposition.

2. Methods

2.1 Overview of MONDRIAN model

For this study, we enhanced an existing model of wetland community-ecosystem processes, the MONDRIAN model, to include net emissions of greenhouse gases (GHGs) CO_2, CH_4 and N_2O. MONDRIAN is a process-based simulation model of wetlands that operates on a daily time step and that spans multiple levels of ecological organization, including individual plant physiology, plant population growth and decline, plant community shifts through competition, and dynamics in ecosystem biogeochemistry including complete C and N cycles (Currie et al., 2014). Recent MONDRIAN versions integrate more detailed plant physiology and competition, including clonal branching and light competition (Martina et al., 2016, Goldberg et al., 2017). Nitrogen (N) cycling in MONDRIAN was also recently enhanced by adding nitrification and denitrification (Sharp et al., *in revision*). The model has previously been applied in Great Lakes coastal wetlands. However, the model processes are general enough that it could be used to study inland wetlands and wetlands in other regions.

MONDRIAN is a spatially-explicit, individual-based model, meaning individual plants compete for nutrients, light, and space. Plant growth, population dynamics, and community composition shift in response to environmental drivers, including water level (which can fluctuate daily), temperature, and N inflows. Resource limitation (N and light) together with competition and nutrient-cycling feedbacks result in intrinsic emergent ecosystem properties. At the individual level, MONDRIAN simulates C and N uptake within each plant and available N is competed for among neighboring plants within spatially explicit grid cells, leading to heterogeneous N availability. At the population level, plants reproduce clonally by creating daughter ramets using C and N reserves from connected parent rhizomes. This C and N demand links resource competition among individuals to population dynamics in a heterogeneous environment. Plants also experience mortality which can lead to the loss (and conversion to litter) of individual ramets or whole genets. At the ecosystem level, C and N enter the wetland through photosynthetic capture of C and hydrologic inflow of N that is assimilated in living tissue. C and N enter the litter pools after seasonal tissue senescence or from plant mortality. Decomposition of litter then results in the mineralization of organic C and N to their inorganic forms. Rates of litter decomposition can be significantly slowed under low temperature and anaerobic conditions caused by high water level, defined in MONDRIAN by any portion of soil below a 5-day trailing average of water level (Reddy & Delaune, 2008). Thus, flooding enhances C and N accretion in detritus while slowing the release of both C and N from detrital pools via mineralization. Previous applications of MONDRIAN provide greater detail on C and N cycling in the model, including controls on decomposition, decomposition feedbacks on N mineralization, plant growth and uptake of N, hydrology and anaerobic zonation and their effects on C and N cycling (Currie et al., 2014, Martina et al., 2016, Sharp et al., *in revision*).

As in previous applications of MONDRIAN, we conducted over 1000 model simulations (described below) of a 52.5 × 52.5 cm area consisting of 49 grid cells each 7.5 × 7.5 cm in area. This area contains thousands of individual plants that reproduce and branch belowground spatially and that if they leave the space, wrap to the opposite side, making the topology of the space a torus (Currie et al., 2014).

2.2 Net Ecosystem CO_2 Exchange

We drew on the existing complete ecosystem C balance in the MONDRIAN model to calculate Net Ecosystem Exchange (hereafter NEE) of CO_2-C as a model result. It is equal to the CO_2 emission from heterotrophic respiration minus the CO_2 sink in net photosynthesis, with a positive NEE defined as net emission and negative NEE defined as net C sequestration. The NEE calculation replicates what is measured as NEE of CO_2-C.

2.3 Methane flux simulation sub-model

Several process-based models have been developed to estimate global CH_4 emissions. Each had unique methods for dealing with wetland system complexity and CH_4 flux processes (Cao et al., 1996; Tian et al., 2010; Riley et al., 2011; Zhu et al., 2014; Oikawa et al., 2017; Sitch et al., 2003 & Gerten et al., 2004). They all involved water table level as an essential factor in defining anoxic and oxic soil zones where CH_4 is produced and oxidized, to modulate methane fluxes.

We updated MONDRIAN to include sophisticated CH_4 flux using a modified sub-model from Cao et al. (1996), which separately calculated CH_4 production and consumption in soil. Existing MONDRIAN processes first calculated total heterotrophic C respiration in each soil horizon based on model production and inputs of plant detritus together with user-specified decay constants modified by daily temperature and aerobic or anaerobic conditions in the model. The new sub-model then calculated the rate of CH_4-C production as a proportion, $CH_4CHetProp$, of total heterotrophic C respiration that undergoes methanogenesis to CH_4 (eqn. 1). A user-specified parameter (CH_4P_0) specified this proportion under optimal conditions for methanogenesis, which is then constrained each day by temperature and soil water status (eqns 2-5).

In other wetland modeling studies, values of the proportion CH_4P_0 ranged from 0.1 to 0.3 (Riley et al., 2011; Wania et al., 2010; Zhu et al., 2014). We tested values of 0.1, 0.15, 0.2, 0.3, 0.4 and 0.47 in MONDRIAN during sub-model development using in-field data from 5 sites in North America (Minnesota, Ontario, Alaska, Michigan, California). When CH_4P_0=0.2, we obtained the least square error in testing our results against field measurements from the literature.

$$CH_4CDay = CH_4CHetProp * CHetCell \qquad (1)$$

The annual production of CH_4 was written as (1), Where CH_4CDay is CH_4 production on each day, $CHetCell$ is the total C lost from C pool in one cell in one day (includes CO_2-C and CH_4-C).

$$CH_4CHetProp = CH_4P_0 * f_{WLP} * f_T \qquad (2)$$

$$f_{WLP} = 0.383 * e^{(0.096 * 100 * TAWL)} \qquad (3)$$

$$\begin{cases} f_T = \dfrac{e^{(0.0693 * WT)}}{8} & (WT>0) \\ f_T = 0 & (WT \leq 0) \end{cases} \qquad (4)$$

$$\begin{cases} WT = 3.4+0.785*T_{day}Air & (T_{day}Air > 0) \\ WT = 3.5 & (T_{day}Air \leq 0) \end{cases} \qquad (5)$$

Where f_{WLP} is a function of water level position (cm), representing an index from zero to 1 that lowers CH_4 production based on non-ideal conditions of aerobic related to water level (3). We define *TAWL* (cm) using a trailing average water level of 5 days. Function of temperature (°C) is f_T (eqn. 4), in this equation, *WT* represents water temperature, which is calculated as eqn.5. An index f_T from zero to 1 that lowers CH_4 production based on water temperature with maximum value at 30 °C, and a value of 0.12 at 0 °C (Cao et al., 1996; Dunfield et al., 1993). If water temperature is zero or below, CH_4 production is halted by setting f_T to zero.

$$CH_4CHetProp = CH_4CHetProp^* (1-CH_4Ox) \qquad (6)$$

MONDRIAN did not explicitly simulate fine-scale processes of CH_4 transport by diffusion, ebullition and transport through plant tissues, which were implicitly included in the model scaling parameters for CH_4 production and oxidation. In MONDRIAN, we set 43% of CH_4 oxidized to CO_2 before emitting to the atmosphere when muck is aerobic, (Roslev & King, 1996) and no CH_4 is oxidized under anaerobic, inundated conditions (6). These oxidation rates (CH_4Ox) of CH_4 were user-defined inputs in MONDRIAN and could be changed to reflect conditions different from those in the current study.

2.4 N_2O flux simulation sub-model

Denitrification produces two species of gaseous N: these are N_2O and N_2. N_2O is a GHG with high radiative forcing but N_2 is not. In wetlands, oxygen availability is an important condition regulating N_2O production. Aerobic conditions enable nitrification, the production of NO_3^-, the primary reactant for N_2O production. Nitrate (NO_3^-) either flowing into a wetland or produced through nitrification then requires anaerobic conditions to be converted to N_2O. Oxygen availability also controls the

N_2O yield in denitrification (N_2O/ (N_2O +N_2)) (Tiedje, 1988). In MONDRIAN, total denitrification was calculated by NO_3^- availability, rate of heterotrophic CO_2 production and anaerobic zone proportion (Sharp et al. in revision). For the present study, we augmented the existing sub-model of total denitrification to further calculate the N_2O yield. We used water level and flooding days to represent oxygen ability and set N_2O yield to be 50% on the first day of flooding, 8% between 2 days to 4 days of flooding, and 1% after 4 days of flooding to. We use daily water levels to represent aerobic and anaerobic in the N_2O sub-model but all detrital pools (or proportions thereof), including above-and belowground litter, muck, and mineral soil organic matter (MSOM) pools lying below the level of the 5-day trailing average in water level are considered anaerobic.

N_2O yield as a proportion of total denitrification (N_2O / (N_2O+N_2)) is typically described in the literature as decreasing with increasing soil water content (Colbourn & Dowdell, 1984; Davidson, 1992; Rudaz et al., 1999), particularly when the soil water content exceeds 75% water filled pore space (Davidson, 1992; Weier et al., 1993). High ratios of N_2O yield have also been observed in the field and lab experiments on the first day of flooding events, relative to subsequent days because the transition from aerobic to anaerobic conditions increased the formation of N_2O (Kester et al., 1997, Cai et al.,1997, Ciarlo et al., 2007, Hansen et al., 2014; Lewicka-Szczebak et al., 2015). Experiments with ^{15}N isotopes showed that N_2O yield decreased from 50% to below 5% after 4-days flooding (Hansen et al., 2014, Lewicka-Szczebak et al., 2015). Mean N_2O yield of 8.2% was measured in freshwater wetlands and flooded soils (Schlesinger, 2009), and mean N_2O yield of 0.9% in streams and rivers (Beaulieu et al., 2011). Average N_2O yield in soils under natural recovering vegetation is 49.2% (Schlesinger, 2009). When wetlands are not flooded, we consider it as dry soils with vegetation.

2.5 Model Parameterization and Simulations

In this study, we conducted sets of contrasting simulation model runs (model run = one 40-y simulation), resulting in 480 combinations of model drivers and parameters. Each combination was replicated three times with stochastic differences both in initial plant distributions and spatial movements during clonal reproduction. In all model runs, our key dependent variables stabilized by 30 to 40 y and so for all statistical tests and figures, the average of the last 5 y (years 36 to 40) of each model run was used.

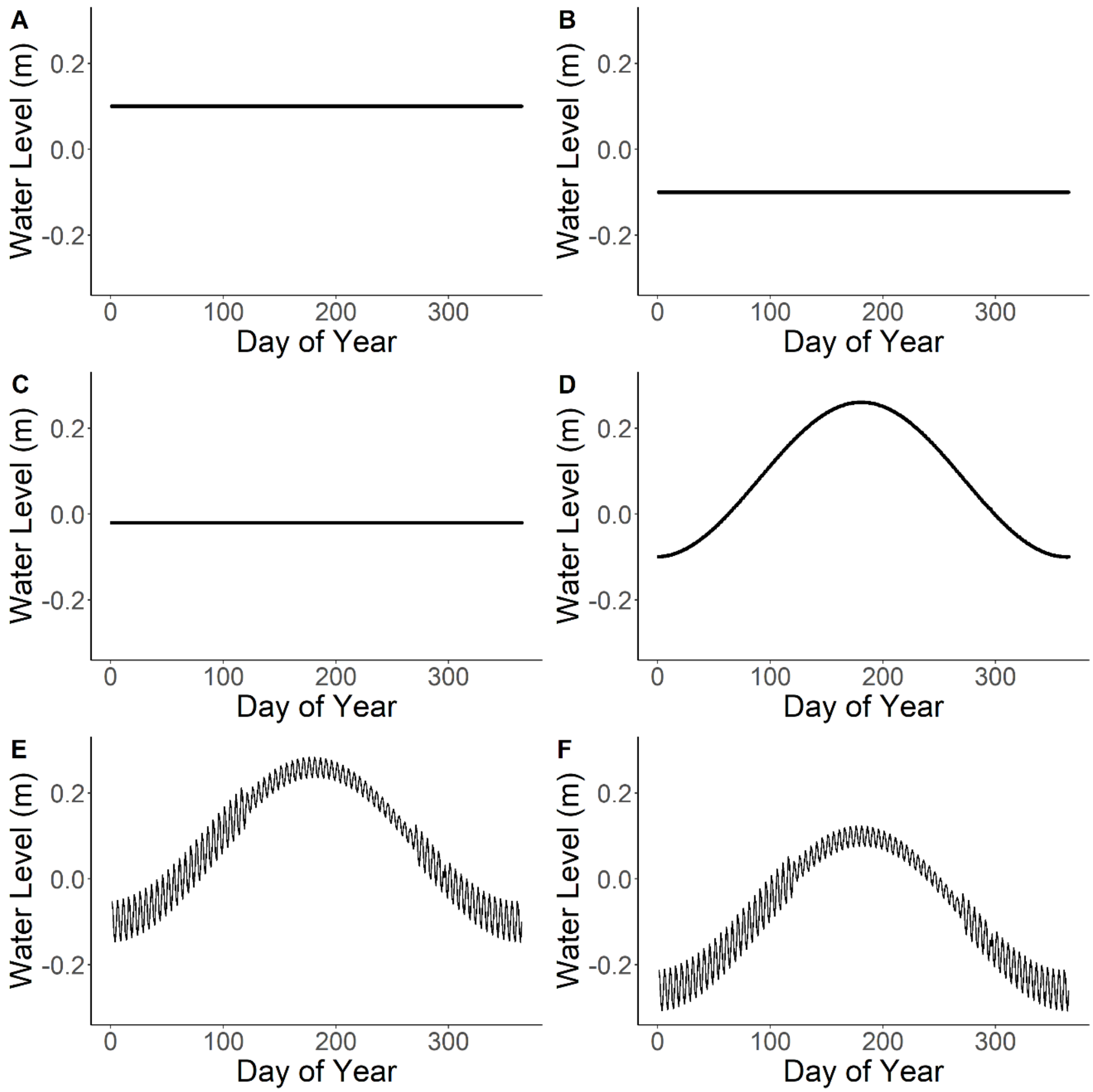

Fig. 1. Annual patterns in daily water level (meters) of six water level scenarios used in the present study. Scenarios A, B, C had constant water level, whereas D, E, and F had seasonally fluctuating water levels. Scenarios E and F superimposed an additional 5-day fluctuation on seasonal fluctuations.

We selected six water level scenarios to represent possible water levels found in coastal wetlands in Michigan (Fig. 1). The six hydrologic regimes were as follows: (1) always anaerobic (constant water level 10 cm above the MSOM surface); (2) always aerobic (water level constant at 10 cm below the MSOM surface); (3) always aerobic (water level constant at 2 cm below the MSOM); (4) sinusoidal fluctuation in the water level of -10 to 26 cm about the MSOM surface with an annual hydroperiod (highest in July and lowest in January) ("NOAA Tides and Currents," n.d.); (5) sinusoidal fluctuation in the water level of -10 to 26 cm about the MSOM surface with an annual period together with a smaller, 5-day fluctuation superimposed; and (6) sinusoidal fluctuation in the water level of -26 to 10 cm about the MSOM surface with an annual period together with a smaller, 5-day fluctuation superimposed (Fig. 1).

We included 5 nitrogen loading levels in this research: 1, 5, 10, 15, and 20 g N m^{-2} y^{-1}. Earlier modeling results (Martina et al., 2016) showed that *Phragmites* invasions, which dramatically change the ecosystem, failed at N loading < 4 g N m^{-2} y^{-1} and a threshold for highly successful invasion usually occurred between 12-18 g N m^{-2} y^{-1}. Our choices of N loading levels span across the range of this threshold area, resulting in both successful and unsuccessful invasion.

There are not a lot of measurements of water residence time in Great Lakes Coastal wetlands. Sierszen et al (2012) used isotopes to measure the water residence time in coastal wetlands and found that water residence time ranged from 0.16 to 46 days in their study sites. We estimated a wide range based on the variety of coastal wetlands in the region (Sharp et al., *in revision*), including 1 day, 10 days, 33 days, and 100 days.

We set 4 temperature levels (10.2 °C, 11.5 °C, 13.5 °C, 14.5 °C), seasonal temperatures will vary around the average temperature. 10.2 °C was the average annual temperature in 1951 (GLISA, n.d.), 11.5°C was the default value representing current temperature. 13.5 °C and 14.5 °C were estimated annual average temperatures in the Great Lakes by midcentury under low and high emissions (Hayhoe et al., 2010).

Climate change and warming are predicted to lengthen growing seasons in many parts of the world. Furthermore, increases in temperature have been demonstrated to affect the growing season start and end dates unequally resulting in the growing season start in the spring advancing by more days than the growing season end date is delayed in the fall (Linderholm, 2006). With 1°C increase in temperature the average annual growing season has advanced by 4 to 10.8 days in spring and been delayed by 1 to 7 days in autumn (Menzel & Fabian,1999; Chmielewski, 2001; Zhou et al., 2001; Wolfe et al., 2005; Song et al., 2010; Ibáñez et al., 2010). Therefore, we represent growing season length in our simulations as a function of temperature. We set plant growing season changes for all four plant species in MONDRIAN with 7 days advance in spring and 4 days delay in autumn for each 1°C temperature increase.

Species parameters used in this study are three native species (*Eleocharis palustris, Juncus balticus*, and *Schoenoplectus acutus*) and one invasive species (*Phragmites australis*) commonly occurring in Great Lakes coastal wetlands. Native species were randomly distributed in the modeling area in year one. Invader (*Phragmites*) plants were introduced at random locations in year 15, after natives had become well established.

2.6 Calculation of GWP

Global warming potential (GWP) is a metric widely used to compare emissions of various GHGs by standardizing their radiative effects in the atmosphere over a specific time horizon. Here we use GWP_{20} and GWP_{100} to denote 20 and 100-year time horizons. GWP is defined as the relative radiative effect of 1 kg of a GHG compared to 1 kg of the reference gas CO_2 (IPCC, 1990). Thus, GWP values are reported as kg CO_2 equivalents (kg CO_2-eq). Here we use the latest available conversion factors from the IPCC including climate-carbon feedback (IPCC, 2013). GWP conversions for methane (CH_4) are 86 for GWP_{20} and 34 for GWP_{100}; for N_2O the values are 268 for GWP_{20} and 298 for GWP_{100}. For results reported here, in addition to GWP conversions to CO_2-eq, the fractions (44 g CO_2/12 g C), (16 g CH_4/12 g C), and (44 g N_2O/28 g N) were also used to convert from fluxes on a C or N mass basis in MONDRIAN model output (g CO_2-C m^{-2} y^{-1}, g CH_4-C m^{-2} y^{-1}, and g N_2O-N m^{-2} y^{-1}) to the compound masses of the gases used in GWP conversions. In addition, results reported here were converted to represent the net emission of each gas over one hectare of wetland over one simulated year, thus reported as kg CO_2-eq ha^{-1} y^{-1}.

2.7 Statistical Analysis

We used ANOVA to assess differences in gas fluxes by water level scenario, water residence time, N inflow, and year using database software R studio (R Core Team 2020).

3. Results

We found the emission of CH_4, N_2O and net sequestration of C (i.e. negative

NEE) increased with increasing water residence time and N inflow, primarily driven by increased plant productivity and N uptake. Our simulation results for the summed GWP_{20} and GWP_{100} (i.e. summed GWP of CH_4, N_2O, and NEE) were dominated by the GWP of CH_4. The GWP of NEE was negative under most circumstances, meaning wetlands were net sinks of carbon in our simulations as wetland plants fix atmospheric CO_2 in net photosynthesis and plant detrital pools accrete under inundated (anaerobic) soil conditions. GWP of N_2O is negligible considering although N_2O has high radiative forcing, the amount of N_2O emitted from wetlands was very small. The summed GWP (i.e. sum of CH_4, N_2O, and NEE) mainly depends on how much GWP of CH_4 can be offset by negative GWP of NEE (CO_2). Water level scenarios also had an effect on GHG exchanges by modulating conditions between aerobic and anaerobic states. Generally, higher temperature promoted higher GWP but due to the modest range of temperature increases expected by the midcentury in this region, its effects were smaller than others.

3.1 CH_4 emission

CH_4 emissions ranged from nearly 0 to 73 g C m^{-2} y^{-1} in our results. Teasing apart the main controls on CH_4 emissions in our results was challenging because there were a large number of significant main effects and significant interactions among drivers ($p<0.01$). However, among model runs, CH_4 emission increased the greatest and most consistently both with increasing levels of N inflow and with longer water residence time (Fig. 2). Furthermore, more flooding (A, D, E; Fig. 2) and higher temperature resulted in more CH_4 production.

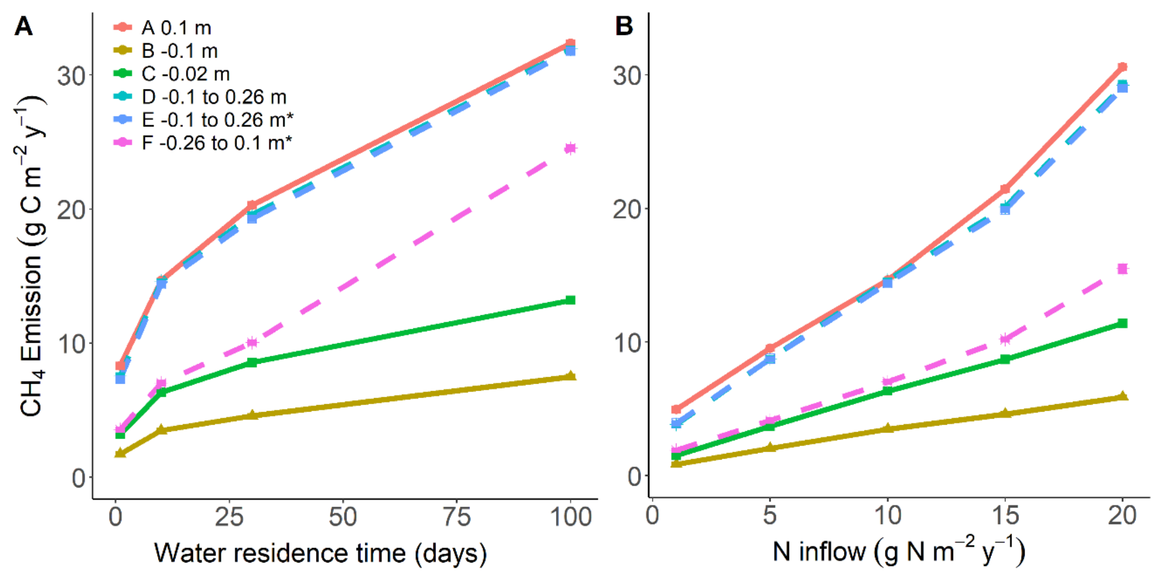

Fig. 2. MONDRIAN model results for CH_4 emissions (as g C m^{-2} y^{-1}) under current temperature conditions (annual mean 11.5 °C) as functions of water residence time (left panel) and wetland N inflow (right panel) in our simulations. Different lines refer to six different WL (water level) scenarios with constant (A-C) and seasonally fluctuating (D-F) water level. Asterisks (*) on legend indicate smaller 5-day fluctuations in water level superimposed on season fluctuations (Fig. 1). Note that lines (D) and (E) are overlapping in both panels. Error bars represent standard errors among 3 replicate model runs; note that some error bars are within the size of the symbols and thus too small to be visible.

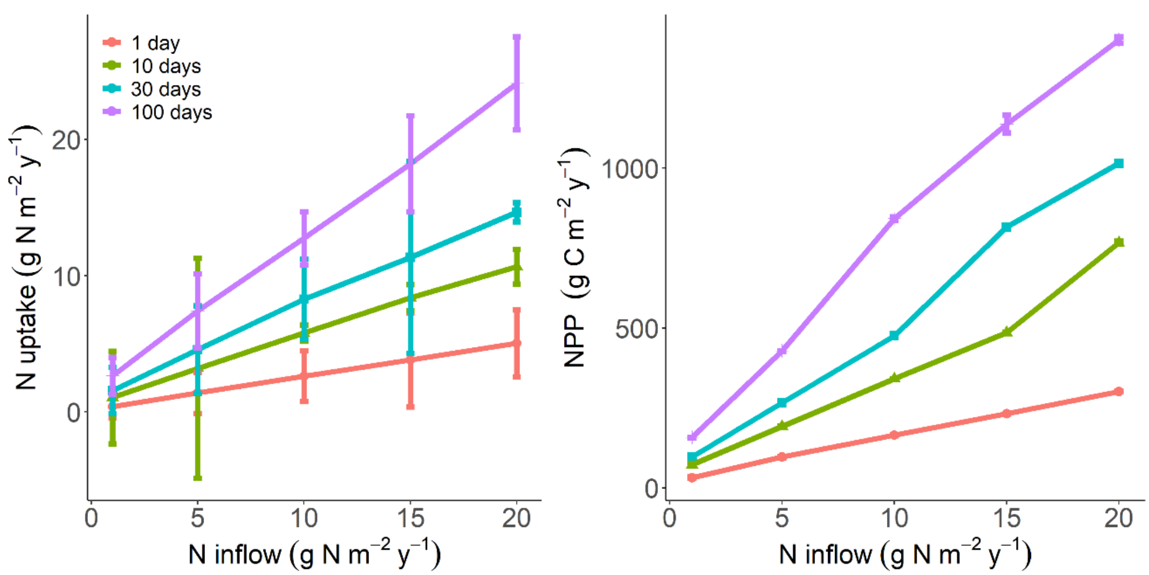

Fig. 3. MONDRIAN model results for N uptake by plants (left panel) and NPP (right panel) as a function of wetland N inflow under scenarios with current temperature (annual mean 11.5 °C) and water level scenario D (Fig. 1). Different lines refer to different values of water residence time (days). Error bars represent standard errors among 3 replicate model runs; note that some error bars are within the size of the symbols and thus too small to be visible.

NPP increased with increasing N inflow and water residence time as pools of available N were larger (reflected in plant uptake) thus facilitating increased plant growth (Fig. 3). Higher N inflows provided more nitrogen in the ecosystem and under longer water residence time nitrogen could stay in the ecosystem longer instead of being flushed out, promoting more N uptake by plants. Greater plant N uptake led to greater NPP, resulting in more litter production and deposition and higher levels of heterotrophic respiration. In MONDRIAN, CH_4 production was a proportion of heterotrophic respiration, calculated as a function of water level, temperature and a coefficient. N inflow and water residence time had limited effects on it.

When controlling for N inflow, hydraulic residence time, and temperature, water-level (WL) scenarios (Fig. 1) had an important impact on the rates of CH_4 emission (Fig.2A). The most striking pattern was that the two WL scenarios where water levels were constantly below zero (WL scenarios B and C) had the lowest CH_4 emissions (3.13- 269 kg C ha^{-1} y^{-1}) and were significantly lower than other WL scenarios (p-value < 0.05). WL scenarios that had flooded periods, whether constant flooding at 0.1 m (WL scenario A) or seasonally fluctuating around the high level at 0.08 m (WL scenarios D, E) had highest CH_4 emissions, but the three flooded WL scenarios (A, D, E) were not significantly different from one another ($p = 0.99$).

Fluctuation around an average lower water level (WL scenario F, -0.08 m) with fewer days of the year flooded (132 days) had lower CH_4 emissions than fluctuating WL scenarios with high average water level (WL scenario D and E; 0.08m) and more days of the years flooded the (237 days; $p < 0.05$). Surprisingly, wetlands with a constant water level above the soil surface (0.1m; WL scenario A) emitted less CH_4 than wetlands with fluctuating water around a positive mean (WL scenarios D, E) despite being flooded longer. Although higher temperature stimulated higher CH_4 emissions, compared with N inflows and water residence time, temperature's effects on CH_4 were small. This may be because we set a small range of temperature compared with water residence time and N inflow. Only with the difference of temperature greater than 2°C were simulations significantly different ($p < 0.05$).

3.2 Net Ecosystem exchange of CO_2 (NEE)

Similar to CH_4, NEE was strongly controlled by nitrogen inflow and water residence time (Fig. 4) because increasing these variables (i.e. more N inflow and longer residence time) increases N availability, which in turn increases ecosystem productivity, including photosynthesis and respiration. Because rates of photosynthesis and respiration largely determine rates of NEE, this component of GWP is highly integrated with nitrogen availability. Under low nitrogen inflow (5 g N m^{-2} y^{-1} or less) and low water residence time (10 days or less), negative NEE values (negative indicating net C sequestration) were relatively small in all simulations (ranging ca 25 g C m^{-2} y^{-1} to - 60 g C m^{-2} y^{-1}). But under high nitrogen inflow (20 g N m^{-2} y^{-1}) and long water residence time (100 days), negative NEE values were relatively large, ranging from ca -150 to -270 (g C m^{-2} y^{-1}). When controlling for water residence time and temperature, greater levels of N inflow contributed to greater sequestration of C (negative NEE) in all WL scenarios. (Fig. 4).

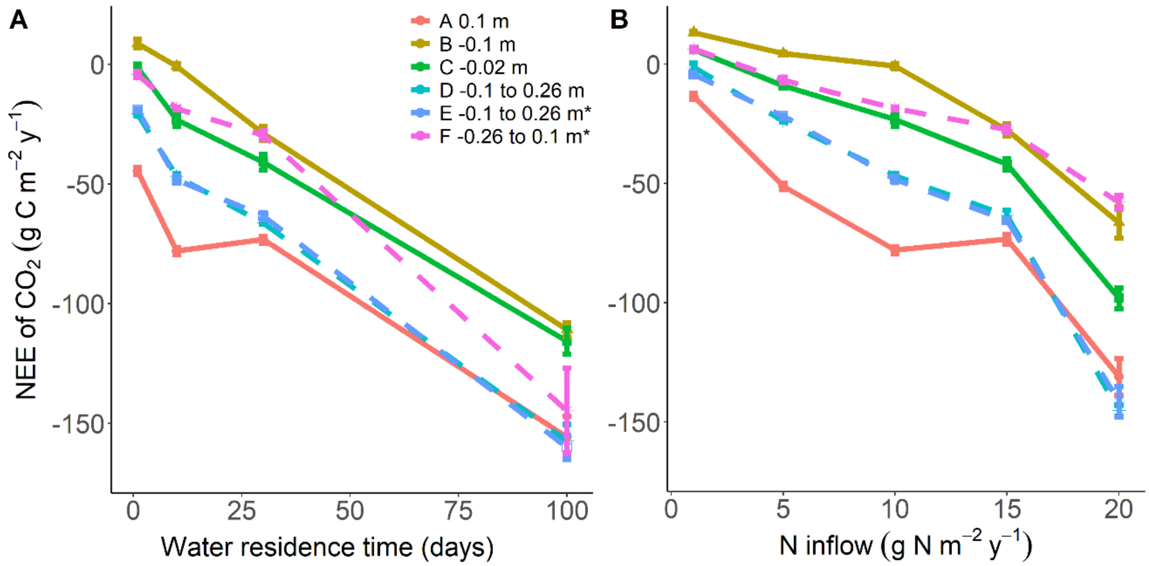

Fig. 4. Net Ecosystem Exchange (NEE) of CO_2 as a function of (A) wetland water residence time and (B) N inflow under current temperature (annual average 11.5 °C). Negative values of NEE indicate a wetland sink of CO_2. Different lines refer to six different WL (water level) scenarios with constant (A-C) or seasonally fluctuating (D-F) water level (Fig. 1). Asterisks on legend indicate smaller 5-day fluctuations superimposed on seasonally fluctuating water levels. Model results in panel (A) used an intermediate rate of N inflow of 10 g N m^{-2} y^{-1}; model results in panel (B) used an low-intermediate water residence time of 10 days. Error bars represent standard errors among 3 replicate model runs; note that some error bars are within the size of the symbols and thus too small to be visible.

WL scenarios had a much smaller effect on NEE with longer flooding (e.g. WL scenarios A, D, E) generally having more negative NEE by promoting more wetland C storage (Fig. 4). Yearlong constant flooding (water scenario A) had more C storage than flooding for more than half a year (WL scenario D, E). WL scenarios D and E had more C storage than flooding for less days (WL scenario F) and water scenarios with no flooding (B, C). 5-day fluctuation has no effects on NEEs that NEE in WL scenario D and E are very similar in that 5-days fluctuation didn't change the total flooding days in one year. At short water residence time (1 day $p<0.001$, 10 days $p<0.001$, 30 days $p<0.01$), the difference between water-level scenarios were significant but not under long water residence time (100 days; $p=0.34$).

Temperature differences had minor overall effects on NEE in our simulations. Higher temperatures simulated greater negative values of NEE, but the difference only became significant when the difference of temperature was greater than 2°C. Under the same N inflow, water residence time and WL scenario, the differences of NEE between 10.2°C to 14.5°C were small. This change ranged from -16.6 to 68.8 g C m^{-2} y^{-1} (median 11.1 g C m^{-2} y^{-1}), average proportion of change 17.2%.

3.3 N_2O emission

N_2O emissions also increased with higher nitrogen inflows by increasing available N for denitrification and with longer water residence time by lowering wetland N export and increasing wetland N pools. However, unlike CH_4 emissions and NEE, 5-days fluctuation promoted more N_2O emissions compared to WL scenarios with only annual fluctuation. Additionally, N_2O had much lower emission rates (0 to 0.375 g N m^{-2} y^{-1}) compared to CH_4 (0.313 to 73 g C m^{-2} y^{-1}) and NEE (-271 to 16 g C m^{-2} y^{-1}). In all water level scenarios, there were no N_2O emissions when water residence time was low (1 day) and N inflow was low (1g N m^{-2} y^{-1}). Under low nitrogen inflow level, as water residence time increased, N_2O emissions increased slowly (0-0.08 g N m^{-2} y^{-1} from residence time of 1 to 365 days) while at high nitrogen inflow levels, N_2O emissions increased rapidly from 0 to 0.15g N m^{-2} y^{-1}. Greater levels of N inflow magnified the denitrification effects of longer water residence time.

Under the conditions of sufficient N inflow ($\geq$ 10 g N m^{-2} y^{-1}) and long enough residence time (100 days), the two fluctuating WL scenarios that included 5-day fluctuations (WL E and F) produced the greatest N_2O emissions. Fluctuation provided more transitions from aerobic to anaerobic, which increased the N_2O yield from denitrification. Yet, although 5-day fluctuations affected N_2O emission from denitrification compared to WL scenarios without 5-day fluctuations, this difference did not affect total N removed via denitrification (N_2 + N_2O). Despite different average water levels, water scenarios E and F had very similar denitrification, nitrification, N uptake, and N retention, which also explained why water scenario E and F did not show greater CH_4 emissions and higher negative value of NEE. At constant -0.1 m water level (WL B), there was zero N_2O emission because this was below the 'active zone' that we set as a model parameter.

N_2O emissions increased with temperature but it was not significant.

3.4 Global warming potential

Global warming potential (GWP) is a metric that integrates GHG emission that was modulated by the same drivers as GHGs. Water residence time, N inflows, and WL scenarios are the most important drivers of GWP (Fig. 5) just as they are of the various GHGs that comprise GWP, including NEE (CO_2 exchange), CH_4 emission, and N_2O emission. High N inflow and longer water residence time produced larger values of negative NEE but also more CH_4 emissions. The negative value of NEE, representing a wetland sink for CO_2-C, meant that the contribution of CO_2-C to the summed GWP partially offset the higher positive contributions of CH_4

to GWP (Fig.6). The GWP of CH_4 consistently outweighed the negative GWP of NEE and increased summed GWP at 20 years (GWP_{20}) under higher N inflow and longer water residence time. But at 100 years, summed GWP_{100} for low water level scenarios decreased with high nitrogen inflows and long water residence time (Fig. 5) because of the GWP of per unit CH_4 decreased in 100 years.

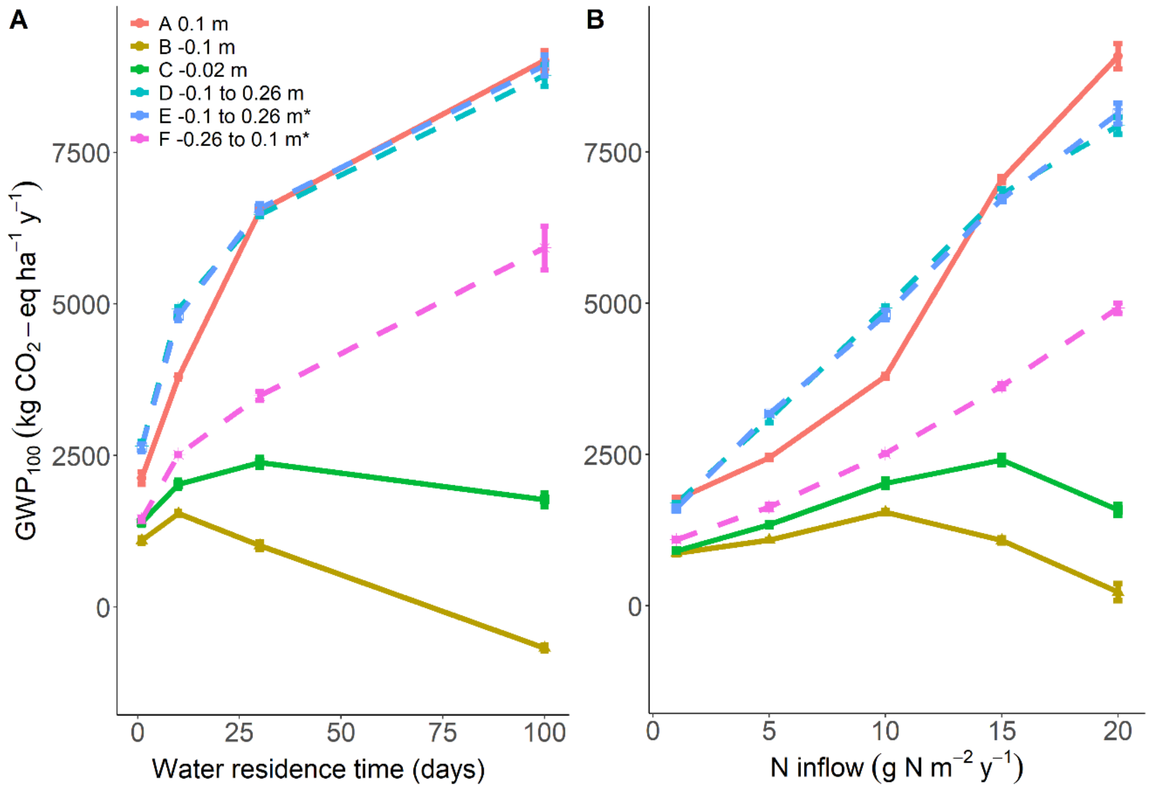

Fig. 5. Model results for summed global warming potential (GWP) of three greenhouse gases as CO_2 equivalents (kg CO_2-eq ha^{-1} y^{-1}) in the 100-year time horizon as functions of water residence time and N inflow under annual mean temperature 11.5°C. Different lines refer to 6 different WL (water level) scenarios with constant (A-C) and seasonally fluctuating (D-F) water level. Dashed lines indicate seasonally fluctuating WL scenarios with added smaller 5-day fluctuations. Model results in panel (A) used an intermediate rate of N inflow of 10 g N m^{-2} y^{-1}; model results in panel (B) used an low-intermediate water residence time of 10 days. Error bars represent standard errors among 3 replicate model runs; note that some error bars are within the size of the symbols and thus too small to be

visible.

Across all N inflows, water residence times, temperatures, and WL scenarios, CH_4 was consistently the largest contributor for GWP_{20}. NEE was the second largest contributor, with negative GWP to offset the summed GWP. The amount of emitted N_2O was very small. Although the GWP for per unit mass of N_2O was highest in three, its total GWP was limited compared with other two gases.

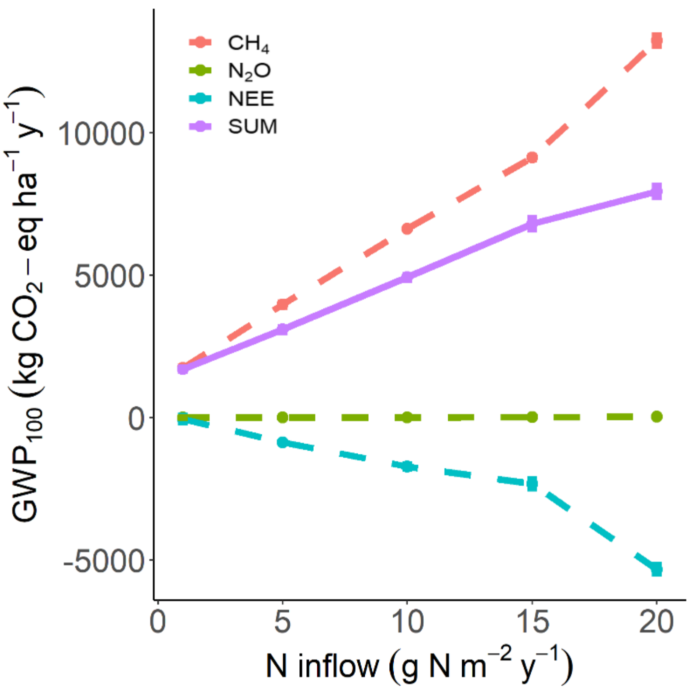

Fig. 6. MONDRIAN model results for GWP of each GHG in the 100-year time horizon (GWP_{100}) as functions of N inflow under mean annual temperature 11.5°C, water residence time 10 days and WL scenario D. Error bars represent standard errors among 3 replicate model runs; note that some error bars are within the size of the symbols and thus too small to be visible. NEE = net ecosystem exchange of CO_2; Sum = summed GWP from three gases shown.

At the 100-year time horizon, across all N inflows, water residence times, and temperatures, CH_4 was the greatest contributor for GWP in flooded water scenarios

(A, D, E, F), NEE was the second and N_2O was the least. In water scenario B and C (constant negative water level) where CH_4 emissions were smaller, NEE had a larger contribution and offset the GWP of CH_4 and N_2O under high nitrogen inflows and long water residence time. In water scenario B, under water residence time 30 and 100 days and N inflow of 20 g N m^{-2} y^{-1}, negative NEE counteracted GWP of CH_4 and N_2O and made the summed GWP negative. In water scenario C, NEE had similar contribution with CH_4 under long water residence time and high N inflow. Negative GWP of NEE was still less than the positive GWP of CH_4 and failed to counteract its influence. However, summed GWP in scenario C was much smaller than other water scenarios.

Similar to its component gases, summed GWP was also affected by WL scenarios. Flooding water level scenarios (WL scenarios A, and E, fluctuated from -0.1 to 0.26 m) had the highest summed GWP. Water scenario B and C (constant negative water level) were significantly lower than others after controlling water residence time, nitrogen inflow and temperature. Generally, summed GWP increases with temperature, but the effect of temperature on summed GWP is small.

The summed GWP_{20} of one-hectare wetland ranged from 819 to 76,400 (kg CO_2-eq ha^{-1} y^{-1}). The smallest number appeared in water level scenario C, when temperature is 10.2 °C, water residence time is one day and nitrogen inflow is 1 g N m^{-2} y^{-1}. The highest GWP_{20} appeared in water scenario E, when temperature is 13.5 °C, water residence time is 100 days and nitrogen inflow is 20 g N m^{-2} y^{-1}. GWP_{100} of one-hectare wetland ranged from -1730 to 26,600. The smallest number appeared in water level scenario B, when temperature was 11.5 °C, water residence time was 100 days and nitrogen inflow was 20 g N m^{-2} y^{-1}. The highest GWP_{100} appeared in water scenario E, when temperature was 14.5°C, water residence time is 100 days and nitrogen inflow was 20 g N m^{-2} y^{-1}.

4. Discussion

In our simulations, Great Lakes coastal wetlands exhibited net sinks for CO_2 but net sources for CH_4 and N_2O. These broad findings are consistent with a global meta-analysis of natural coastal wetlands, riparian wetlands, and peatlands in that wetlands were generally net sinks of atmospheric CO_2 and net sources of CH_4 and N_2O (Tan et al., 2020). However, the summed global warming potential (GWP) in 20 years and 100 years (sum of CH_4, NEE and N_2O) was positive in our simulations, which differed from the general finding of negative GWP in the same global meta-analysis (GWP_{100} −900 to −8,700 kg CO_2-eq ha^{-1} y^{-1}) (Tan et al., 2020). CH_4 made the biggest contribution to summed GWP while the effects of N_2O was very limited. NEE was negative and it offset the GWP of CH_4 and N_2O. Water residence time, N inflow and WL scenarios were most essential to three GHGs and summed GWP because they controlled N uptake by plants and plant productivity, which determined the amount of C transferred to CH_4.

4.1 Comparison with measured data

CH_4 emission rates ranged from nearly 0 to 73 g C m^{-2} y^{-1} in our results. These results fell in the range of CH_4 flux from wetlands measured in empirical studies, which have ranged from -11.4 g C m^{-2} y^{-1} to 13,870 g C m^{-2} y^{-1} in different wetlands types (Table 1). Rates of NEE in our results ranged from small positive numbers (representing emission of CO_2), up to 16 g C m^{-2} y^{-1}, to much larger negative numbers (representing a net ecosystem sink for CO_2), up to ca -270.7 g C m^{-2} y^{-1}. Most of our estimated NEE was within the range of those observed in empirical studies (field measurements) of -30 to -2,200 g C m^{-2} y^{-1} (Table 1). There was a small amount of estimated positive NEE in our results that were out of the range of those published from empirical studies. Low water level (including low constant water level scenario B, C and low seasonal fluctuated water level scenario F) showed a net CO_2 emission (positive NEE out of measured data range) under low N inflow and low water residence time, but such sites would not be wetlands if they are continuous unflooded. In our results, in most circumstances, wetlands were net sinks of C. But there also existed a few sets that simulated small C sources. This is consistent with previous findings that wetlands can be both sources and sinks of carbon, depending on their age, operation, and the environmental boundary conditions such as location and climate (Kayranli et al., 2009). Emissions of N_2O in our simulations ranged from 0 to 0.375 g N m^{-2} y^{-1}. In field measurements in wetlands from the literature, estimated N_2O emissions ranged from 0.013 g N m^{-2} y^{-1} to very high levels of 365 g N m^{-2} y^{-1} (Table 1). However, values in the literature above 0.28 g N m^{-2} y^{-1} occurred in constructed wetlands (Table 1), making our modeling results in good agreement with the range of N_2O observed in non-constructed wetlands across a range of studies.

Site	Time	CH_4 g C m^{-2} y^{-1}	Methods	Reference
Sub-arctic mire, Sweden	June 16th to September 1st	1.31 to 237	Closed chamber technique	Ström & Christensen (2007)
Constructed wetland, Estonia, Finland, Norway, and Poland	Summer and winter season, 2001-2003	-11.7 to 13,900	Dark chamber	Søvik et al. (2006)
Freshwater marsh, China	November to March	1.58 to 4.38	Single column sampling-separation system equipped with flame ionization detector	Zhang et al. (2005)
Coastal saline wetlands, China	September 2012 to August 2013	-3.23 to 43.4	Closed static chamber	Xu et al. (2014)
Restored wetlands, Skjern Meadows, Denmark	2009–2011	8.25 to 12.8	Eddy Covariance Technique	Herbst et al., (2013)
Peatland, Minnesota, United Stats	2009-2011	11.8 to 24.9	Eddy Covariance Technique	Olson et al., (2013)
Current study		**0.313 to 73**		

Site	Time	NEE g C m^{-2} y^{-1}	Methods	Reference
Peatland, Minnesota, United States	2009-2011	-21 to -39.5	Eddy Covariance Techniquea	Olson et al., (2013)
Restored wetlands, Skjern Meadows, Denmark	2009–2011	-195 to -983	Eddy Covariance Techniquea	Herbst et al., (2013)
Cattail marsh, Canada	May 9th 2005 to May 30th 2006	-264	Eddy Covariance Techniquea	Bonneville et al., (2008)

Sedge fen, Finland	2004-2005	-55.5	Eddy Covariance Techniquea	Aurela et al., (2007)
Sub-arctic mire, Sweden	June 16th to the September 1st	-2,390 to -2990	Closed chamber technique	Ström & Christensen (2007)
Bogs and mires, Finland		-15 to -35	Estimated C accumulation from dry mass of peat	Turunen et al., (2005)
Current study		**-271 to 16**		
Site	**Time**	**N_2O g N m^{-2} y^{-1}**	**Methods**	**Reference**
Constructed wetland, Netherlands	April to September 2009	0.32 to 1.21	Estimated denitrification with nitrogen budget	de Klein & van der Werf (2014)
Natural wetlands, Sanjiang Plain, China	Early May to late September (2002 -2005)	0.11 to 0.28	Static dark chamber and gas chromatography techniques	Song et al.,(2009)
Freshwater marsh, Sanjiang plain, China	July 7th to September 27th in 2005	0.071	Gas chromatograph (Agilent 4890)	Yang et al., (2013)
Peatland, Ontario, Canada	2005	0.013	Data not report	Bubier et al., (2007)
Restored emergent freshwater marsh, California, United States	February 20th 2014 to February 20th 2015	0.062	Permanently deployed chambers	McNicol et al., (2017)

Constructed wetland (subsurface flow, free surface water, and overland and groundwater flow wetlands), Estonia, Finland, Norway, and Poland	Summer and winter season, 2001-2003	-0.77 to 365	Dark chamber	Søvik et al. (2006)
Current study		**0 to 0.375**		

Table 1. CH_4 emissions, NEE (as CO_2) and N_2O emissions in wetlands. Negative values of NEE indicate a wetland C sink.

In general, in our results, our simulated wetlands were large sinks of CO_2, small sources of N_2O and modest sources of CH_4 (McNicol et al., 2017; Beringer, 2013; Wang et al., 2016; Tan et al., 2019). But in contrast with some previous studies in which CO_2 was the dominant gas contributing to overall GWP (Krauss & Whitbeck., 2012), CH_4 was the main contributor to summed GWP in our study (Wang et al., 2016).

We set the 0.2 as the value of $CH_4P_{0,}$ and assumed 43% methane gets oxidized before being emitted to the atmosphere when muck is aerobic. The final proportion of CH_4 from heterotrophic respiration ranging from 0.01 to 0.1 depending on WL scenarios. 3% to 60% of total decomposed carbon (CH_4-C and CO_2-C) was reported to transform to CH_4 depending on the environment (Moore & Knowles, 1990; Yavitt et al., 1987; Tsutsuki & Ponnamperuma, 1987; Cao, 1996). Our CH_4 proportion is relatively low compared to others. If we set a higher value of CH_4P_0, CH_4 would dominate even more than it already does. In MONDRIAN CH_4 simulation, we didn't explicitly simulate fine-scale processes of CH_4 transport by diffusion, ebullition and transport through plant tissues. This process may bring more CH_4 into atmosphere and increase the proportion of CH_4 from heterotrophic respiration.

It is commonly considered that increased N uptake promoted greater C storage by plants. But at the same time, with the increase of NPP, more C came to litter and decomposition. CH_4 production also increased. Considering the GWP of N_2O was negligible, the trade-off between NEE and CH_4 emissions controlled the summed GWP in wetlands and the summed GWP mainly depends on whether NEE is able to offset the GWP of CH_4. In open-water wetlands, net CO_2 storage did not offset CH_4 emission, producing an overall positive radiative forcing effect of 35000±3000 kg CO_2-eq ha^{-1} yr^{-1} (McNicol et al., 2017). However, in other studies, negative GWP of NEE offset the GWP of CH4 and N_2O and made the summed GWP negative (Beringer, 2013, Tan et al., 2020). Under most circumstances, our estimated GWPs were positive, which means NEE didn't offset the GWP of CH_4 and N_2O. This is mainly due to the high CH_4 emissions. We set in MONDRIAN that all C will come from litter, however, in reality, there should have some standing plant tissues. The overestimated litter increased the C in heterotrophic and promoted more CH_4.

Land use, land cover, vegetation, nutrients, humidity, water table, salinity, soil pH, and temperature are considered to influence the GHG emissions (Oertel et al., 2016; Tan et al., 2020). The summed GWP of GHG also varies by climate, wetland types, vegetation and nutrients. Most field measurements only focused on one wetlands class and in one season and brought the varieties of calculated GWP.

4.2 Drivers of greenhouse gas emissions

4.2.1 N inflow and water residence time

Our results showed N inflow, water residence time and WL (water level) scenarios had significant effects on CH_4 emissions, sequestration of C (negative NEE), N_2O emissions and summed GWP in both 20 years and 100 years.

Increasing soil N content generally leads to higher soil respiration and to higher net ecosystem exchange (NEE), if carbon is not limiting (Niu et al., 2010; Peng et al., 2011). In MONDRIAN, higher levels of N inflow and water residence time promoted greater N cycling because there was more N flow into the system and longer water residence time decreased the daily flushing rate of N from the wetland to downstream and allowed greater wetland N retention (Sharp et al., *in revision*). Greater N cycling promoted greater plant NPP and greater sequestration of C (negative NEE) by regulating plant N uptake. In MONDRIAN, N inflow caused wetland C storage (Martina et al., 2012). However, the version of the model used by Martina et al. and their analysis did not include denitrification and variable water residence time, and they looked only at C stocks, not NEE.

Carbon storage acts as reservoirs for CH_4 production and emission. CH_4 emissions have been found to have positive correlations with net ecosystem production, around 3% productivity will be emitted as CH_4 (Whiting & Chanton, 1993; Le Mer & Roger, 2001). Our results also showed this pattern that CH_4 emissions increased with plant N uptake and NPP. Besides, our results also showed that high correlation between N uptake and net primary productivity, which means the increased N uptake encouraged better plant productivity and then allocated more

C to CH_4 emissions.

It was widely considered that N deposition will reduce GWP owing to increased net CO_2 uptake (Wang et al., 2017). However, our study indicated that although high N inflow increased the sequestration of C, CH_4 emissions also increased and brought the uncertainties of summed GWP. Negative GWP of NEE was unable to offset the N stimulated GWP of CH_4 and N_2O emissions in 20 years. In the 100 years' time horizon, summed GWP in WL scenario B and C (low constant) decreased with high N inflow and water residence. NEE's negative GWP offset the N stimulated GWP of CH_4 and N_2O in these WL scenarios. Liu & Greaver (2009) pointed out that different ecosystems had different responses to GHG with increased N that N increased the GHG sink strength for forest ecosystems but agricultural ecosystems were sources for GHG emissions under intensive N application.

4.2.2 Water level scenario

Our model results on constant water level scenarios are consistent with previous findings that high water table increases CH_4 emissions (Moore & Dalva, 1993; MacDonald et al., 1998; Blodau & Moore, 2003; Yang et al., 2014). WL scenarios where water levels were constantly below zero (WL scenarios B and C) had lower CH_4 emissions than WL scenarios A (constant above ground) because the aerobic soil condition decreased CH_4 production and increased the oxidation. Five-days fluctuation in WL scenario E had limited effects on CH_4 emissions because it didn't influence the annual number of flooded days and trailing average water level compared to WL scenario D.

Water level scenarios also influenced NEE. But it is not as obvious as CH_4.

We speculated it is because although in the lowest water WL scenario B (-0.1m constant), plants can still get enough water to live and it didn't influence plant's productivity.

Because of the high CH_4 emissions reduction caused by low water level, above ground WL scenarios (including constant and seasonal fluctuating) had much higher summed GWP than below ground WL scenarios in 20 years and 100 years. In a field experiment in Tibetan wetlands, 20cm water table lowering reduced GWP from 337.3 to -480.1 g CO_2-eq m^{-2}, mostly because of decreased CH_4 emissions (Wang et al., 2017).

4.2.3 Temperature

It was recognized that an increase of soil temperature leads to higher emissions and higher soil respiration rates as a positive feedback response of increased microbial metabolism. CO_2 was analyzed to be mainly regulated by annual temperature by Lu et al (2017). CH_4 and N_2O fluxes also displayed strong and asynchronous seasonal dynamics (McNicol et al., 2017).

All of the GHG emissions we simulated are sensitive to temperature in MONDRIAN. However, we found that temperature differences, together with associated differences in growing season length, were less important than hydrology and nutrient inflows in controlling GHG emissions from wetlands in our simulations. The temperature's effects were small in all three GHGs and summed GWPs and only became significant between over 2°C's difference. We set the temperature according to the prediction of temperature in the Great Lakes region by mid-century, the range of temperature was small (10.2 to 14.5°C) compared with other elements: range of N inflow (1 to 20 g m^{-2} y^{-1}), water residence time (1 to 100 days) and water level (-30 cm to 28 cm). For each temperature level, we only changed the growing season of plants but not the growth rate, this may also consist of why temperature's influence was small. Under field conditions, moisture and temperature effects always overlap, which may make it difficult to separate the two effects (Fang & Moncrieff, 2001). This also explains why temperature was least important in our results.

5. Conclusion

In our simulations, Great Lakes coastal wetlands exhibited net sinks for CO_2 but net sources for CH_4 and N_2O and had positive summed GWP under most conditions, which suggested wetlands are sources for global warming. In all three GHGs, CH_4 made the biggest contribution to summed GWP in our results and deserved more attention in future. Water residence time, N inflow and water level scenarios were most essential to three GHGs and summed GWP because they controlled N uptake by plants and plant productivity, which determined the amount of C stored by plants and how many C transferred to CH_4. More N uptake encouraged better C storage but at the same time, provide more substrates for CH_4 production. Thus, the balance of CH_4 emission and C sequestration become the key for summed wetlands GWP. Temperature was the least important in our study considering the limitation of temperature range. However, our understanding on how temperature influenced GHGs is insufficient. Measurements and experiments from field are needed to fill the data gap.

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Chapter 2: Wetlands biogeochemistry

1. Carbon cycle in wetlands

Fixation of atmosphere carbon in plants, soils and sediments is considered as the major source of carbon to wetland and aquatic ecosystem (Mitsch & Gosselink., 2015). The balance between inputs and outputs of organic carbon determines long-term accumulation of carbon in wetlands. Wetlands receiving increased inputs of nutrients from flows were more productive than closed wetlands only received input from precipitation.

A large proportion of wetland carbon is stored in soil organic matter and sediment. Major sources of organic matter and sediment are litter and belowground biomass. Soil organic matter and sediment are considered as the detrital pools providing material for decomposition. Microbial composers drove energy and carbon from detrital and soil organic matters by decomposing.

Carbon mineralization within wetlands is a complicated process that involves both aerobic and anaerobic processes. Carbon dioxide and methane (CH_4) are two gaseous end products of decomposition of organic matter under anaerobic conditions, whereas only carbon dioxide is produced under aerobic conditions. Under aerobic conditions, as long as there is oxygen present, the other oxidants that microorganisms can use are not reduced. Oxygen is used preferentially because it took electrons from the reductant material more readily than other oxidants. When oxygen becomes limiting, the other oxidants begin to accept electrons and keep respiration of certain microorganisms going, anaerobes use electron acceptors other than oxygen (Reddy &

DeLaune., 2008). Decomposition of organic substrates under anaerobic conditions results in the accumulation of reduced species like CH_4. Under anaerobic conditions, organic matter decomposition is often slower, because of the lack of oxygen, a main factor that drives rates of plant detritus turnover and makes decomposition in wetland differs from decomposition in upland ecosystem because the predominance of anaerobic condition slow down the decomposition process. Methanogens are the only carbon dioxide reducing bacteria in anaerobic environments, and also the major contributor of atmosphere CH_4 (Mitsch & Gosselink., 2015).

Oxygen supply in wetlands is restricted to the water column and a thin layer of surface soil. Seasonal fluctuation in hydrology and water table could bring more oxygen into soil profile. Aerobic process is restricted to the small column of oxygenated soil, whereas in the remaining anoxic soil, the dominant microbial group were anaerobes.

Carbon sequestration in wetlands is closely coupled to the moisture regime. Many wetlands were moist for only part of the year. When soil is submerged, anaerobic decay dominates. The amount of carbon sequestered during a year depends on the timing and duration of anaerobic and aerobic conditions. Net ecosystem emission of CH_4 becomes more positive as water table depth increase. Wetlands hydrology changes by precipitation and climate changes, which strongly influences the carbon dynamics in wetlands. Long-hydroperiod marsh was found to be a net annual CO_2 source while the short-hydroperiod marsh was a net CO_2 sink (Jimenez et al., 2012). Variable hydrology may have contrasting effects on different respiratory products.

Beside carbon, the water table of wetlands also influences CH_4 emission, influencing the amount of CH_4 emitted to the atmosphere, and also the oxidation of CH_4. The water table level predominantly determines the presence of aerobic and anaerobic conditions occurring at different depths of wetlands. These conditions control the methanogenic and methanotrophic processes. Methanogenesis is an anaerobic process, and it is evoked during flooding periods, when the water table level rises. In contrast, with a decrease in flooding periods, CH_4 production decreases.

Relatively high CH_4 emissions could be observed when the groundwater table was high and soil temperatures were higher than 12°C. Vegetated organic sediments at different water table depths below the surface was compared with vegetated inundated sediments and it was found that due to the high-water holding capacity of organic sediments, rates of methanogenesis and CH_4 emission in organic sediments with a water table of 8 cm below the sediment surface were only slightly, but not statistically significantly different from rates in inundated sediments (Grünfeld & Brix, 1999). The mean position of the water table level was reported as the best indicator of CH_4 emissions such that a water table depth greater than 18 cm does not produce high emissions, since CH_4 production (methanogenesis) decreases and its consumption increases (methanotrophy) (Moore & Dalva, 1993). However, when the depth of the water table was 12 cm below the surface of peat, or exceeds it, CH_4 fluxes were high. Peatlands convert from a source to a sink of CH_4 when the water table drops to 25 cm below the peat surface due to increased CH_4 oxidation (Roulet et al., 1993). Across a tidally flooded riverbank in North Carolina, USA, the highest

CH_4 fluxes were observed when the water level close to the surface, and the lowest fluxes at both high and low water table levels (Kelley et al., 1995).

2. N cycling in wetlands

N cycling involves the nitrogen transformations within soil, plant, water and atmospheric systems, including mineralization, immobilization, nitrification, denitrification, ammonia (NH_3^-) volatilization, ammonium (NH_4^+) fixation and nitrate (NO_3^-) leaching (Zaman et al., 2012). Mineralization, immobilization, nitrification and denitrification are microbially driven biotic processes, occurring with microbial and enzymes. NH_3 volatilization, NH_4^+ fixation and NO_3^- leaching were abiotic processes, involving only chemical and physical processes.

Nitrogen mineralization converts organic N (e.g. protein, amino acids, amines, amides, urea, chitin and amino sugars) into an inorganic form of N (mainly NH_4^+) with a sequence of microbial and enzymatic activities, which is always considered as the first step of N cycling (Mitsch & Gosselink., 2015). Inorganic N then serves as a substrate for nitrification by a diverse group of microorganisms (Zaman et al., 1999). Final productions of N cycling were gaseous N, including ammonia (NH_3), nitrogen oxide (NO), nitrogen dioxide (NO_2), nitrous oxide(N_2O) and dinitrogen (N_2). In all of the emission gases, N_2O drew the most attention because it is the key greenhouse with high GWP.

Soil microbial processes accounts for major N_2O production include nitrification, denitrification (Tiedje, 1988; Smith, 1979; Cavigelli & Robertson, 2001) and dissimilatory NO_3^- reduction to NH_4^+ (Silver et al., 2001). These microbial processes occurrs in soils, muck and sediments across the different landscapes depending on the physical (O_2 level or moisture content) and chemical conditions [NO_3^-, NH_4^+, pH and C contents].

2.1 Nitrification

Nitrification, the transformation of NH_4^+ to NO_3^-, has two pathways in soils: autotrophic nitrification and heterotrophic nitrification. Autotrophic nitrification is the oxidation of ammonia to nitrate via hydroxylamine and nitrite (Wood, 1986).

Autotrophic nitrification is carried out by chemolitho-autotrophic bacteria. O_2 worked as a terminal electron acceptor in this process. In autotrophic nitrification, NH_4^+ or NH_3 are first oxidized to NH_2OH by ammonia monooxygenase (Wood, 1986). Two electrons are needed for the reduction of one of the atoms of O_2 in this step. Two electrons are derived from the next step, the oxidation of NH_2OH to NO_2^-. The next step in NH_4^+/NH_3 oxidation is from NH_2OH to NO_2^-. This reaction is catalyzed by the enzyme hydroxylamine oxidoreductase (McCarty,1999). The NO_2^- production is further promoted by NO_2^-oxidizers or secondary nitrifiers Nitrobacter and Nitrococcus (Bremner & Blackmer, 1981) in a one-step reaction to NO_3^-. In addition to NO_2^- production during the first two stages of autotrophic nitrification, several intermediate and unstable compounds such as nitrosyl (NOH) are also formed. Ammonia oxidizers consumed relatively large amounts of molecular O_2 during this first stage, causing anaerobic conditions in microsites within soil and presapce, which then leds to a reduction of NO_2^- to N_2O and N_2 (Poth & Focht, 1985; Firestone & Davidson, 1989; Zart & Bock, 1998).

Heterotrophic nitrification is the oxidation of reduced N compounds or NH_4^+ to NO_3^- in the presence of O_2 and organic C (Wood, 1990). Nitrifiers in heterotrophic nitrification use organic carbon as a source of energy while nitrifiers in autotrophic nitrification used nitrification as an energy source. The substrate, intermediates and products of heterotrophic and autotrophic nitrification were the same but the enzymes of two processes has been shown to be different (Wrage et al., 2001). Besides, under aerobic conditions, heterotrophic nitrifiers produced much more N_2O than autotrophic nitrification although the production of N_2O from nitrification was only a minor source (Anderson et al., 1993).

Sufficient soil O_2 level, adequate NH_4^+ concentrations, a favorable soil temperature above 5°C (optimum 25 to 35°C), and soil pH above 5 (optimum 7 to 9) were among the known soil and environmental conditions which control the rate of nitrification (Linn & Doran 1984; Grundmann et al., 1995; Zaman et al., 2009). Among these factors, NH_4^+ and O_2 concentrations were considered the most critical factors affecting autotrophic nitrification. Thus, autotrophic nitrification was expected to be a dominant N transformation process in well-drained pastoral or agriculture systems, where oxygen and NH4+ were abundant in soils (Zaman et al., 1999). High rates of heterotrophic nitrification relative to autotrophic nitrification have been measured in a riparian wetland soil with a pH close to 7, which was exposed to O_2 (Matheson et al., 2003).

2.2 Denitrification

Denitrification is the stepwise reduction of NO_3^- to N_2. Dinitrogen (N_2) gas was the end product of denitrification, and nitrous oxide (N_2O) is the by-product under incomplete denitrification. It is a predominantly microbial process by which NO_3^- and NO_2^- are reduced to N_2O and N_2 in a respiratory metabolic process. During respiratory denitrification, N-oxides are reduced and organic carbon is oxidized by denitrifies under anaerobic conditions and produce adenosine triphosphate by phosphorylation (Linn & Doran, 1984; Cavigelli & Robertson, 2001).

Nitrifiers require aerobic conditions in that the enzyme needs molecular oxygen to oxidize ammonium (NH_4^+) or ammonia (NH_3) to hydroxylamine. In contrast, denitrifies are facultative anaerobes and are able to work in anaerobic conditions and use nitrogen oxides as electron acceptors in place of oxygen when oxygen was limited in the soil (Poth, 1986; Tiedje, 1988; Remde and Conrad,1990).

Microbially driven oxidation-reduction (redox) reaction, like denitrification, require e^- acceptors and e^- donors as an energy source. In the saturated zone, organic carbon--a common e^- donor, tended to be oxidized preferentially by the e^- acceptor that yield the most energy to denitrifying bacteria. Aerobic bacteria used O_2 to oxidize organic carbon until oxygen supplies become limiting. At this point, facultative anaerobes switched to use NO_3^- and O_2 as e^- acceptors. As O_2 levels decrease, obligate anaerobes begin to use alternative e^- acceptors (NO_3^-). When O_2 levels increase, aerobic bacteria will return to O_2 respiration because of the increased energy economy NO_3^- is the next e^- acceptor to oxidize organic carbon (heterotrophic denitrification). After NO_3^- concentrations become limited, manganese (Mn^{4+}) and ferric iron (Fe^{3+}) and then sulfate ($SO4^{2-}$) are reduced. As mentioned previously, if NO_3^- is introduced to any reducing zone below a denitrifying zone, NO_3^- can serve as an e- acceptor, and reduced inorganic species such as Mn^{2+}, Fe^{2+}, and HS^- can serve as e^- donor. In this process, bacteria in an anaerobic environment used NO_3^- as a terminal electron (e^-) acceptor in their metabolic processes.

Therefore, biological denitrification requires: (1) N oxides (NO_3^-, NO_2^-, NO, and N_2O) as a terminal electron acceptor when O_2 is absent, (2)available organic carbon as an electron donor, (3) anaerobic conditions or restricted O_2 availability, suitable soil pH, which generally ranges from 5 to 8 (optimum at 7) and a soil temperature range between 5 and 30 °C (optimum 25 °C) (Ryden, 1983; Goodroad & Keeney, 1984; Scholefield et al., 1997; Swerts et al., 1997; Aulakh et al., 2001). The most critical factors are the NO_3^- concentrations, anaerobic conditions and the availability of organic C.

Denitrification is an important N transformation process in areas where soils and sediments are subject to water logging (e.g. wetlands), where they contained sufficient organic C and intercepted inputs of NO_3^- or NO_2^- in groundwater or surface water, or after nitrification. Thus, denitrification is generally recognized as the major process for N_2O production in soils, but also a mechanism for N_2O consumption by further reducing N_2O to N_2 (Firestone et al., 1980).

2.3 Factors influencing N_2O emissions

N_2O emissions are considered to be more driven by reduction (denitrification) than oxidation (nitrification) processes in soil although N_2O is also produced by nitrification (Bergsma et al., 2002). The ratio of denitrification production N_2O yield (N_2O/ N_2O +N_2) is generally considered to be regulated by nitrogen concentration in soils, carbon availability, oxygen, temperature, redox potential effects and soil pH.

2.3.1 NO_3^- concentration

The NO_3^- concentration is one of the key factors that influence the yield ($N_2O/ N_2O + N_2$) of denitrification, with higher NO_3^- concentrations apparently inhibited the conversion of N_2O to N_2, usually resulting in a higher N_2O yield (Weier et al., 1993). A higher level of NO_3^- in soils was known to result in incomplete and thus higher N_2O yield due to suppression of nitric oxide synthase activity, which was the enzyme responsible for conversion of N_2O to N_2 (Cho et al., 1997; Scholefield et al., 1997; Stevens & Laughlin, 1998). In long-term mineral N treated sandy loam soils with different KNO_3 concentrations experiments, long-term organic manure treated sandy loam soils and Lavesum soils show lower N_2O yield for the treatments where NO_3^- concentrations were $\leqslant$2 mM, and the ratios were clearly lower in manure fertilized than in mineral fertilizer treated soil. Much higher N_2O yield were found for the treatments with$\geqslant$10 mM NO_3^-, and the ratios were remarkably independent of the soil fertilizer history (Senbayram et al., 2012).

However, in aquatic ecosystem, Beaulieu et al. (2011) suggested higher NO_3^- concentration increases N_2O production, but does not increase the N_2O yield. Stream NO_3^- concentrations predicted N_2O emission rates when NO_3-N exceeded 95 μg·L-1 ($P = 0.01$, $r^2 = 0.16$), but below this concentration N_2O emission rates were uniformly low and unrelated to NO_3^- concentration.

2.3.2 Soil C

It is generally considered that increasing C availability decreases the ratio of N_2O yield (Dendooven et al., 1998) because organic carbon works as an electron donor for NO_3^- reduction. When carbon availability is high relative to the supply of the electron donor NO_3^- (high C:NO_3^-) Denitrification tends to yield more N_2, while low C:NO_3^- can result in more N_2O (Firestone et al., 1980). The ratio of e^- acceptor (NO_3) to CO_2 emission (a proxy for e^- donor availability) was a reliable (R^2=0.50%) predictor of the N_2O yield in the intact soils. All of the soils showed stable N_2O yield when NO_3/CO_2 was high and decreasing N_2O yield as NO_3/CO_2 approached 0 (Del Grosso et al., 2000).

However, some studies suggest that in anaerobic zones of fertilized soils, NO_3^- concentration may control the N_2O yield, while labile C concentration controls the denitrification rate (Tiedje, 1988; Weier et al., 1993). In streams and rivers, the N_2O yield was not related to the ratio of stream water NO_3^- concentration to dissolved or particulate organic carbon concentration.

2.3.3 Temperature

Because the activation energy of N_2O reduction was higher than the activation energy of N_2O production, low temperature affected $^-$ reductase enzymes to a greater extent than N_2O -producing enzymes (Holtan-Hartwig et al., 2002), it has been suggested that N_2 production decreases more drastically at low temperature than does N_2O production, more N_2O is produced at low temperatures and as a result, N_2O yield is increased (Avalakki et al., 1995). Laboratory studies with saturated soils have found that N_2O yield increased when temperature decreased (Bailey & Beauchamp,1973). N_2O yield increased in the cold seasons (autumn and winter) in all experiment plots (Hernandez & Mitsch, 2007). However, there are some studies reported a decrease in the N_2O yield with increasing soil temperature (Maag & Vinther, 1996, Rudaz et al. ,1999).

2.3.4 Water content

Tiedje (1988) suggested that in aerobic systems, oxygen availability is the main limiting factor of denitrification, whereas in anaerobic systems, NO_3 availability may be the key limiting factor. Water content was recognized as an essential factor to control denitrification as it controls anaerobic conditions or restricted O2 availability. The N_2O yield has often been found to decrease with increasing soil water content, particularly when the soil water content exceeds 75% WFPS (Davidson, 1992; Rudaz et al., 1999).

Soil moisture both affect soil redox status and oxygen diffusion, but resulted in the literatures are contradictory. The greatest N_2O fluxes from pasture soils was found at water-filled porosity space (WFPS) values higher than 60% when NO_3^- concentration was non-limiting (Dobbie & Smith 2003). The greatest N_2O emissions occurred at 80 and 100% WFPS where conditions were not reductive enough to allow the complete reduction to N2, but the N_2O yield was lowest under 120% WFPS and increased with decreasing soil moisture content (Ciarlo et al., 2007).

However, The N_2O yield has often been found to decrease with increasing soil water content (Davidson, 1992; Rudaz et al., 1999), particularly when the soil water content exceeded 75% WFPS (Davidson, 1992; Weier et al., 1993). Similarly, the measured N_2O yield was highest ($\geq$0.5) under dry conditions during summer and early autumn when denitrification was relatively inactive (RuzJerez et al., 1994). The N_2O emitted during water-logging was very little while N_2O emissions reached peak when drained the waterlogged soil (Flessa & Beese 1995). N_2O was lowest at soil water contents above 60% water filled pore space, and it was further declined in the presence of a well-developed plant canopy (Rudaz et al. 1999). Entice soils from

Canada displayed greater N_2O values with WFPS lower than 30% with respect to soils at WFPS higher than 50% (Elmi et al. 2003); at the latter WFPS values, probably a greater reduction of N_2O to N_2 occurred. An increase in the WFPS from 45.4% to 96.9% strongly decreased the N_2O yield. In dry soils the N_2O yield tended to be high and the emission of N2 was favored over the emission of N_2O with the increasing soil moisture (Rudaz et al., 1999).

In wetlands, permanently flooded wetlands showed low N_2O yield with a maximum of 4.5% in autumn 2005 and a minimum of 0.15% in spring 2005. In the permanently saturated zones, N_2O yield were more variable, ranging from 1.2% in spring 2004 to 19% in autumn 2005. N_2O yield increased in the cold seasons (autumn and winter) in all plots (Hernandez & Mitsch 2007). In flooded areas, average N_2O yield (11%) is higher than drained area (2%) (Davidsson & Leonardson ,1997).

Despite the extensive research, the effect of either soil moisture or a superficial flooding water layer on both N_2O and N_2 emissions was not clear and could not be used as a signal to predict the N_2O in denitrification separately.

2.3.5 Effects of redox potential

Many published papers in the literature found that soil Eh was significantly higher when fields were unflooded, or well-drained, compared to periods when the fields were flooded. Soil Eh increased up to 300 to 450 mV six days after drainage at 5 mm depth (Cai et al., 2001). Under submergence, the soil Eh values were highly negative and N_2O emissions were low (Majumdar et al., 2000). After seven days of incubation, the Eh values apparently decreased in the investigated soils by 3–121 mV

(Wlodarczyk et al., 2003). After flooding for 20 days, soil redox potential decreases to -100mV (Jiao et al., 2006).

It is also well recognized that the Eh increasing during drainage period reflecting the anoxic condition. Under laboratory conditions, soil Eh values significantly correlated with N_2O yield, suggesting that this soil parameter regulates the proportion of N gases emitted as N_2O (Ciarlo et al., 2007). Decreasing water levels were accompanied by high soil Eh, which will increase N_2O emissions. However, how soil redox potential decreased with anaerobic conditions and how reducing influence denitrification is still unknown.

Denitrification occurs when soil redox potential decreased to below 340 mV (Stumm, 1979) while nitrification activities normally occurs when soil Eh value is greater than 200 mv (Chen et al., 1997, Bauza et al., 2002). 0 mV is considered to be the most suitable soil redox potential for N_2O production with the addition of KNO_3 (Kralova et al., 1992). But there is no significant N_2O evolution occurred at 0mV Eh and N_2 evolution rates did not differ significantly where soil Eh stayed at about 100 mV in the same phase according to Cai et al., (2001). N_2O emission from rice paddy soils with various redox potentials, ranging from +500 to –250 mV (Masscheleyn et al., 1993). Two maximums N_2O evolution points were found at +400 mV where nitrification was the source and at 0 mV where N_2O was produced by denitrification. The more reducing the soils, the more N gases are emitted but the smaller the N_2O yield of resulting gas. The important effect of reductive conditions was supported by the significant and positive relationship between N_2O yield values and soil Eh values.

It should be emphasized that the Eh value above 400mV corresponded with the lowest N_2O emission after the first day of incubation (Wlodarczyk et al., 2003).

No agreement was reached that denitrification was most suitable at which level soil Eh and no quantitative results showed the relationship of soil redox potential and the gas productions from denitrification because of some unknown mechanisms. It may be caused by different respiration rates if two soils with the same moisture could have very different redox potentials (Li et al., 2000).

2.3.6 Soil pH

Soil acidity is known to influence the N_2O yield of denitrification. At lower soil pH the N_2O yield increased. It was reported that ample evidence from numerous studies stated that when the pH of soil is decreased, denitrification liberated more N_2O and the N_2O yield was increased (Šimek & Cooper, 2002). Increasing soil pH above 6.0 may offer a mechanism to mitigate N_2O emissions by shifting the balance between N_2O and N_2 (Zaman & Nguyen, 2010). In the pH range 4.0–8.0, the denitrification N_2O yield declined in linear (Liu et al., 2010). The N_2O yield increased with decreasing pH due to changes in the total denitrification activity, while no changes in N_2O production were observed (Čuhel et al., 2010).

The N_2O yield went down with the increase of pH from 6.2 to 7.4. And the plot means of N_2O yield decreased exponentially with increasing pH values above a threshold value of approximately pH=6.9 (Dannenmann et al., 2008). Similar trend of N_2O yield ratio was illustrated by Sun et al., (2012) that N_2O yield decreased in power function and has a dramatic decrease when pH was greater than 6.7. N_2O yield declined in asymptote from pH 4 to 7 with N_2O yield approach to a flat between 5.5

to 7 (Van den Heuvel et al., 2011). N_2O reduction to N_2 was halted until NO_3^- was depleted at low pH values, resulting in the construction of N_2O. As a consequence, N_2O yield decreased exponentially with pH.

It is more credible that the pH influences the ratio of denitrification production in a threshold. From literature listed above, between 5.5 to 7 pH, there is no significant difference in N_2O yield caused by pH.

3. GWP Calculation

3.1 Introduction of GWP

Global warming potential (GWP) is an emission metric defined to compare emissions of various components under a specific time horizon. GWP index of component is defined by a pulse emission of 1 kg of compound relative to that of 1 kg of the reference gas CO_2 based on the time-integrated global mean radiative forcing, which was developed (IPCC, 1990) and adopted for use in the Kyoto Protocol. GWP of CO_2 is 1 in 20 years, 100 years and 500 years as a reference gas. Direct GWP for CH_4 and nitrous oxide and other components was first estimated in the second IPCC report and updated in the fourth and fifth report in 2013 with inclusion of climate-carbon feedback. Gillett and Matthews (2010) included climate–carbon feedback in calculations of GWP for CH_4 and N_2O suggested that climate–carbon feedback should be considered and parameterized when used in simple models to derive metrics. Here we use the latest GWP values from the IPCC fifth report with the inclusion of climate-carbon feedback. CH_4 is 86 (CO_2 equivalents) in 20 years and 34 in 100 years. Nitrous oxides are 268 in 20 years and 298 in 100 years.

	Lifetime (years)		GWP_{20}	GWP_{100}	GTP_{20}	GTP_{100}
CH_4[b]	12.4[a]	No cc fb	84	28	67	4
		With cc fb	86	34	70	11
HFC-134a	13.4	No cc fb	3710	1300	3050	201
		With cc fb	3790	1550	3170	530
CFC-11	45.0	No cc fb	6900	4660	6890	2340
		With cc fb	7020	5350	7080	3490
N_2O	121.0[a]	No cc fb	264	265	277	234
		With cc fb	268	298	284	297
CF_4	50,000.0	No cc fb	4880	6630	5270	8040
		With cc fb	4950	7350	5400	9560

Notes:
Uncertainties related to the climate–carbon feedback are large, comparable in magnitude to the strength of the feedback for a single gas.
[a] Perturbation lifetime is used in the calculation of metrics.
[b] These values do not include CO_2 from methane oxidation. Values for fossil methane are higher by 1 and 2 for the 20 and 100 year metrics, respectively (Table 8.A.1).

Fig. 1. Table of GWP and GTP with and without inclusions of climate-carbon feedbacks in response to emissions of the indicated non-CO_2 gases. From Climate Change 2013: The Physical Science Basis Chapter 8 Anthropogenic and Natural Radiative Forcing p. 714.

Mondrian tracks CO_2, CH_4 and N_2O by the mass of C and N with the unit of g C m^{-2} y^{-1} and g N m^{-2} y^{-1}. To calculate the GWP for 20 years and 100 years, we first transfer the mass of C and N to the atomic weight of CO_2, CH_4 and N_2O components and then transfer the unit of g to kg. Then we can get the global warming of CO_2, CH_4 and N_2O per meter square per year. The estimated GWP is very similar with the GWP estimated by the CO_2 equivalent methods in Mosier et al. (2006) (1 kg N_2O ha-1=296 CO_2 kg ha-1, 1 kg CH_4 ha-1=23 CO_2 kg ha-1) and Brander, M., & Davis, G. (2012) (1kg CH_4= 25 kg CO_2). The difference is caused by different numbers of selected GWP indexes.

3.2 Calculation of GWP

Global warming potential of 1-hectare wetland for 20-year time horizon:

$$GWP_{20}\text{-}CO_2\ (\text{kg } CO_2\text{-eq ha}^{-1}\ \text{y}^{-1}) = CO_2\text{-C}\ (\text{g C m}^{-2}\ \text{y}^{-1}) \times \frac{44\ (atomic\ weight\ of\ CO2)}{12\ (atomic\ weight\ of\ C)} \times \frac{1\ (GWP\ of\ CO2\ in\ 20\ years)}{1000\ (g\ to\ kg)} \times 10000$$

$$GWP_{20}\text{-}CH_4\ (kg\ CO_2\text{-eq}\ ha^{-1}\ y^{-1}) = CH_4\text{-}C\ (g\ C\ m^{-2}\ y^{-1}) \times \frac{16\ (atomic\ weight\ of\ CH4)}{12\ (atomic\ weight\ of\ C)} \times \frac{86\ (GWP\ of\ CH4\ in\ 20\ years)}{1000\ (g\ to\ kg)} \times 10000$$

$$GWP_{20}\text{-}N_2O\ (kg\ CO_2\text{-eq}\ ha^{-1}\ y^{-1}) = N_2O\text{-}N\ (g\ N\ m^{-2}\ y^{-1}) \times \frac{44\ (atomic\ weight\ of\ N2O)}{28\ (atomic\ weight\ of\ 2N)} \times \frac{268\ (GWP\ of\ N2O\ in\ 20\ years)}{1000\ (g\ to\ kg)} \times 10000$$

Global warming potential of 1-hectare wetland for 100-year time horizon:

$$GWP_{100}\text{-}CO_2\ (kg\ CO_2\text{-eq}\ ha^{-1}\ y^{-1}) = CO_2\text{-}C\ (g\ C\ m^{-2}\ y^{-1}) \times \frac{44\ (atomic\ weight\ of\ CO2)}{12\ (atomic\ weight\ of\ C)} \times \frac{1\ (GWP\ of\ CO2\ in\ 100\ years)}{1000\ (g\ to\ kg)} \times 10000$$

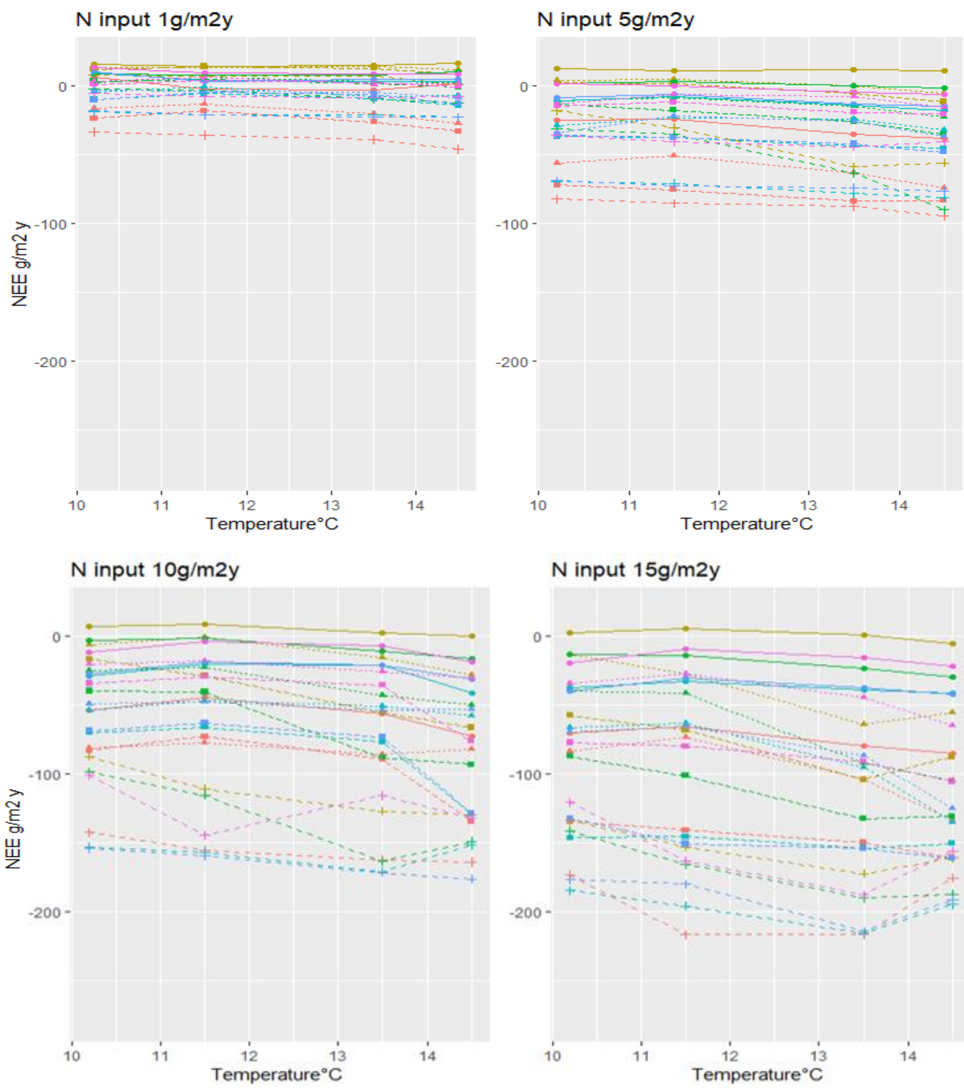
$$GWP_{100}\text{-}CH_4\ (kg\ CO_2\text{-eq}\ ha^{-1}\ y^{-1}) = CH_4\text{-}C\ (g\ C\ m^{-2}\ y^{-1}1) \times \frac{16\ (atomic\ weight\ of\ CH4)}{12\ (atomic\ weight\ of\ C)} \times \frac{34\ (GWP\ of\ CH4\ in\ 100\ years)}{1000\ (g\ to\ kg)} \times 10000$$

$$GWP_{100}\text{-}N_2O\ (kg\ CO_2\text{-eq}\ ha^{-1}\ y^{-1}) = N_2O\text{-}N\ (g\ N\ m^{-2}\ y^{-1}) \times \frac{44\ (atomic\ weight\ of\ N2O)}{28\ (atomic\ weight\ of\ 2N)} \times \frac{298\ (GWP\ of\ N2O\ in\ 100\ years)}{1000\ (g\ to\ kg)} \times 10000$$

4. Temperature's effects on GHG emissions

Compared with N inflow, water residence time, water level (WL) scenarios, temperature had the smallest effects on all three greenhouse gases. Only with the difference of temperature greater than 2°C were simulations significantly different ($p<0.05$).

Under low nitrogen inflow, low water residence time, our simulations show similar NEEs of CO_2 under four temperature levels in all water scenarios. As nitrogen inflow reached 10 g N m^{-2} y^{-1}, under short water residence time (1day), all water scenarios got lowest NEEs at highest temperature 14.5 °C. This may be caused by the longer growing season came with higher temperature, or greater internal N cycling. But under longer water residence times, NEEs were more variable among different temperature levels. Lowest NEEs happened in temperature 13.5°C. This may because higher temperature and longer growing season encouraged plant growth but also promoted plants and soil respirations and then released more CO_2 into atmosphere. Water residence time had positive effects on nitrogen cycling, in longer water residence time, more nitrogen emitted to atmosphere as N_2O by denitrification and left less for plants. This may also explain why NEE reaches lowest at temperature 13.5°C in long water residence time but not short.



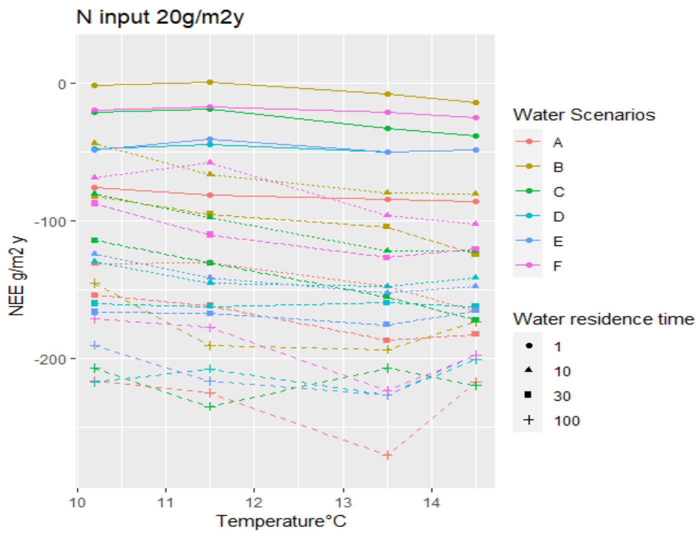


Fig. 2. MONDRIAN model results for NEE of CO_2 (as g C m^{-2} y^{-1}) as functions of temperatures in our simulations. Different lines refer to six different WL (water level) scenarios with constant (A-C) and seasonally fluctuating (D - F) water level. Different symbols refer to different water residence time.

CH_4 emissions increased with temperature under low N inflow ($\leqslant$10 g N m^{-2} y^{-1}). But under high N inflow (20 g N m^{-2} y^{-1}) and long water residence time (100 days). CH_4 emission under temperature 13.5°C was slightly higher than 14.5°C. Considering negative NEE also reached the greatest value at the temperature of 13.5°C, we speculate that in MONDRIAN, 13.5°C is the optimal temperature for ecosystem C storage, considering the tradeoff between N cycling and decomposition. Plant stored most carbon under 13.5°C, so more carbon comes to the litter pool and heterotrophic respiration.

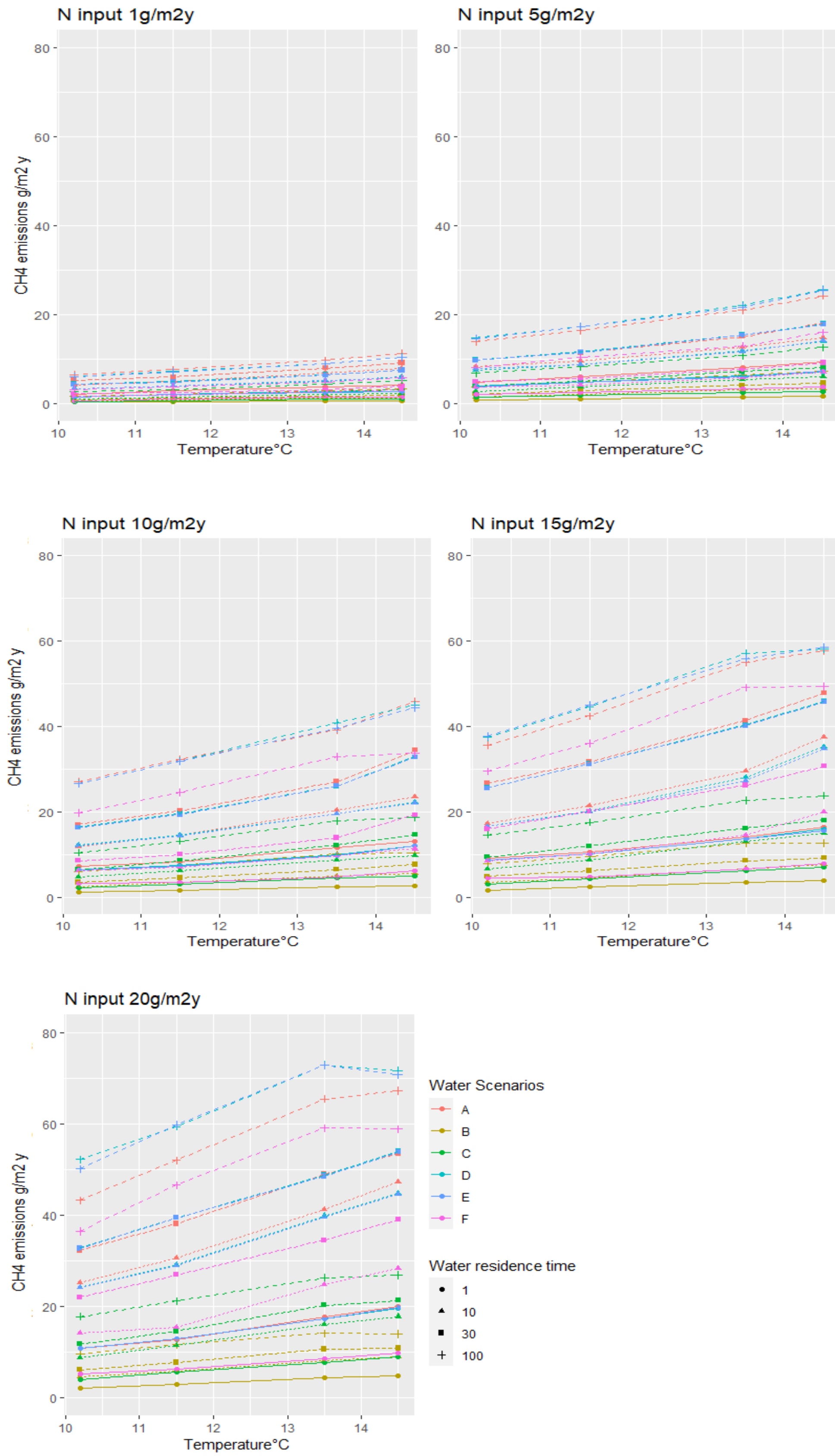
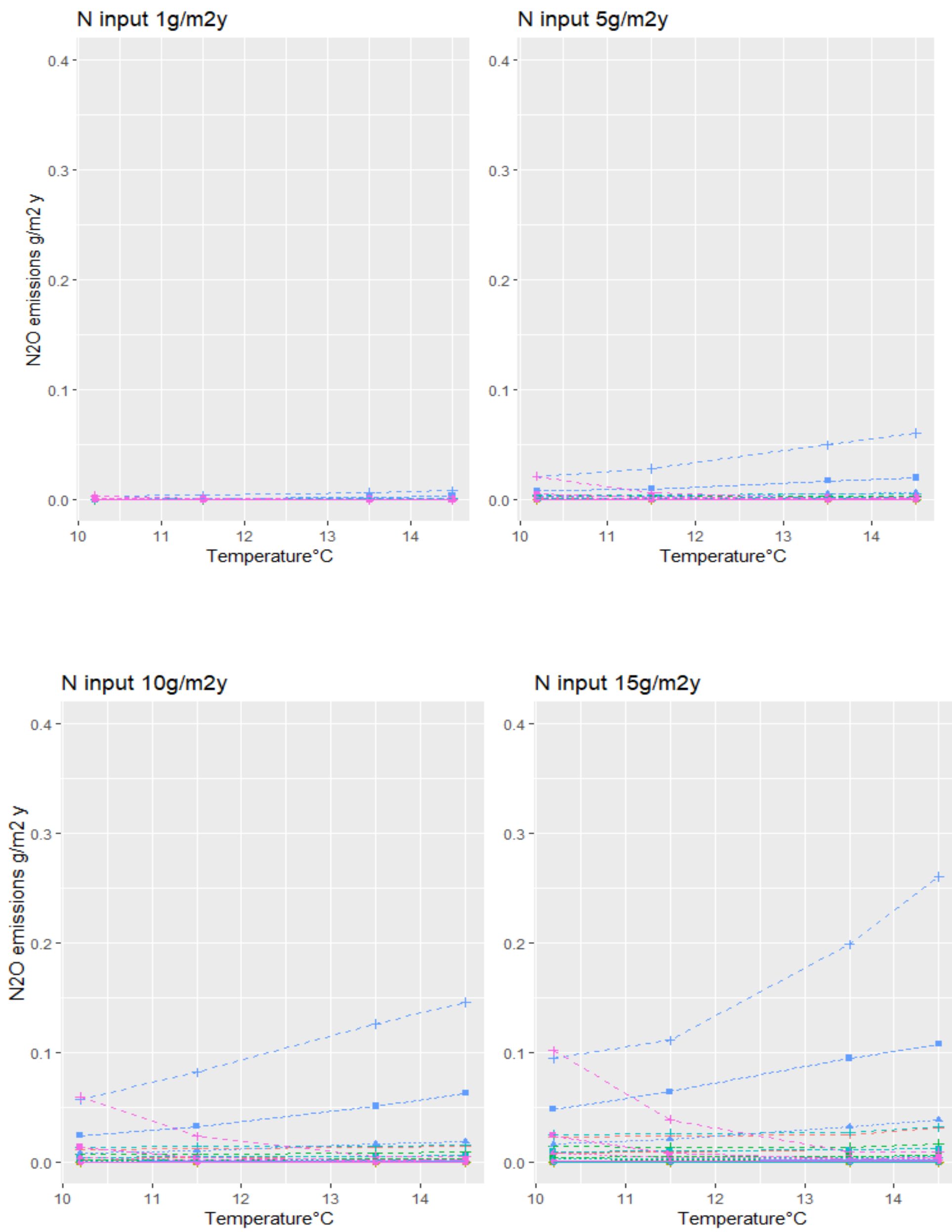

N input 1g/m2y
N input 5g/m2y
N input 10g/m2y
N input 15g/m2y
N input 20g/m2y
CH4 emissions g/m2 y
Temperature°C
0
20
40
60
80
10
11
12
13
14
Water Scenarios
A
B
C
D
E
F
Water residence time
1
10
30
100

Fig. 3. MONDRIAN model results for CH_4 emissions (as g C m^{-2} y^{-1}) as functions of temperatures in our simulations. Different lines refer to six different WL (water level) scenarios with constant (A-C) and seasonally fluctuating (D-F) water level. Different symbols refer to different water residence time.



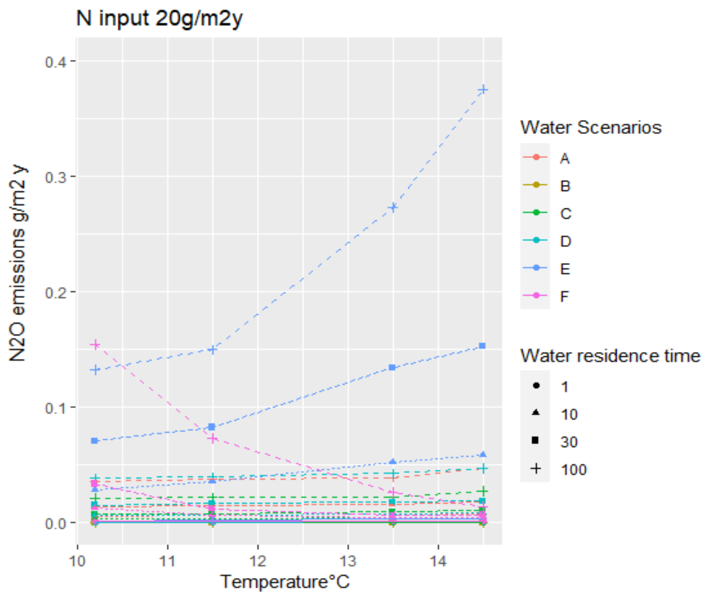


Fig. 4. MONDRIAN model results for N_2O (as g N m^{-2} y^{-1}) as functions of temperatures in our simulations. Different lines refer to six different WL (water level) scenarios with constant (A-C) and seasonally fluctuating (D-F) water level. Different symbols refer to different water residence time.

Besides water scenario F, N_2O emissions increased with temperature, which was different from NEE and CH_4 that had the greatest value under 13.5°C. Denitrification was not dominant by plants in MONDRIN, while there was some trade-off between respiration and photosynthesis in plants when temperature increased. In water scenario F, for some unknown reason, N_2O emissions exhibited an opposite pattern.

5. Strengths and weaknesses of our modeling approach

There are only a few models that model three greenhouse gases together, most ecosystem models only focus on one or two greenhouse gases. MONDRIAN simulated three greenhouse gases at the same time under the same environment conditions, which could illustrate the linkage and interaction between plant, N cycle and C cycle.

Different from field experiments and measurements that only look at one or two environment factors at one time, Mondrian has the strength to simulate variable environment factors. This provided us enough data to find which environment factor is the most essential for GHG emissions and GWP. Mondrian also has the strength to model water residence time, which is difficult to be done in experiments.

However, in Mondrian, we didn't include some environment elements such as pH and Eh into sub-models for GHG simulation because the agreements of how pH and Eh influence GHG emissions haven't been reached and we also don't know the exact values of soil pH and Eh in Great Lakes coastal wetlands. They may bring uncertainties to our estimated GHG emissions. CH_4 and N_2O are more sensitive to pH and Eh than NEE, which may also influence the summed GWP. pH and Eh varies between different wetlands and they will cause the spatial heterogeneity of wetlands GHG emissions GWP.

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