Flow velocity and nutrients affect CO$_2$ emissions from agricultural drainage channels in the North China Plain

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Abstract

Background

Groundwater is typically over-saturated in CO$_2$ with respect to atmospheric equilibrium. Irrigation with groundwater is a common agricultural practice in many countries, but little is known about the fate of dissolved inorganic carbon (DIC) in irrigation groundwater and its contribution to the CO$_2$ emission inventory from land to the atmosphere. We performed a mesocosm experiment to study the fate of DIC entering agricultural drainage channels in the North China Plain. Specifically, we aimed to unravel the effect of flow velocity and nutrient on CO$_2$ emissions.

Results

All treatments were emitting CO$_2$. Approximately half of the DIC in the water was consumed by TOC production (1-16%), emitted to the atmosphere (14-20%), or precipitated as calcite (CaCO$_3$) (14-20%). We found that DIC depletion was stimulated by nutrient addition, whereas more CO$_2$ evasion occurred in the treatments without nutrients addition. On the other hand, about 50% of CO$_2$ was emitted within the first 50h under high flow velocity. Thus, in the short term, high nutrient levels may counteract CO$_2$ emissions from drainage channels, whereas the final fate of the produced biomass (burial versus mineralization to CO$_2$ or even CH$_4$) determines the duration of the effect.

Conclusion

Our study reveals that both hydrology and biological processes affect CO$_2$ emissions from groundwater irrigation channels. The estimated CO$_2$ emission from total groundwater depletion in the North China Plain is up to 0.52 ± 0.07 Mt CO$_2$ y$^{-1}$. Thus, CO$_2$ emissions from groundwater
irrigation should be considered in regional CO₂ budgets, especially given that groundwater depletion is expected to acceleration in the future.

**Keywords:** CO₂ emissions; agricultural irrigation drainage; controlled experiments; groundwater; North China Plain.
1. Background

Groundwater is a critical water resource around the globe ensuring food and water security (Giordano 2009). Irrigation with groundwater for agricultural activities is a common practice in many arid and semi-arid regions (Siebert et al. 2010). However, over exploitation of groundwater has led to severe groundwater depletion in several regions of the world (Famiglietti 2014). Areas most affected by groundwater depletion are California and Midwest in the U.S., Northern India, and the North China Plain (NCP) (de Graaf et al. 2019). In the NCP approximately 70% of the irrigated area is currently groundwater-fed (Wang et al. 2012; Zhu et al. 2013) which causes the groundwater level to drop by more than 2 cm per year (Feng et al. 2013). While several studies focus on the importance and influence of the dramatic groundwater level drop, the further fate of the pumped irrigation water is much less studied (Jahangir et al. 2012).

Groundwater is typically 10-100 fold over-saturated with CO$_2$ (Macpherson 2009), even up to 250 times the atmospheric equilibrium value (Borges et al. 2018). Thus, if it is pumped to the surface, CO$_2$ is released. First estimates show that CO$_2$ emissions from groundwater pumping probably represent a globally significant source of CO$_2$ (Wood and Hyndman 2017), with both CO$_2$ liberation from the water and CO$_2$ production due to pump energy generation contributing to the negative climate impact of groundwater irrigation (McGill et al. 2018). CO$_2$ has been recognized as the dominant driver of climate change resulting in tremendous deteriorative impacts on the environment and society at a global scale (Myhre et al. 2013). As one of the major emission sources of CO$_2$, agricultural land plays an important role in the global carbon cycle (Liang et al. 2016). Direct CO$_2$ emissions from agriculture have been well-documented in many regions (Houghton et al. 2012; West and Marland 2003; Zamanian et al. 2018). However, indirect emission sources, such as irrigation drainages and rivers receiving drainage water, may
account for a large part of the uncertainties in the carbon budgets of agricultural ecosystems (Koschorreck et al. 2019; Butman et al. 2016; Hotchkiss et al. 2015; Schrier-Uijl et al. 2011).

If CO₂ containing water equilibrates with the atmosphere, not only the dissolved CO₂ but also other species of the carbonate system have to be considered (Stumm and Morgan 2012). Existing estimates of CO₂ emissions from groundwater pumping assume complete evaporation of the pumped water, leaving solutes and solids at the surface. Under such conditions, each molecule of CO₂ outgassing is theoretically produced from two molecule of carbonate hardness (refers to HCO₃⁻ + CO₃²⁻) to re-equilibrate with atmospheric CO₂ accompanied by one molecule of carbonate precipitation simultaneously (Wood and Hyndman 2017; Duvert et al. 2019). Thus, maximum CO₂ liberation from groundwater dissolved inorganic carbon could be calculated from the bicarbonate content of the groundwater (Macpherson 2009). When a large part of dissolved inorganic carbon (DIC) containing irrigation water drains into surface waters, DIC may have four different fates: evasion as CO₂, carbonate precipitation, fixation into biomass by TOC production, and downstream transport (Cole et al. 2007).

Streams are recognized as important CO₂ sources to the atmosphere (Borges et al. 2015; Raymond et al. 2013). In streams the distribution among the four fates of groundwater inorganic carbon is controlled by both hydrological and biochemical processes and their complex interactions (Halbedel and Koschorreck 2013; Borges et al. 2018). Flow velocity, characterized by fluctuating hydraulic conditions due to flood irrigation or excessive utilization of water resources, usually results in enhanced carbon export from terrestrial and wetland habitats to fluvial networks that subsequently become a source of CO₂ (Dinsmore et al. 2013; Borges et al. 2015; Borges et al. 2019). Turbulence at the air-water interface, which is dependent on the river geomorphology and the river flow, affects the gas transfer coefficient of CO₂, which ultimately
determines fluvial CO₂ emissions (Gómez-Gener et al. 2015; Liu et al. 2017; Liu and Raymond 2018). On the other hand, increasing nutrient levels stimulate biological processes such as algal growth, which decrease DIC concentration by converting CO₂ to organic carbon via photosynthesis (Crawford et al. 2016). Agricultural drainage water is typically high in inorganic nutrients. Thus, our hypothesis is that both nutrients and flow velocity mediate the relative importance of uptake versus outgassing of CO₂ accompanied with calcite precipitation from the dense agricultural drainage channels transporting pumping groundwater.

However, quantifying these processes of DIC depletion remains challenging. It is difficult to disentangle the effects of both factors on the fate of inorganic carbon from field observations only, primarily due to uncontrolled environmental conditions. We therefore performed a mesocosm experiment in the field to explore how CO₂ emissions from irrigation groundwater respond to nutrients and flow velocity treatments. The goals of this study are to 1) quantitatively testify the effects of nutrients and flow velocity on CO₂ emissions and the carbon budget of irrigation drainage channels in a typical agricultural region in China, and 2) provide implications to CO₂ emission potential from the irrigation groundwater in the NCP as well as other similar regions worldwide.

2. Methods

2.1 Study area

Our study was conducted in the Yucheng Comprehensive Experiment Station of Dezhou Irrigation District (DID) between 115°45′- 117°36′ E and 36°24′ - 38°00′ N, located in the North China Plain. The annual-averaged precipitation is 587 mm (ranges from 286 to 1034 mm). Precipitation occurs mostly from June to September, which accounts for 75% of the total annual amount. Annual evaporation is between 900 and 1400 mm and annual mean temperature is
12.8°C (Zhao et al. 2018). The groundwater for agricultural irrigation is characterized by high alkalinity and enriched with agricultural nutrients when it enters the drainage channels (Zhou et al. 2012). Groundwater bicarbonate concentrations in the NCP can range between 1.55 to 7.65 mmol L\(^{-1}\) (Chen et al. 2005). The ditches and canals are mainly artificial and lined with concrete.

Historically, DID has been characterized by anthropogenic activities, particularly intensive agriculture development, which has been causing a high demand of water resources in the NCP (Zhang et al. 2015). Irrigation drainages were built during the 20\(^{th}\) century to increase crop yield in the salinized soil by diverting water from the lower reaches of the Yellow River to DID. Given that the surface water cannot fulfill the demand from agricultural and industrial production, over-exploitation of groundwater had been frequently observed through the sharp decrease of the groundwater table and heavy pollution therein (Shao et al. 2013). To eliminate the influence of soil salinity on crop growth, flooding irrigation is still commonly applied among local farmers. This enhances nutrient inputs from irrigated groundwater into the surface water network that subsequently become a source of CO\(_2\). Based on farmer’s practice when they irrigate the crops, our experiment simulate that stream drainage collected from groundwater-irrigated agricultural land. For better representation of local groundwater, we used groundwater from a local irrigation well as inlet water to our experimental system.

2.2 Mesocosm setup

Cubic mesocosms (volume 0.2 m\(^3\)) were constructed to mimic drainage channels. The physical design of our mesocosms follows that from Petersen et al. (2003). The systems are composed of sixteen cuboid polyvinyl chloride plastic tanks with 0.9 m in length, 0.3 m in width, and 0.6 m in depth. Depth of water was set to 0.5 m. Mesocosms were placed outdoor and remained open and in contact with the field atmosphere to ensure natural light and weather conditions. The
containers were sunk into the ground to buffer heating from ambient atmosphere temperature and solar radiation. The electrical wiring for power supplying was also buried. The upper edge of the tanks was 10 cm above the ground so that no surface runoff could flow into containers during rainstorms. The containers allow a factorial design combining two nutrient levels with two flow velocity levels in four replicates (Figure S1). The tanks were equipped with two alternative submerged pumps to mimic river flowing. Each mesocosm had an individual pump (65W or 15W) to provide continuous flowing condition and to preclude water pressure differences of connected pipes when sharing the same pump under the same treatment. The pumps were placed in mesh cages to prevent snails, insects, and floating fragments from suction into the pump and to reduce the risk of clogging. The inlet of the pump was on the shorter side of the tank to simulate a unit of water channel (Figure 1). We set the length to width ratio as 3:1 to establish a realistic flow regime in the central part of our setting. The middle section along the longitudinal direction of these tanks can be considered a homogeneous flow field with simple physical boundaries.

2.3 Experimental procedure

Groundwater was collected from a nearby agricultural irrigation well from a depth of 5 m and pumped into the pre-cleaned tanks without sediments. Nutrients were added into the tanks at the beginning of the experiment for the high-nutrient treatment, while low-nutrient tanks received no additional nutrients. Particularly, high-nutrient tanks were instantaneously fed with 40 mg P m⁻³ and 4000 mg N m⁻³ as K₂HPO₄ and Ca(NO₃)₂, respectively. We set the nutrient enrichment level by mimicking the two alternative states existing in the local drainage system. The nitrate and ammonia concentrations of the study groundwater well were approximately 0.02 mg N L⁻¹ and 5.8 μg N L⁻¹, respectively, while the nitrate concentration of drainages in a field survey in
Yucheng (on 16th and 17th of September) varied from 0.02 to 0.42 mg N L\(^{-1}\) with a mean value of 0.17 mg N L\(^{-1}\) (Table 1). Other parameters in the experimental water were comparable to that in the surface water as well (Table 1). We designed the initial nitrate concentration for the high nutrient experimental group at a level above the average nitrate concentration (0.3 mg N L\(^{-1}\)). Phosphorous was added with the N: P molar ratio of 10:1 following Lone et al. (2005).

We choose flow velocities in surrounding drainage channels as a reference. Flow velocity of local drainages varied from 0.001 to 0.340 m s\(^{-1}\) during our field sampling. Accordingly, two levels of flow velocity were set to 0.1 and 0.4 m s\(^{-1}\). Pumps were cleaned manually every three days. It is expected that there was little CO\(_2\) degassing through pumping itself, since the submerged pumps were tested for air-tightness before usage and it is expected that any artifact would be equal between low and high nutrient treatments because the same pumps were used.

Overall, there were four (2×2) treatments with 4 replicates each in our experimental design, which are denoted as: high nutrient and high flow velocity (A+H); high nutrient and low flow velocity (A+L); low nutrient and high flow velocity (N+H); and low nutrient and low flow velocity (N+L).

The experiments was conducted between 31st August and 15th September 2018. Sampling and measurements of the physical and chemical parameters was performed at 0, 4, 16, 32, 64, 112, 160, 280 hours. The experiment measurement was finished after 12 days when the CO\(_2\) concentration had reached equilibrium with the atmosphere. Due to the mesocosm malfunction, the N+H treatment has only one replicate after 50 h.

2.4 Sampling and analysis

Water temperature, dissolved oxygen (DO), and electrical conductivity (EC) were measured using multi-parameter probes (Hach H40d, USA). Water level and flow velocity were recorded
by using a flow meter (HR-2, China) in parallel to each sampling. Water samples were collected to quantify concentrations of nitrate, ammonium, DIC, alkalinity, and TOC. For determination of NO$_3^-$-N and NH$_4^+$-N concentration, water samples were filtered using 0.45 μm filters by spectrophotometry (TU-1810DSPC, China). Calibration curves were produced using reference samples according to quality control standards and were then applied to evaluate data from each set of samples. Reagents, procedural blanks, and samples were measured twice in parallel, with average values reported. The differences between two replicates were within 5% of the mean value for all samples. NO$_3^-$ and NH$_4^+$ concentrations could be measured at precisions of 2.6% and 8.6%, respectively. DIC and TOC were analyzed with a Vario TOC Analyzer (Elementar Analysensysteme GmbH, Germany). The detection limits of DIC and TOC were 4 and 1 μg L$^{-1}$ with precisions of 1.5% and 5%, respectively. Alkalinity was determined by titration with ~0.01 M H$_2$SO$_4$ at a precision of 6%. While the measured TOC data could not be directly used. We used two methods to quantify CO$_2$ emissions during our experiments: A carbon budget approach and direct flux measurements using floating chambers (see Supporting Information for method details).

2.5 Calculation of C budgets

Changes of DIC in the mesocosms can be separated into three parts: carbon dioxide evasion, calcite precipitation, and total organic carbon (TOC) production (Figure 1):

$$\Delta DIC = \Delta CO_2 + \Delta CaCO_3 + \Delta TOC$$ (1)

To verify whether carbonate precipitation was likely to occur within the mesocosm, we calculated calcite saturation indices (SIs) using PHREEQC (Parkhurst and Appelo 2013). Because we did not measure calcium concentrations in the mesocosm, we used historical rainy season data from irrigation ditches in Dezhou District (Li et al., 2014) and derived possible SIs.
with 1.28 ± 0.16 (mean value ± standard deviation). Therefore, we assumed calcite precipitation occurred in all mesocosms, with 1 mol each of CO₂ outgassed and CaCO₃ precipitated from 2 mol of HCO₃⁻ according to Wood and Hyndman (2017):

\[ 2HCO_3^- + Ca^{2+} = CO_2 \uparrow + CaCO_3 \downarrow + H_2O \]  

(2)

CO₂ evasion depends on CO₂ concentration and the physical gas transfer velocity (Liu and Raymond 2018). The CO₂ concentration is affected by the thermodynamic carbonate equilibrium. TOC formation is a biological process that converts inorganic carbon into organic matter. At any time, the variation for DIC is denoted as:

\[ \Delta DIC_0 - \Delta DIC_t = \Delta CO_2 + \Delta CaCO_3 + (TOC_t - TOC_0) \]  

(3)

Equation (3) is based on our hypothesis that CO₂ in the system was over-saturated and TOC was generated during the experiment, \( DIC_0 \) and \( TOC_0 \) is the amount of DIC and TOC at the initial time, respectively, and \( DIC_t \) and \( TOC_t \) is the amount of DIC and TOC at time \( t \), respectively. \( \Delta CO_2 \) and \( \Delta CaCO_3 \) is the amount of CO₂ outgassing and calcite precipitating during time 0 to time \( t \), respectively. Combined with equation (2),

\[ \Delta CO_2 = \Delta CaCO_3 \]  

(4)

This is a conservative estimate as we note that the ratio of \( \Delta CO_2:\Delta CaCO_3 \) can range from 1.18 to 1.88 (Macpherson 2009). The CO₂ evasion could be deduced by the difference between the variation amount of DIC and the variation amount of TOC, re-arranging equations (3) with (4) gives:

\[ \Delta CO_2 = \frac{(DIC_0 - DIC_t) - (TOC_t - TOC_0)}{2} \]  

(5)

Because TOC data were not available, we estimated the TOC generation indirectly from total inorganic nitrogen (TIN) consumption. Assuming the molar C:N ratio in freshwater being higher than the Redfield ratio of 106:16 (Hecky et al. 1993; They et al. 2017), TOC production could be
estimated from the consumption of nitrate and ammonium, which are the main species of nitrogen in the groundwater system with nitrate accounting for the majority, based on a C:N ratio of 10:1 (Stubbins 2016). We assume that denitrification as a process that removes N from the system can be neglected in our case because our system was turbulent and well aerated.

Our mass balance was calculated by multiplying the concentrations with the varying water volume in the setup (mesocosm bottom area \( \times \) decreasing water level with negligible volume of the water in pipes and pump), so the evaporation would not influence our result.

We performed a series of analysis of variance (ANOVA) to explore the patterns of DIC, TOC, and CO\(_2\) and their relationship to nutrient and flow velocity. The concentration of CO\(_2\) at given DIC and alkalinity was calculated using standard dissociation constants of the carbonate system (Zeebe and Wolf-Gladrow 2001). Data were log-transformed to satisfy assumptions of residuals normal distribution. ANOVA was applied to test for overall statistical differences among treatments. The ratio to the initial amount of the above parameters for each of the mesocosm was carried out to test for the treatment effects using ANOVA. In the model, nutrient and flow velocity were treated as the fixed effect, and temporal pseudo-replication from repeated sampling over time was considered as nested within each mesocosm as random effects. The comparison of DIC and CO\(_2\) changes is given by the different slope of a first-order reaction of \( \log_{10} \) DIC or \( \log_{10} \) CO\(_2\) over time to test for statistical differences for each treatment and mesocosm. All calculations, statistical analysis, and data visualization were performed using R version 3.5.1 (R Core Team 2019).
3. Results

3.1 Significant differences among four treatments

The differences of flow velocities and nutrients among the four treatments were significant at the beginning of the experiment (Table 2). The nitrate concentration was similar between high and low flow with a larger variation range in high flow treatments. Because of some clogging of the pumps, the flow velocity fluctuated at a larger range at high flow compared to the low flow velocity.

At first, DO saturation increased exponentially over time in all mesocosms (Figure 2). The initial DO concentration at high flow was higher than that at low flow at the starting time, probably because more turbulences at high flow mixed more oxygen into the water before the first sampling. DO saturation varied dissimilarly over time and treatments as well. Mesocosms with nutrient additions developed a clear over-saturation, showing that TOC production was stimulated by nutrient additions. The A+L treatment reached the highest over-saturation. On the contrary, the control mesocosms rapidly reached equilibrium with atmosphere. As expected, equilibration was faster at high flow.

EC in the high flow velocity treatments showed a similar trend with a sharp decrease from 2.24 mS/cm to 1.95 mS/cm in the first 150 h after which it stayed constant (Figure 2). The low flow velocity treatments showed a steadily decrease from 2.24 mS/cm to 1.95 mS/cm from the start to the end of experiment.

DIC and alkalinity were used to calculate the CO2 concentrations at the beginning and in the end. At the end of the experiment in the high nutrient treatment, pCO2 in water was below that in the atmosphere, indicating CO2 uptake. Assuming alkalinity has a linear decrease over time accompanied with known DIC changes (Figure 3, a-d), we calculated the pCO2 at any time in
each mesocosm using the CO2SYS program (Lewis et al. 1998). Thus, the time when $p\text{CO}_2$ in each mesocosm was equal to $p\text{CO}_2$ in the atmosphere ($p\text{CO}_2\text{air} = 395$ μatm) could be estimated. After about 125 and 235 h, the systems switched to CO2 uptake under the A+H and A+L treatments, respectively (Figure S2). The N + L treatment reached CO2 equilibration with atmosphere until the end of experiment.

3.2 DIC and TOC

The DIC amount in all treatments decreased continuously by 31-48% during the experimental period (Figure 3). Decrease of DIC was largest in the A + H treatment and lowest in the N + L treatment. The amount of DIC in the system was significantly different between the two nutrient treatments ($p = 0.041$), as well as between the two flow velocities ($p = 0.020$). DIC in the N + H treatment decreased rapidly at the beginning of the experiment (particularly at the first 50 h). The decreasing rate of DIC under the A + H treatment surpassed that under the N + H treatment, while the rate was relatively slow but steadily after 170 h. The rate of DIC decrease was also strongly related to flow velocity ($p = 0.006$) but had insignificant relationship with nutrients. Moreover, there was a significant interaction of flow velocity and nutrients in the DIC decrease slope showing a combined effect between the two factors ($p = 0.043$).

The TOC increase in the high nutrient treatments was evidently much higher than the one in the treatment without nutrients addition (Figure 3) and independent of flow velocity. In the low nutrient treatments, TOC did not significantly change during the experiment, indicating little TOC production in these systems. This is consistent with the DO data which showed no O2 oversaturation in the low nutrient treatments (Figure 2).
3.3 CO₂ evasions among four treatments

All mesocosms were net sources of CO₂ during the experimental period (Figure 4). Always positive fluxes (except at the end of the experiment) were confirmed by our floating chamber measurements (Figure 4, e-h). The high flow treatments reached CO₂ equilibrium between water and atmosphere faster (Figure S2). The rate of CO₂ change also shows the significant difference between flow velocity treatments (p = 0.024). High flow velocity sped up CO₂ evasion. More CO₂ was emitted significantly under the high flow velocity (p = 0.005) and low nutrient condition (p = 0.096). CO₂ emission from the low nutrient treatments was 35% higher than that in the high nutrient treatments in average.

CO₂ evasions of the N+H treatment increased rapidly during the first 80 h, and remained nearly constant after 150 h. The A+H treatment emitted markedly a lot of CO₂ at the beginning but the flux became lower over time. CO₂ evasion from the two low flow treatments exhibited a similar behavior with relatively gentle and steady CO₂ emissions, and the N+L treatment released evidently more CO₂ than the A+L treatment.

Combined with the result of pCO₂ changes (Figure S2), CO₂ uptake could occur by the time when pCO₂ concentration dropped below pCO₂air. The floating chamber measurement also showed that some CO₂ was taken up (CO₂ flux < 0) under the high nutrient treatments at the time of 280h. The rate of CO₂ uptake can be calculated from pCO₂ and the gas transfer velocity (k₆₀₀):

\[ f_{CO₂} = k₆₀₀ \cdot k_H \cdot (pCO₂ - pCO₂air) \]  

\( k_H \) is Henry’s constant for CO₂ at a given temperature and salinity (Weiss 1974). Gas transfer velocity (k₆₀₀) could be calculated from the initial DIC depletion in the low nutrient treatments assuming that there was little TOC produced in these systems (Figure 3 g, h). Assuming k₆₀₀ being constant and equivalent under the same flow velocity treatments, k₆₀₀ was 0.93 and 0.23 m
$d^1$ in the high and low flow velocity treatments, respectively. Using these $k_{600}$ values and the final $pCO_2$ we can calculate the CO$_2$ flux at the end of the experiment using equation (6). Multiplying that flux with the duration of the under-saturated period results in an average total CO$_2$ uptake of 42 and 9.5 μmol in the A+H and A+L treatments, respectively. This is much lower than the observed changes in DIC. Thus, uptake did not significantly contribute to the total C budget of the experiment (Figure 4).

4. Discussion

4.1 Carbon dynamics

Our results show that flow velocity and nutrient level determine the rate and amount of CO$_2$ evasion, respectively. CO$_2$ evasion depends on both CO$_2$ concentration and the gas transport coefficient ($k$) in equation (6) (Alin et al. 2011; Raymond et al. 2012). With the CO$_2$ evasions under the same flow treatments showing similar tendency over time, flow velocity altered $k$, which determined the rate of CO$_2$ emission. Meanwhile, treatments with the same nutrient level ended with similar amount of CO$_2$ evasion, suggesting that the nutrient level ultimately dictates the quantity of CO$_2$ emission. Providing that more TOC was generated in the high nutrient treatment, our results confirm that TOC generation reallocate the depletion of inorganic carbon.

Our results also highlight the interaction of the flow and nutrient speeding up the depletion rate of DIC in drainage channels ($p = 0.043$). However, there was no significant synergistic effect of velocity and nutrients on the final DIC amount remaining in the system ($p = 0.40$). Flow velocity significantly altered the slope of DIC and CO$_2$ over time, indicating that flow velocity dominated the rate of DIC consumption and CO$_2$ emissions. Simultaneously, flow velocity influences the quantity of DIC consumption as well, possibly by means of regulating on ecosystem metabolism. High flow can intensify the capacity of an ecosystem to store and process
carbon (Aristi et al. 2014). TOC production at high flow velocity could be enhanced by higher light and nutrient availability throughout the water column due to better mixing (Moss 2009). Low flow on the other hand may promote sedimentation, thereby improving water clarity which may increase TOC production (Crawford et al. 2016). Nutrients affect the quantity of both CO₂ and DIC by altering the pattern of the inorganic carbon utilization through ecosystem processes (i.e. gross primary production, ecosystem respiration) (Benstead et al. 2009; Williamson et al. 2016). Nutrient enrichment may accelerate TOC processing, transformation, and export, potentially altering food-web dynamics and ecosystem stability in the long term (Benstead et al. 2009). Higher water temperature enhances photosynthesis enzyme activity that favors the biomass growth (Hall Jr. et al. 2015). In our study, the synergy of both factors cannot be explained by light availability or temperature because turbidity was low due to lack of sediment and temperature did not differ between treatments (mean water temperature of 25.0 ± 1.0 °C within each sampling). Most probable, better mixing at high flow prevented possible local nutrient limitation of photosynthesis in our experiment.

4.2 Uncertainty

4.2.1 Effects of C:N ratio on carbon budgets

Our TOC results are sensitive towards the chosen C:N ratio (10:1 in our case). We examined the responsiveness of the C:N ratio to the DIC allocation in our experiment by calculating carbon mass balances for different C:N ratios (C:N = 5, 106:16 (Redfield ratio), 10 (used in this study), and 15) (Figure S3). Variation of the C:N ratio changed the absolute amount of CO₂ emitted from the high nutrient treatments but did not change the general pattern.
4.2.2 Alkalinity dynamics

In a closed system changes in alkalinity only occur by processes including either a solid phase or conversion to a gas, which then escapes to the atmosphere (Koschorreck and Tittel 2007). Beside the definition of the alkalinity as acid neutralizing capacity of a solution titrated to the CO₂ equivalence point, the alkalinity can be also described by the equivalent sum of conservative cations (those that do not affect alkalinity) minus the sum of conservative anions:

\[
\text{Alkalinity} = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + 2[Mn^{2+}] + [NH_4^+] + 2[Fe^{2+}] - [Cl^-] - 2[SO_4^{2-}] - [NO_3^-]
\] (7)

The changes of alkalinity caused by nitrate and ammonium consumption can account for 0.1-26.2% of the total alkalinity variation. The continuous EC decline during the experiment (Figure 2) was also observed indicating that not only nitrogen transformation occurred, but there was also ion precipitation inducing alkalinity dropping down. The main ions in the groundwater were SO₄²⁻, HCO₃⁻ (affects the DIC change), Na⁺, and Ca²⁺ (Zhang et al. 2013). Chemical theory predicts that upon evaporation, half of the bicarbonate in the groundwater will re-equilibrate with the atmosphere releasing CO₂ while the other half precipitates, mostly as calcite (Wood and Hyndman 2017). Thus, calcite precipitation must have affected our pCO₂ calculations and led to alkalinity decrease through Ca²⁺ removal from the system. Assuming the measured alkalinity changes (153 μmol L⁻¹ in average) were completely caused by calcite precipitation, then there would be 77 μmol L⁻¹ Ca²⁺ being utilized for CaCO₃ formed in each mesocosm. This is roughly consistent with our CO₂ emission calculations because assuming one calcite formed per emitted CO₂ would result in 69 - 168 μmol L⁻¹ Ca²⁺ being utilized for CaCO₃ formed.
4.2.3 Method uncertainties in CO2 flux measurement

We used two methods to quantify CO2 emissions during our experiments: A carbon budget approach and direct flux measurements using floating chambers. Theoretically, the cumulative CO2 flux measured by the chamber should match the cumulative C loss from the water,

$$ S \int_{0}^{t} f(t) dt = (c_t - c_0)V $$

where \( S \) is the surface area of the water; \( f(t) \) is the CO2 emission flux as a function of time; \( V \) is the volume of the water, \( c_0 \) and \( c_t \) are the CO2 concentrations at time 0 and \( t \), respectively.

We found that the results of the direct flux measurement and the DIC calculation were not consistent. The flux chamber method resulted in a twenty-time overestimation of the CO2 evasion especially at higher flow (Figure 4). This is likely because of the artificial turbulence generated by the floating chamber (Lorke et al. 2015; Raymond and Cole 2001). Deployment of floating chamber in the mesocosm system could cause a large overestimation of the CO2 evasion compared with the one in natural waters (Vachon et al. 2010; Marino and Howarth 1993), which would lead to an unrealistic carbon budget with all carbon removed from the system by outgassing in our carbon budget. Thus, floating chamber measurements cannot be used to quantify CO2 emissions in flume experiments.

4.3 Implications and upscaling

Drainage channels receive irrigation water from agriculture and route the nutrient containing groundwater directly into streams. High flow velocity accelerates the CO2 evasion to the atmosphere rapidly (Figure 5), leaving less opportunity for channel metabolism and processing (Liu and Raymond 2018). Previous research also suggests that CO2 concentrations are largely reduced by intensive primary production in rivers (Houser et al. 2015). Thus, nutrient additions have the potential to attenuate CO2 emissions. The formed biomass is transported downstream
and could be trapped in lentic parts of the drainage network where particle sedimentation mainly occurs. Notably, collected particulate carbon needs to be properly buried or dredged. Otherwise methane production is likely to take place in the sediment accumulations. That would largely increase the GHG effect of the drainage network due to the larger global warming potential of methane compared to CO2 (Gómez-Gener et al. 2015; Schrier-Uijl et al. 2011). Alternatively, in-stream plankton could potentially be mineralized by heterotrophic respiration (Vannote et al. 1980; Hotchkiss et al. 2015). In that case, CO2 would only be temporarily bound and later liberated further downstream.

At a given rate of CO2 emission, the flow velocity determines the required distance until the CO2 concentration in a drainage ditch equilibrates with the atmosphere. In a hypothetical drainage system of infinite length with no biological processes involved, it could be anticipated that the only fate of inorganic carbon is to outgas into atmosphere. Our study suggest that up to 20% of DIC would be converted to CO2 and 58% of the initial DIC would be transported downstream considering no other processes were involved until the pCO2 in the water equilibrates with the atmosphere. Previous study reported large variations of the release rate of atmospheric carbon from rivers to the atmosphere (2-30%) (Li et al. 2012). From field measurements of GHG emissions, Ran et al. (2015) concluded that 35% of the carbon exported into the Yellow River network was degassed from the entire watershed during fluvial transport, which is comparable with our estimation.

Irrigation in the study area mainly occurs in March-April (to ensure the water requirement of winter-wheat during the growth period), and October (before wheat sowing). In the case of extreme drought in summer, irrigation is also needed for maize growth in July or August. During other periods the water residence time in the agricultural drainage is quite long, because runoff in
irrigated agriculture is mainly related to the intensity of irrigation and rainfall events in comparison to the infiltration capacity of the soil (Foster et al. 2018). In NCP, the streamflow has dramatically decreased because of the human activities. Low level of groundwater and large evaporation potential in this semi-arid region often lead to lentic water in drainages (Varis and Vakkilainen 2001). High primary production in the stagnant drainage channels will make them a carbon sink.

The median bicarbonate concentration of aquifer systems in the NCP is approximately 241 mg L\(^{-1}\) based on representative samples from three plain types (Chen et al. 2005). Using the conservative assumption that when groundwater reaches the surface, half of the bicarbonate (121 mg L\(^{-1}\)) is converted to CO\(_2\) (Wood and Hyndman 2017) which is equivalent to 87 mg L\(^{-1}\) CO\(_2\). Annual groundwater net depletion in NCP was estimated as a volume of 8.3 ± 1.1 km\(^3\) y\(^{-1}\) (Feng et al. 2013). The estimated annual CO\(_2\) emissions due to groundwater depletion in the NCP are thus approximately 0.52 ± 0.07 Mt (1 Mt = 10\(^{12}\) g). The irrigation efficiency in this region is about 0.5 as reported earlier (Qu et al. 2012). Thus, half of the pumped groundwater reaches the drainage channels. However, we do not know how much of the CO\(_2\) is set free already on the fields and which part of it is entering the drainage channels. Furthermore, no biological carbon fixation is considered. This makes our estimate a worst case scenario. Indeed, high CO\(_2\) emissions during irrigation the fields have been observed (Tang et al. 2018). Agriculture is always an integrative practice with soil management, fertilization, and irrigation. Further studies are needed to understand how much groundwater CO\(_2\) is emitted during the agricultural management and how much ends up in the drainage channels.

Groundwater depletion in the NCP contributed a great number of CO\(_2\) which is quite close to the groundwater CO\(_2\) efflux in U.S. and India (Table 3), and accounted for ~5 % of the global
groundwater extraction. CO₂ released from groundwater depletion has not yet been included in the Chinese carbon inventory (Shan et al. 2018). A previous study indicates that groundwater loss in the NCP was approximately 50 km³ within 8 years, which is greater than the capacity of China's Three Gorges Dam (39.3 km³), the world’s largest power station (Feng et al. 2013). Thus, CO₂ emissions from groundwater pumping should be considered in global carbon budgets (Currell et al. 2010; Mishra et al. 2018). This is especially relevant because groundwater depletion is expected to acceleration in the future (Zhao et al. 2019).

5. Conclusions

Up to now, carbon dioxide emissions from irrigation drainage networks remain poorly understood. Mesocosm experiments help to unravel the effect of different drivers by experimental manipulation and replications. Here, we applied controlled mesocosm experiments to investigate the impact of flow velocity and nutrients on carbon dynamics in irrigation groundwater entering drainage channels in an intensive agricultural landscape. High nutrients contributed to TOC generation and in turn reduce CO₂ evasion on a short term. High flow velocity, on the other hand, promoted rapid CO₂ evasion at high nutrient level. Overall, TOC production counteracted CO₂ evasion, whereas both of the flow velocity and nutrients stimulate DIC depletion. For a proper quantification of the real CO₂ emissions from the entire network, information about flow velocity and residence time of the water in the ditch network as well as information about the fate of organic matter formed in the ditches is necessary. Controlled mesocosm experiments are a useful tool to disentangle the interaction of the various processes involved.
Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Availability of data and materials
The data of this article can be found online at https://figshare.com/articles/Raw_Data_xlsx/9874394.

Competing interests
The authors declare that they have no competing interests.

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Authors' contributions
PL and FL designed the mesocosm experiment. PL, KD, and ZL were involved in performing the mesocosm experiment and collecting the samples. PL, CG, and MK analyzed and interpreted the data. PL drafted the manuscript. MK contributed to the study design and revised the manuscript.

All authors read and approved the final manuscript.

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Table 1. Characteristics of the groundwater and surface water in the study area

(pH and alkalinity data in the groundwater were from Li et al. (2014); NO$_3$-N and NH$_4$-N data in groundwater were from this study; pH, DIC, NO$_3$-N, and NH$_4$-N data in surface water were unpublished from the field survey in September, 2018.)

| Parameter | Unit | Groundwater | Surface water |
|-----------|------|-------------|---------------|
| pH        | -    | 7.31 ± 0.13 | 7.06 ± 4.13   |
| alkalinity| μmol L$^{-1}$ | 785 ± 123   | -             |
| DIC       | mg L$^{-1}$ | -          | 3.83 ± 1.30   |
| NO$_3$-N  | mg L$^{-1}$ | 0.02 ± 0.01 | 0.17 ± 0.10   |
| NH$_4$-N  | μg L$^{-1}$ | 5.8 ± 1.1   | 3.2 ± 5.8     |
Table 2. Flow velocities and chemical parameters at start (t = 0 h) and the end (t = 280 h) of the experiment among four treatments.

| Treatment Abbreviation | Flow velocity (m s⁻¹) | Time (h) | NO₃-N concentration (mg L⁻¹) | NH₄⁺-N concentration (µg L⁻¹) | DIC concentration (mg L⁻¹) | Alkalinity (µmol L⁻¹) | pCO₂ (µatm) |
|------------------------|-----------------------|----------|-----------------------------|-------------------------------|-----------------------------|----------------------|-------------|
| Add + A + H            | 0.37 ± 0.21           | 0        | 0.33 ± 0.01                 | 5.6 ± 0.4                     | 9.53 ± 4.79                 | 721.2 ± 83.8        | 3537 ± 2670 |
| High                   | 0.21 ± 0.07           | 280      | 0.06 ± 0.07                 | 0.03 ± 0.03                   | 6.21 ± 3.18                 | 571.2 ± 14.5        | 43.3 ± 34.8  |
| Add + A + L            | 0.11 ± 0.07           | 0        | 0.33 ± 0.03                 | 6.3 ± 1.2                     | 10.11 ± 5.06                | 794.8 ± 17.0        | 3270 ± 2259 |
| Low                    | 0.07 ± 0.05           | 280      | 0.13 ± 0.05                 | 0.11 ± 0.12                   | 6.40 ± 0.86                 | 629.3 ± 60.4        | 439 ± 612   |
| Non + N + H            | 0.32 ± 0.22           | 0        | 0.01 ± 0.01                 | 6.2 ± 1.6                     | 9.85 ± 4.94                 | 758.3 ± 53.0        | 1889 ± 1349 |
| High                   | 0.22 ± 0.00           | 280      | 0.01 ± 0.00                 | 0.01 ± 0.00                   | 7.02 ± 3.51                 | 588.9 ± 22.1        | 15.2 ± 15.8  |
| Non + N + L            | 0.09 ± 0.06           | 0        | 0.02 ± 0.00                 | 5.8 ± 0.9                     | 9.33 ± 4.78                 | 719.6 ± 81.9        | 3549 ± 1943 |
| Low                    | 0.06 ± 0.00           | 280      | 0.01 ± 0.00                 | 0.03 ± 0.05                   | 7.25 ± 3.64                 | 591.1 ± 25.1        | 383 ± 605   |
Table 3. Comparison of CO\(_2\) emissions from groundwater pumping in the NCP with other regions of the world as well as with other CO\(_2\) sources in the NCP.

| CO\(_2\) emissions | Description | References |
|---------------------|-------------|------------|
| 9.7 – 13.5 Mt CO\(_2\) y\(^{-1}\) | Groundwater irrigation global estimate | (Wood and Hyndman 2017) |
| ~ 10 Mt C y\(^{-1}\) | Global groundwater extraction | (Macpherson 2009) |
| ~0.72 Mt CO\(_2\) y\(^{-1}\) | Groundwater irrigation in India | (Mishra et al. 2018) |
| 1.7 Mt CO\(_2\) y\(^{-1}\) | Groundwater irrigation in the U.S. | (Wood and Hyndman 2017) |
| 0.52 ± 0.07 Mt CO\(_2\) y\(^{-1}\) | Groundwater depletion in the NCP | this study |
| 8.72 Mt CO\(_2\)e y\(^{-1}\) | GHG emissions of energy use for irrigation water pumping in the NCP | (Qiu et al. 2018) |
| 120.87 Mt CO\(_2\)e y\(^{-1}\) | GHG emissions from agricultural production process in the NCP by life cycle assessment | (Zhang 2019) |
| 121 Mt CO\(_2\) y\(^{-1}\) | CO\(_2\) emissions from central heating supply due to natural gas usage in the NCP | (Cui et al. 2019) |
| 15.99 Mt CO\(_2\) y\(^{-1}\) | Crop burning emissions during harvest seasons in the NCP | (Liu et al. 2015) |
Figure 1. Conceptual diagram of a single container with a pump. The up-right insert panel shows a conceptual model of DIC transformation in the mesocosm. The fate of DIC was categorized into four pathways: CO$_2$ evasion, TOC production, calcite precipitation, and downstream transport.
Figure 2. Variations of DO saturation (a-d) and EC (e-h) during the experiment. The black dashed lines show the exponential fits and colored areas indicate its 95% confidence intervals. The red dashed lines show 100% of the DO saturation.
Figure 3. DIC depletion (a-d) and TOC generation (e-h) in each container over time among four treatments, the dashed lines in a-d show the exponential fits ($p < 0.001$), and the dashed lines in e-h show the linear fits with $p$ values and colored areas indicate 95% confidence intervals.
Figure 4. Cumulative CO$_2$ emissions in each container over time among four treatments calculated from DIC (a-d) and from floating chamber measurements (e-h), the dashed lines show the exponential fits ($p < 0.001$) and colored areas indicate 95% confidence level, the red dots indicate the negative CO$_2$ fluxes, namely there was CO$_2$ uptake occurring.
Figure 5. (i) Fitted curves of temporal changes of the DIC, TOC, and cumulative CO₂ emission among the four treatments (a, c: exponential regression, b: linear regression) and (ii) the percentage fate of the dissolved inorganic carbon in the mesocosm.
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