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Rapid Loss of Dissolved CO_2 From a Subtropical Steep Headwater Stream

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High-gradient headwater streams are major participants in the carbon (C) cycle because of their capabilities of emitting a significant amount of carbon dioxide (CO_2). Notwithstanding, their CO_2 emissions have been largely overlooked in previous studies owing to their small water surface area and are sometimes strenuous to be measured because of their narrow channel widths and strong turbulence. This study examined the spatial and seasonal variabilities of CO_2 dynamics of a subtropical steep headwater stream fed by groundwater. Our study found that the pH and dissolved oxygen exhibited a general increasing trend away from the source of the headwater whereas the partial pressure of carbon dioxide (pCO_2) showed a downward trend. The stream water pCO_2 in the upper reach was found to be higher than the ambient level by 19–114 times, with an average drop of >70% at just 9.2 m from the groundwater source, demonstrating the potentially large emission of CO_2 into the atmosphere within this short distance. Additionally, the sampling works conducted further downstream revealed that the CO_2 derived from groundwater could almost completely dissipate within approximately half a kilometer downstream of the source. The concentrations of dissolved organic carbon and pCO_2 were also lower during the period with lower air temperatures in the headwater stream, indicating temperature-dependent metabolism and decomposition of organic matter in soil might modulate the C dynamics in the headwater stream, although the rapid gas exchange along the stream remained the determinative factor. Our findings reassert that headwater streams are an essential source of CO_2 and disregarding them from the studies of greenhouse gas emissions of inland waters would underestimate their potency to influence the global C cycle.

Keywords: carbon dioxide, carbon dioxide emissions, groundwater, carbon cycle, headwater streams

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INTRODUCTION

There has been a growing number of studies showing that carbon dioxide (CO_2) emissions from inland waters into the atmosphere have substantial repercussions on the regional and global carbon (C) cycle. Headwater streams are a crucial component of the water cycle because they dominate the riparian interface in the world and account for approximately 80% of the Earth's perennial channels (Downing et al., 2012; Schneider et al., 2020). Headwater streams are also important players in the global C cycle as they receive different forms of C from surrounding environments, with running waters as the "vehicles" that transport these C downstream (Duvert et al., 2018). They can also provide an environment for the development of metabolic processes such as respiration that lead to gaseous C emissions, while aquatic sediments do not typically store substantial amounts of terrestrial

C (Bernal et al., 2013; Argerich et al., 2016; Schneider et al., 2020). Studies that analyzed rivers and streams worldwide also showed that greenhouse gas (GHG) emissions decrease with increasing Strahler stream orders, and the amount of annual GHG emission from first order headwater streams is the highest, highlighting they are a hotspot for GHG emissions (Ran et al., 2021a; Li et al., 2021). A regional study on the CO_2 emissions from inland waters also observed 61% of the flux is attributable to first and second order streams in China (Ran et al., 2021a). Additionally, past research on the partial pressure of CO_2 (pCO_2) of stream networks in boreal regions revealed a general decreasing trend of pCO_2 and CO_2 evasion flux with stream order (Crawford et al., 2013; Wallin et al., 2013). It has been suggested that approximately 36% of the global CO_2 emitted from lotic systems is sourced from headwaters (Marx et al., 2017). During the high-flow period when the hydrological connectivity is the highest in a year, CO_2 evasion from headwater streams can even dominate the aquatic CO_2 loss (Gómez-Gener et al., 2016). These studies unequivocally demonstrated that headwater streams have a significant role to contribute to the global C cycle. In addition, when a headwater stream is connected to a CO_2-enriched groundwater source, the rapid evasion of CO_2 along the stream may also enable it to serve as an important conduit for terrestrially-respired C (Johnson et al., 2008; Duvert et al., 2018). For determining the extent to which a system is affected by groundwater input, measurement of radon-222 concentration has been identified to be one of the promising solutions (Wu et al., 2004; Mullinger et al., 2007).

Despite the prominence of headwater streams in the C cycle, they have largely been overlooked in C cycle studies because of their narrow width and strong turbulence, making them difficult to use traditional methods, including floating chamber or tracer gas, to estimate the GHG emissions. Furthermore, their water surface area is subject to significant seasonal variations which is the underlying cause of the huge uncertainties in documenting the length and area of streams on both regional and global scales (Benstead and Leigh, 2012; Wallin et al., 2013; Horgby et al., 2019b). These systems can have particularly high emission rates due to their common associations with steep slopes, high flow velocities, and rough riverbeds (Schelker et al., 2016; Maurice et al., 2017; Aho and Raymond, 2019; Horgby et al., 2019b; Ulseth et al., 2019). The substantial differences in the CO_2 concentration between headwater streams and the ambient air is another factor that elevates the emission rate of CO_2. Headwater streams are typically supersaturated in CO_2 owing to a number of factors, such as the mobilization of organic C arising from the degradation of organic matters, the input of CO_2-enriched groundwater, as well as the influence of carbonate-dominated catchment lithology (Davidson et al., 2010; Marx et al., 2017; Duvert et al., 2018). It has also been postulated previous studies might have underestimated the magnitude of catchment-scale CO_2 degassing flux because samples were collected distant from the groundwater source, thereby having a great potential of underestimating the contribution of groundwater inputs and obscuring the impacts of CO_2 evasion (Johnson et al., 2008; Duvert et al., 2018).

Although the relatively small water surface area covered by a single headwater stream signifies that the GHG emissions from an individual headwater stream may not be significant, they are still likely to make a substantial contribution to the global C budget due to their sheer numbers on a global scale. It has been estimated that first—third order systems comprise nearly 48% of the surface area of all rivers and streams globally (Li et al., 2021), implying a substantial fraction of GHG emissions from lotic systems are contributed by low-order headwater streams. Furthermore, the CO_2 dynamics (i.e., pCO_2 and CO_2 emission rate) of headwater streams are spatially and temporally heterogeneous, adding to the difficulty in the accurate quantification of their roles in the global C cycle (Crawford et al., 2017). Although the difficulty of this task cannot be understated, given the above factors, there is a genuine need to better characterize and quantify GHG emissions from headwater streams in order to render greater accuracy to relevant studies in the future. When these studies are more accurately reflective of the actual scale of the GHG emissions, a more comprehensive understanding of the factors contributing to climate change may be gained.

In this study, the spatio-temporal patterns of pCO_2 of a high-gradient forested headwater stream fed by groundwater in subtropical Hong Kong were analyzed. We paid particular attention to the rate of CO_2 degassing from this headwater stream into the atmosphere. The relationships of pCO_2 with selected environmental and hydrological variables, such as pH, dissolved oxygen (DO), and dissolved organic carbon (DOC), were also investigated to identify the potential drivers that have regulated the C dynamics in the studied headwater stream.

MATERIALS AND METHODS

Study Site

This study was conducted in a headwater stream in the Pokfulam catchment (area: 1.7 km^2) in subtropical Hong Kong (22°16′00″N—22°16′08″N, 114°08′25″E—114°08′41″E, **Figure 1**). The bedrock geology of the study area is dominated by early Cretaceous volcanic rocks (Fletcher, 1997). The annual precipitation is approximately 2,400 mm and the climate is classified as Cwa (monsoon-influenced humid subtropical climate) according to the Köppen climate classification (Cheung et al., 2019). The altitude of the groundwater resurgence is 258 m above the sea level (m.a.s.l.) (**Figure 1C**). It was fed by groundwater and the groundwater resurgence was visible. A total of nine sampling campaigns were conducted at a monthly interval from June 2020 to February 2021 at the beginning of each month and 7 water samples were taken from the first 520 m of the headwater stream at the sampling sites of 0 m (Site A, the groundwater resurgence), 1.3 m (Site B), 3.3 m (Site C), 5.1 m (Site D), 6.7 m (Site E), 9.2 m (Site F), and 520 m (Site G) from the headwater stream respectively during each field campaign (**Figures 1C,D**). Sites A—F and site G are defined as the upper reach and lower reach of the headwater stream, respectively. The average slope of the stream reach from site A to F and site F to G is 24.7 and 7.8%, respectively. There is a

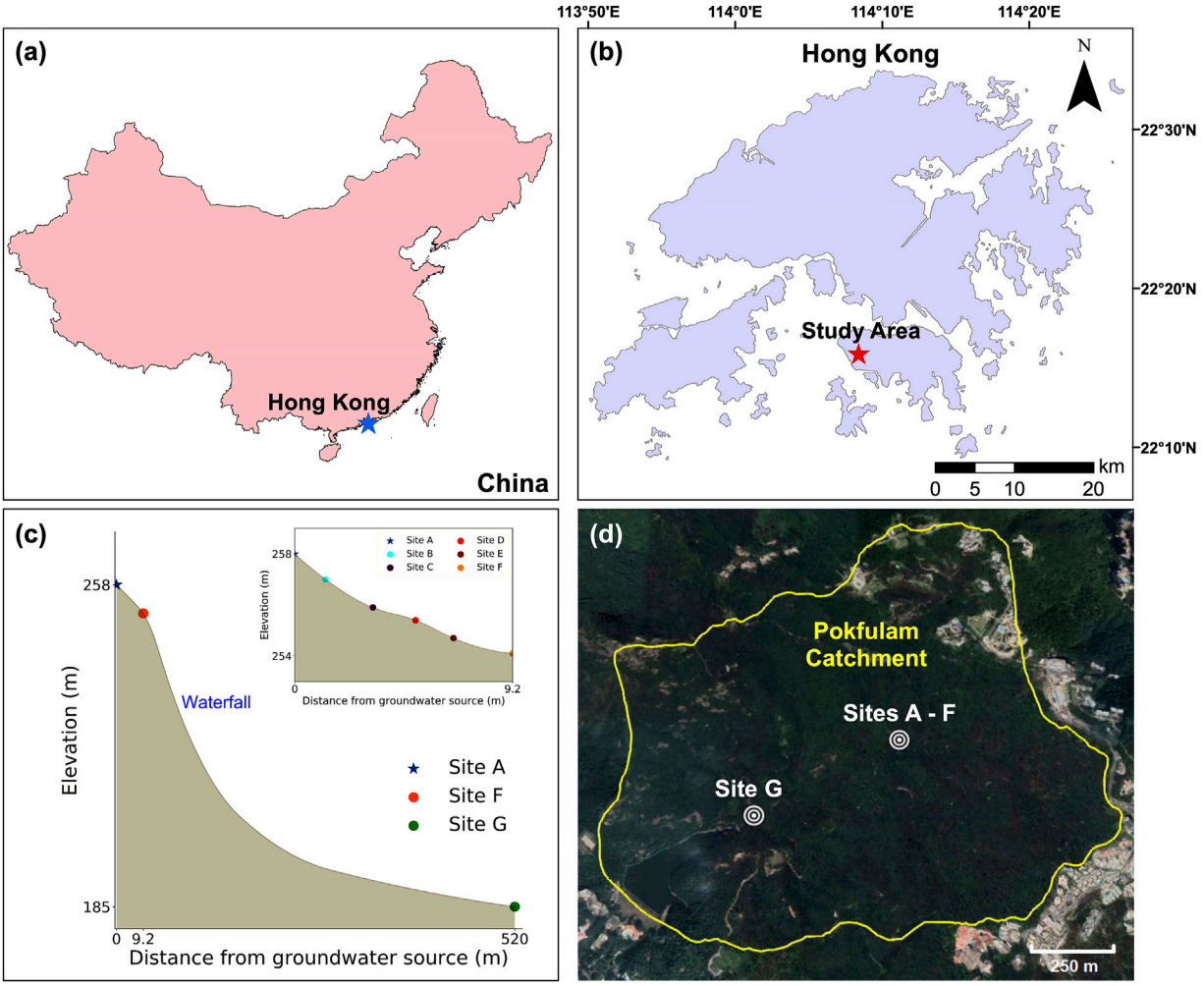

FIGURE 1 | Location map of the study area **(A,B)**, the schematic diagram showing the changes in elevation from site A to G (not scaled) **(C)**, and the enlarged satellite image obtained from Google Earth showing the locations of the study sites, i.e., sites A—F and site G and the boundary of the Pokfulam catchment **(D)**.

waterfall immediately downstream of site F and site G is located downstream of the waterfall (**Figure 1C**). The sampling sites were selected to characterize the potential evasion of CO_2 along the reach and for illustrating the longitudinal changes in water chemistry and C properties. Based on the climatic characteristics of Hong Kong, June to October is defined as the "wet season" and November to February as the "dry season" in this study. The meteorological data from the Hong Kong Observatory suggested that June to October on average account for >70% of the annual precipitation whereas this figure is only around 5% for November to February (Hong Kong Observatory, 2021).

Sampling Procedures and Laboratory Analysis

At each site, approximately 500 ml of stream water was collected by using a polyethylene bottle. All the polyethylene bottles were thoroughly cleaned and sterilized prior to each field campaign and were filled completely with stream water without headspace. At Sites A and G, an additional 9 L of water was collected without headspace for analyzing the radon-222 concentration in the laboratory.

The basic water quality parameters, including pH, electroconductivity (EC), and DO at each sampling site was measured by using a ProDSS Multiparameter water quality meter (YSI, Yellow Springs, Ohio, United States). The water quality meter was calibrated with two pH buffer solutions (pH = 4.00 and 7.00) prior to each sampling work to ensure the accuracy of pH measurement. The water collected in the polyethylene bottle was filtered using 47 mm GF/C filter paper with a pore size of 1.2 µm (Whatman, Maidstone, United Kingdom), and alkalinity and dissolved organic carbon (DOC) were subsequently measured in the laboratory. 20 ml of sample was titrated with 0.05 M hydrochloric acid (HCl) to determine the alkalinity, using methyl orange as the indicator. A 60 ml subsample was prepared from the filtered water and acidified by concentrated sulfuric acid to pH < 2 for the measurement of DOC concentration. The determination of

alkalinity and acidification of the subsample were carried out immediately upon the return of the laboratory and within the same day of the sampling. The acidified subsamples were then preserved in a refrigerator at 4°C until analysis, usually for 1 week. The DOC concentration was assessed by a TOC-L TOC analyzer (Shimadzu, Kyoto, Japan) using high-temperature combustion method with triple injections and an error of <2%. The standard used was 10 mg C L^{-1} potassium hydrogen phthalate. The stream discharge has been measured at sites A and G by using salt dilution gauging as reported in Moore (2004).

The pCO_2 of the stream water at each site was measured by the headspace equilibrium method *in-situ* immediately after sampling (Campeau et al., 2014; Ran et al., 2021b). Briefly, 400 ml of water sample was collected in a reagent bottle with a capacity of 610 ml, while the remaining space was filled with ambient air, thus giving a water to headspace ratio of 1.91:1. The bottle was subsequently closed with a lid and shaken vigorously for at least 2 min for equilibrating the pCO_2 between water and the headspace prior to the connection of a Li-850 CO_2 analyzer (LI-COR, Lincoln, Nebraska, United States). The measurements of the headspace pCO_2 were done in duplicate with repeatability better than 5%, and the values of original stream water pCO_2 were accordingly computed from the headspace ratio, solubility constant of CO_2, and temperature (Koschorreck et al., 2021). The calculation of average areal evasion flux of CO_2 within the headwater stream was done in two steps. Firstly, the total amount of CO_2 loss along the reach was estimated by the differences in the pCO_2 between sites A and F and then multiply by the discharge at site A. Secondly, the average areal evasion flux of CO_2 was calculated by dividing the total amount of CO_2 loss along the reach by the estimated surface area of the reach.

The water collected at sites A and G was analyzed for radon-222 concentration with a RAD7 radon detector (Durridge, Billerica, Massachusetts, United States) in laboratory within 2 h after collection to determine the groundwater signature at sites A and G. It usually took approximately 30–45 min for the reading of radon-222 to reach equilibrium. The gap between the time of water collection and radon-222 measurement was considered unlikely to have a substantial effect on the experimental results because of the relatively short half-life of radon-222, which is about 3.8 days (Dimova et al., 2013).

Statistical Analyses

The statistical analyses were executed by IBM SPSS Statistics (Version 27). Apart from pH, the mean values of the parameters were presented as mean ± standard deviation. The two-sample independent *t*-test was conducted to test for the differences in the mean of variables between the dry season and wet season. The Pearson correlation coefficient (r) was selected to assess the strength of a linear association between two variables. The threshold of the *p*-value to be regarded as statistically significant was 0.05.

RESULTS

Patterns of General Water Chemistry

The mean EC ranged from 43.9 to 50.4 μS cm^{-1}, with a mean of 47.2 ± 1.4 μS cm^{-1} and exhibited a slight downward trend downstream from site A to F (**Figure 2A**). The mean EC at site F was 2.8 μS cm^{-1} lower than that of site A. The DO was always undersaturated with a range from 68.4 to 95.1% and a mean of 85.9 ± 6.3%, exhibiting a significant increasing trend downstream (**Figure 2B**). The mean DO at site F was 14.2% higher than that of site A, and stream water with DO < 80% was observed mainly at sites A and B. The stream water was acidic with pH ranging from 4.53 to 5.63 and a mean of 5.07, exhibiting a significant increasing trend downstream (**Figure 2C**). The mean pH value at site F was approximately on average 0.32 units higher than site A, and stream water with pH < 5 was mostly found at sites A, B, and C. The alkalinity did not display significant spatial differences along the reach, ranging from 125 to 206 μmol L^{-1}, with a mean of 159 ± 22 μmol L^{-1} (**Figure 2D**). The DOC varied between 0.40 and 5.73 mg C L^{-1} with a mean of 1.38 ± 1.10 mg C L^{-1}. There was a generally decreasing trend in DOC downstream during the dry season, with the mean DOC concentration decreased progressively from 1.15 mg C L^{-1} at site A to 0.48 mg C L^{-1} at site F, but this tendency was not observed during the wet season (**Figure 2E**). The discharge measured at site A ranged from 0.23 to 0.63 L s^{-1} with a mean of 0.37 ± 0.13 L s^{-1}, and the average stream width was 0.2 m. The mean discharge during the wet and dry seasons was 0.42 ± 0.18 and 0.33 ± 0.04 L s^{-1}, respectively (**Figure 2F**). Radon-222 concentrations at site A often reached high levels, exceeding 100,000 Bq m^{-3} in most sampling months with a mean of 101,720 ± 18,880 Bq m^{-3} (**Figure 2G**). The mean DOC was significantly lower in the dry season than in the wet season ($p < 0.05$, Two-sample *t*-test, **Figure 2E**), while no significant differences in EC, DO, pH, and alkalinity between the dry and wet seasons were found ($p > 0.05$, Two-sample *t*-test, **Figures 2A–D**).

For site G, the mean EC, DO, pH, alkalinity, and DOC were 92.6 ± 12.9 μS cm^{-1}, 100.5 ± 0.8%, 7.13, 211 ± 21 μmol L^{-1}, and 1.15 ± 0.31 mg C L^{-1}, respectively (**Figures 3A–E**). DO and DOC were significantly higher in the wet season than the dry season ($p < 0.05$, Two-sample *t*-test) while the seasonal differences of the remaining variables were not statistically significant ($p > 0.05$, Two-sample *t*-test). The mean EC, DO, pH, and alkalinity at site G were significantly higher than that of sites A—F ($p < 0.05$, Two-sample *t*-test). The mean radon-222 concentration at site G was 562 ± 168 Bq m^{-3}.

Temporal and Spatial Variations of Partial Pressure of Carbon Dioxide

The atmospheric pCO_2 was determined to be 410 μatm based on the average value in 2020. The stream water at sites A—F was significantly supersaturated with CO_2 with the pCO_2 ranging from 7,890 to 46,750 μatm (mean: 22,940 ± 9,840 μatm), which was equal to supersaturation of 19–114 times with respect to atmospheric equilibrium (**Figure 4**). Concerning the temporal variability of the pCO_2, the mean pCO_2 during the wet season and dry season were 23,680 ± 9,810 and 22,010 ± 10,000 μatm, respectively, with the highest values in September and the lowest values in January (**Figure 4**). The mean pCO_2 at sites A and F were 38,590 ± 5,780 and 10,820 ± 1,880 μatm, respectively, implying approximately 72% of

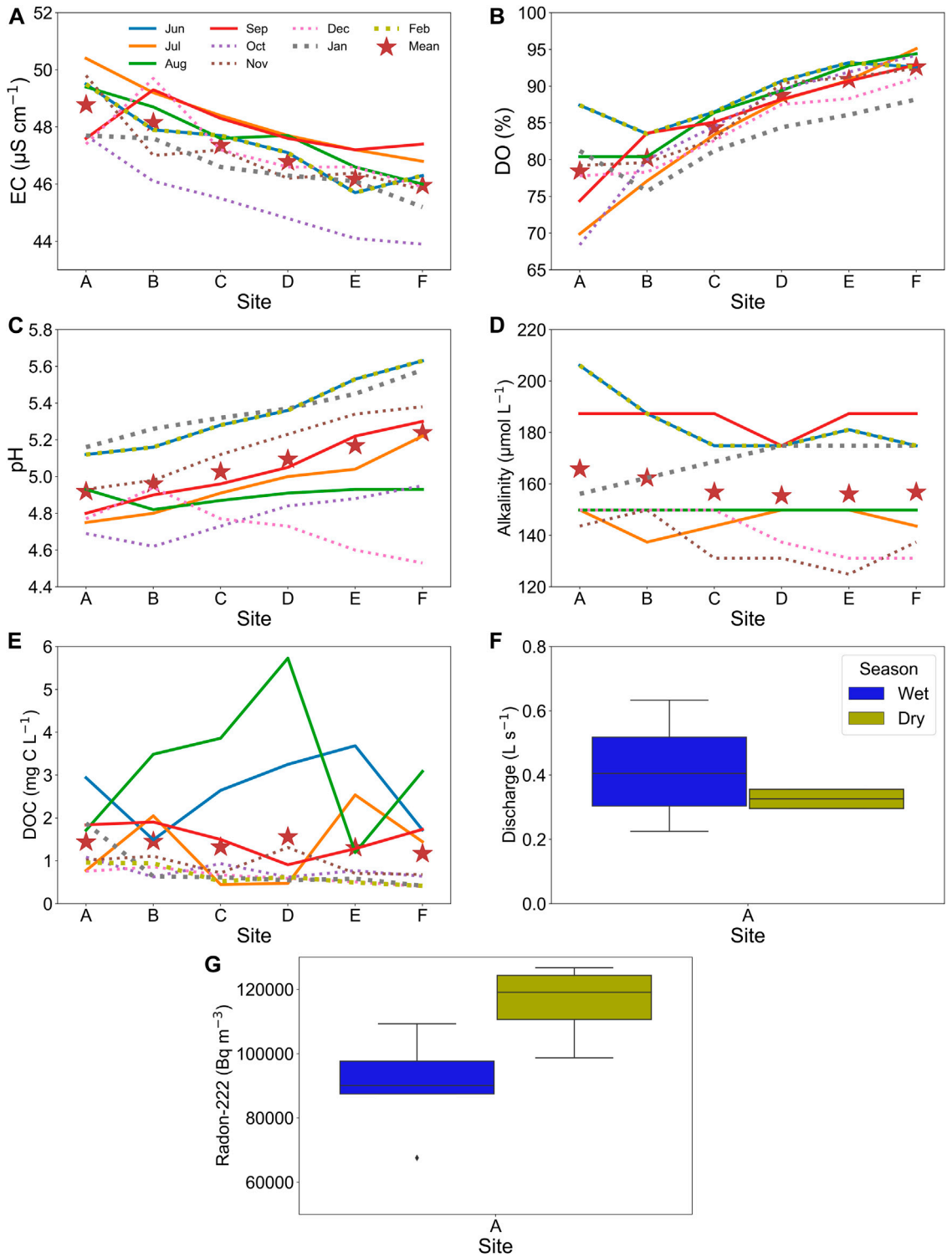

FIGURE 2 | Plots summarizing the monthly water quality variables, including EC **(A)**, DO **(B)**, pH **(C)**, alkalinity **(D)**, and DOC **(E)** of sites A—F, and discharge **(F)** and radon-222 **(G)** of site A between wet and dry seasons in the headwater stream.

the stream CO_2 has been lost over the 9.2-m distance along the headwater stream (**Figure 4**). The pCO_2 recorded at site G was significantly lower than that of sites A—F with the range of 533–1,590 µatm (mean: 778 ± 317 µatm) (**Figure 4**). The mean pCO_2 at site G during the dry and wet seasons were 674 ± 114 and 861 ± 414 µatm, respectively.

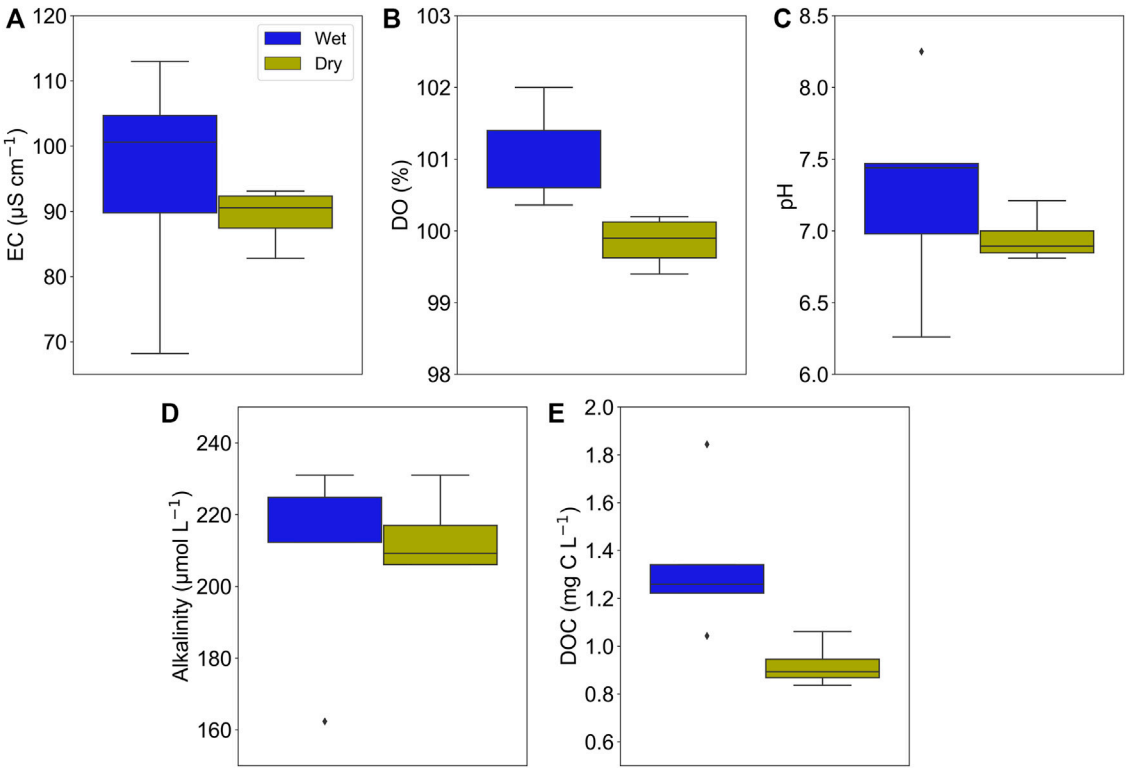

FIGURE 3 | Boxplots summarizing the water quality variables (EC, DO, pH, alkalinity, and DOC) of site G between wet and dry season.

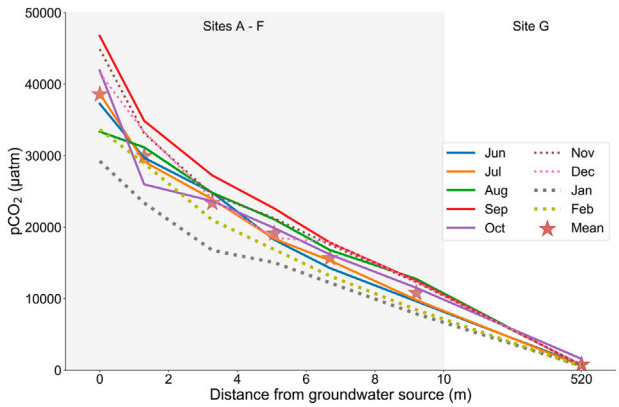

FIGURE 4 | The longitudinal changes in pCO_2 as a function of distance downstream from the groundwater source.

TABLE 1 | The monthly values of Pearson correlation coefficient (r) of pCO_2 with water quality variables in the headwater stream at sites A—F.

	DO	pH	DOC
June	−0.80	−0.97[a]	−0.07
July	−1.00[a]	−0.96[a]	−0.27
August	−0.99[a]	−0.50	−0.05
September	−0.99[a]	−0.95[a]	0.47
October	−0.99[a]	−0.76	0.74
November	−0.90[a]	−0.96[a]	0.44
December	−0.96[a]	0.74	0.88[a]
January	−0.77	−0.97[a]	0.82[a]
February	−0.82[a]	−0.97[a]	0.94[a]

[a]*Correlation is significant at the* $\alpha = 0.05$ *level (2-tailed).*

Relationship of Partial Pressure of Carbon Dioxide With Water Quality Parameters

For sites A—F, the pCO_2 always exhibited a negative relationship with DO, and the correlations of pCO_2 with DO and pH were significant in six out of 9 months with the magnitude of r higher than 0.9 (**Table 1**). The relationship of DOC with pCO_2 was less prominent and consistent compared to that of DO and pH since the r ranged from −0.27 to 0.94, and the relationship was only significant during the dry season from December to February. The values of r of pCO_2 with radon-222 and discharge were 0.33 and 0.01, respectively at site A, and both relationships were not statistically significant. For site G, the pCO_2 had a positive significant relationship with discharge ($p < 0.05$, **Table 2**) while the relationships with DO, pH, DOC, and radon-222 were not statistically significant ($p > 0.05$, **Table 2**).

DISCUSSION

General Chemistry of the Stream Water

Our measurements on the water quality parameters suggested that the chemistry of the headwater stream is heavily influenced

TABLE 2 | The values of Pearson correlation coefficient (r) of pCO_2 with water quality variables at site G of the headwater stream.

Parameters	Correlation Coefficients
DO	−0.03
pH	−0.56
DOC	−0.16
Discharge	0.90[a]
Radon	0.25

[a]*Correlation is significant at the α = 0.05 level (2-tailed).*

by groundwater. Since the EC values remained fairly constant and low under all months of sampling, this indicated that the headwater stream had no signs of saltwater intrusion from the surrounding environment.

The general increase in pH along the downstream direction was a manifestation of the decrease in CO_2 concentration due to degassing (Johnson et al., 2008). There was an occasion in which the pH at sites C—F remained low with the value lower than 5, and this might be attributable to the introduction of anthropogenic acidic substances into the stream or soil which resulted in a drop in the pH value (**Figure 2C**). As the concentration of DO also increased downstream owing to intense gas exchange (Dick et al., 2016), this was likely the reason for the significant positive association between pH and DO in the headwater stream. However, there have been a couple of instances with DO showing a slight decrease from site A to site B, and we suggest that the decomposition of OC along this distance may be a possible reason for this trend. Our measurements were consistent with the theoretical correlation between alkalinity and pH since an increase in pH leads to the production of chemically sequestered bicarbonate ions, a component of alkalinity (Piñol and Avila, 1992; Abril et al., 2015). There was also a general decreasing trend in the DOC concentration within sites A—F of the headwater stream during the dry season (**Figure 2E**), potentially due to in-stream metabolic processes such as mineralization of organic carbon (OC) and by the dilution of DOC-depleted water downstream (Duan et al., 2017). However, this decreasing trend was obscured in the wet season likely because of the capability of heavy rainfall events displacing terrestrially derived OC from the upstream catchment and riparian areas along the reach, which also led to up to more than twofold higher levels of DOC in the headwater stream during the wet season (**Figure 2E**) (Pumpanen et al., 2014; Panton et al., 2020). The generally higher discharge during the wet season might also reduce the water residence time which had the potential to impact the duration of OC mineralization that occurred along the reach (Wickland et al., 2007). Additionally, the variabilities of DOC were higher in the wet season than in the dry season (**Figure 2E**), especially at sites A—F, potentially owing to the sporadic and incidental nature of heavy rainfall events that brought about an increase in DOC levels.

Carbon Dioxide Exchange Dynamics

The pCO_2 was mostly two orders of magnitude higher than the ambient air at sites A—F along the headwater stream, and it was even >100 times higher at sites immediately adjacent to the groundwater source (**Figure 4**), indicating the reach was a consistent source of CO_2. This observation was consistent with the pCO_2 values obtained from headwater stream networks elsewhere in the world (Dawson et al., 2002; Crawford et al., 2013; Winterdahl et al., 2016; Crawford et al., 2017; Li et al., 2021). Because the mean pCO_2 value recorded at site A was in good agreement with the mean value (51,900 ± 1,600 ppmv) of Amazonian deep soil for emergent groundwater reported previously (Johnson et al., 2008) and fell within the range of the groundwater pCO_2 in Swiss mountain catchments and Ganges River catchment (Horgby et al., 2019b; Manaka et al., 2019), it is of high confidence that the high pCO_2 in the headwater stream is contributed by the CO_2-enriched groundwater. The elevated pCO_2 level in groundwater was likely the result of root respiration as well as the microbial respiration of organic matter and its decomposition in surrounding soils (Crawford et al., 2013; Deirmendjian and Abril, 2018; Horgby et al., 2019a; Manaka et al., 2019). The C dynamics of headwater streams located in upper reaches are more profoundly influenced by terrestrially sourced C when compared with large rivers, and therefore they are less sensitive to in-stream metabolism (Johnson et al., 2008; Hotchkiss et al., 2015; Argerich et al., 2016; Deirmendjian and Abril, 2018; Wang et al., 2021). Furthermore, a larger proportion of stream water was in contact with adjacent soil horizons, allowing a stronger hydrological connection between CO_2-rich soils and surface water, contributing to high pCO_2 values in groundwater (Crawford et al., 2013; Schneider et al., 2020). Because the study area is dominated by volcanic rocks without extensive coverage of carbonate rocks, the dissolution of carbonate rocks is highly unlikely to occur and thus cannot be the underlying cause of the elevated pCO_2 in the groundwater (Duvert et al., 2018; Wang et al., 2021).

The rate of decline in pCO_2 along the reach was analogous to the Johnson et al. (2008) study, which developed a model showing a 77% reduction in dissolved CO_2 at 9.2 m from the groundwater spring and was even more rapid than a headwater stream in southwestern France, which exhibited a 70% loss of pCO_2 at 40 m downstream of the groundwater resurgence (Deirmendjian and Abril, 2018). The median percentage of CO_2 loss in the first 100 m from groundwater sources in 15 streams worldwide covering tropical, temperate, and boreal catchments was 76% (Duvert et al., 2018). Our pCO_2 measurement unequivocally indicated the evasion of CO_2 along the reach was very substantial and occurred immediately upon entry of the groundwater into the surface stream (Pu et al., 2019). This observation was particularly salient because it reflected the presence of very active gas exchange triggered by strong turbulence in this high gradient headwater stream fed by groundwater and illustrated that groundwater with exceptionally high CO_2 content had a diminishing effect on stream pCO_2 values with increasing distance downstream (Duvert et al., 2018).

Additionally, our fieldwork results indicated the evasion of CO_2 along the stream via outgassing was responsible for the gradual equilibration of CO_2 in the stream with the atmosphere (Duvert et al., 2018; Schneider et al., 2020). The simultaneous increase in the DO concentrations downstream further

corroborated the strong and rapid gas exchange in this headwater stream since its turbulent nature allowed oxygen to seep and dissolve into the stream water (Dick et al., 2016), and also permitted CO_2 to be released into the atmosphere, yielding the aforementioned pCO_2 and DO trend. In addition, DO and pCO_2 measurements at site G further confirm that water-air gas exchange to reach equilibrium, and complete evasion of groundwater CO_2, was likely to be achieved within 520 m of the groundwater source since the DO consistently reached saturation regardless of the sampling month, while pCO_2 fell to the level similar to the ambient level. This distance was even shorter than that of a previous study which suggested that a majority of the CO_2 in headwater streams sourced from groundwater might be degassed within a few kilometers (Davidson et al., 2010). We argue that this exceptionally large decline in the pCO_2 level might be attributed to the presence of a waterfall between sites F and G. Several previous studies have elaborated on the importance of waterfalls in the emission of CO_2 from freshwater ecosystems due to their abilities in triggering turbulence and favoring gaseous exchange through bubble-mediated transfer, which in turn produced a significant decrease (>50%) in pCO_2 after the stream water passing through waterfalls (Teodoru et al., 2015; Leibowitz et al., 2017; Looman et al., 2021). Because the CO_2 dynamics at downstream locations could be driven by interactions of multiple biogeochemical processes, such as community respiration, primary production, precipitation of minerals, and input of nutrients and CO_2 from immediate surroundings (Davidson et al., 2010; Atkins et al., 2013; Peter et al., 2014; Duvert et al., 2018), the precise quantification of the fraction of groundwater-derived CO_2 remained at site G remains an arduous task. Yet, the enormous decrease in radon-222 concentration by > 99% from site A to G as well as the observed DO and pCO_2 longitudinal trends at least demonstrated that the stream water has lost most of its groundwater signature over this distance.

Our longitudinal pCO_2 results were consistent with the findings observed by Schneider et al. (2020) study, who showed a higher pCO_2 in the upper portion of the stream and declined in the lower reaches, although our study reach was even shorter than the study and the pCO_2 at the source of groundwater was an order of magnitude higher. Another similar study also reported that the significant drop of the differences between the concentration of CO_2 in the stream water and the ambient air in first order streams could be ascribed to highly efficient gas exchange resulting in significant CO_2 loss along the reach (Schelker et al., 2016). Based on the above comparisons, our research data revealed that the evasion of CO_2 along the headwater stream is governed by groundwater input and extremely likely to play a pivotal role in the C dynamics (Deirmendjian et al., 2018). Assuming the decline in pCO_2 derived from groundwater along the reach was solely attributable to the evasion of CO_2 with the contribution of in-stream metabolism being negligible, our measurements on pCO_2 and discharge data estimated that the average areal evasion flux of CO_2 from site A to F and from site F to G amounted to 19,000 and 140 mmol m^{-2} d^{-1}, respectively. The former flux was two orders of magnitude higher than previous CO_2 emission fluxes in stream networks that range from 180 to 920 mmol m^{-2} d^{-1} (Butman and Raymond, 2011; Crawford et al., 2013; Crawford et al., 2014; Wang et al., 2017). Therefore, our measurement indicated the water surface of the upstream region of a catchment is capable of emitting significantly more CO_2 per unit area, in agreement with a groundwater study conducted in an alpine stream network which highlighted the CO_2 emissions from mountainous streams in zones of local groundwater upwelling can outweigh those located in lowland areas (Horgby et al., 2019a). Despite the small water surface area, the CO_2 emission from the first few tens of meters of a groundwater-fed headwater stream is potentially huge and must be considered for obtaining an accurate estimation of the reach-scale CO_2 flux. Waterfalls and cascades along stream reach, on the other hand, may also facilitate the outgassing of CO_2 and their contributions to reach- and catchment-scale CO_2 emissions merit further investigation.

Environmental Factors Affecting Carbon Dioxide Dynamics

The CO_2 dynamics within the headwater stream were found to be statistically correlated with a few water quality and environmental parameters. Firstly, the significant negative correlation between the DO and pCO_2 level in most sampling months (**Table 1**) at sites A—F was consistent with the Li et al. (2021) study covering global rivers, and we anticipated this negative correlation was likely a consequence of rapid gas exchange since the turbulent nature of this headwater stream permits outgassing of a significant amount of CO_2, causing a large decrease in the pCO_2 within a short distance. At the same time, the intense turbulence triggered by steep slopes also resulted in a high rate of reaeration along the stream which led to the rapid replenishment of oxygen from the ambient air and thus a significant increase in DO levels (Huang et al., 2017). At site G, the DO levels were approximately similar regardless of the sampling month, so this could be a potential explanation for the lack of association between dissolved oxygen and pCO_2 levels (**Table 2**). As anticipated, the significant negative pH-pCO_2 relationship (**Table 1**) is likely to be attributed to the dissolution of CO_2 in water lowering the pH.

The lack of strong and consistent association between pCO_2 with the DOC concentration in the headwater stream (**Tables 1** and **2**) has also been documented in previous studies conducted in different parts of the world with varying climate conditions (Nydahl et al., 2017; Horgby et al., 2019a; Luo et al., 2019), and this reflected the mineralization of organic C is unlikely to be the primary source of pCO_2 in this headwater stream (Winterdahl et al., 2016). Although DOC concentration has been hypothesized to be positively associated with pCO_2 level in riverine systems owing to the *in-situ* oxidation of organic matter (Nydahl et al., 2017), the rapid outgassing of CO_2 in this system may attenuate the strength of the pCO_2—DOC relationship along the reach, reflecting the fact that the level of DOC concentration might play an auxiliary role in modulating pCO_2 while the intense gas exchange was still the fundamental factor in controlling the C dynamics. In addition, the increase in DOC is occasionally

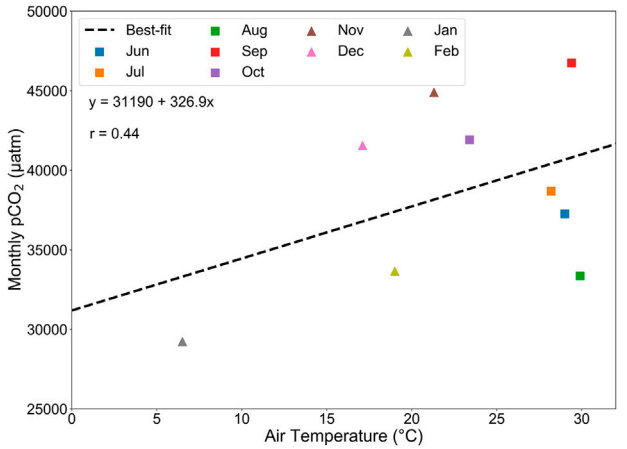

FIGURE 5 | The relationship between monthly pCO_2 at site A and ambient temperature. The dashed line represents the best-fit line of the regression.

associated with an increase in precipitation, but the dilution of stream water CO_2 is possible when precipitation increases, thus obscuring the relationship between the two variables (Luo et al., 2019). Our results support the existence of this precipitation-induced dilution effect since significant positive pCO_2—DOC relationships were only recorded during dry season when the precipitation was low (**Table 1**). Apart from the quantity of DOC, it has also been suggested the chemical properties and degradability of DOC had a role to play in determining the pCO_2 level, while these properties could be impacted by changes in vegetation type and water residence time (Wickland et al., 2007; Dinsmore et al., 2013; Luo and Li, 2021). Thus, a more specific chemical analysis on the properties of DOC in streams is likely to better constrain the processes leading to pCO_2 variabilities in headwater streams. Nonetheless, the results of our current study do not unambiguously preclude the possibility of organic C mineralization in influencing pCO_2 level within the headwater stream, though its effect should be appreciably less influential than that of longitudinal evasive CO_2 loss.

Furthermore, we also found that the CO_2 dynamics of the headwater stream might be influenced by the ambient air temperature since there was a positive relationship between the monthly pCO_2 at site A and air temperature ($r = 0.44$, **Figure 5**). In addition, January and September were the 2 months with the lowest and highest average pCO_2 values in the stream, while the air temperature was the lowest and second highest (**Figure 5**). Thus, we suggested that the observed seasonal variabilities in pCO_2 could be ascribable to the temperature-dependent metabolic activities because the higher temperature in summer months might have facilitated heterotrophic and root respiration in soil, and the downward diffusion of soil CO_2 will lead to a surge in pCO_2 values within the studied headwater stream (Jones and Mulholland, 1998; Deirmendjian and Abril, 2018). This has also been observed in a regional stream study that reported significantly higher pCO_2 levels in summer than spring in headwaters (Jones and Mulholland, 1998). Although the effect of stormwater dilution on groundwater CO_2 has been reported previously (Deirmendjian and Abril, 2018), it might not be a significant factor in regulating the pCO_2 levels in the section of the headwater stream close to the groundwater source because of an absence of the relationships between the discharge and pCO_2 at site A. In contrast, there was a significant positive correlation of pCO_2 with discharge at site G (**Table 2**), and the cause of this relationship might be independent of DOC input since there was no significant relationship between discharge and DOC. Thus, it is hypothesized that such a relationship in the lower reach could be attributable to the increased runoff from the upper catchment area that was enriched in CO_2 (Dinsmore et al., 2013).

Implications for Quantifying Carbon Dioxide Emissions From Stream Networks

Based on our sampling efforts, a close linkage was found between the groundwater and stream networks (Duvert et al., 2018), and the contribution of CO_2 from groundwater and outgassing of CO_2 along the reach was considered to be the primary determinants of C dynamics in this headwater stream. Although other environmental variables including DOC concentration and ambient air temperature might also be capable of regulating pCO_2 levels in the studied headwater stream, the changes were substantially more modest as compared to the longitudinal changes in pCO_2, even at distances of less than 10 m. Additionally, the influence of groundwater in pCO_2 within the catchment was almost varnished at a distance of up to 520 m. This finding is prominent and highlights the necessity of future works focusing on exploring the possibility of other high-gradient headwater streams fed by groundwater having similarly high outgassing rates. On top of that, our study demonstrated that the upstream section of headwaters fed by groundwater are conceivable hotspots of CO_2 emission since the flux can be several orders of magnitude higher than the previously reported stream networks with varying topography and climatic conditions. Because of the rapid gas exchange in high-gradient headwater streams, strong spatial heterogeneities in C dynamics are also occasionally detectable within a catchment. Therefore, the resulting estimates are likely to underestimate the true C flux if these headwater systems are not duly and adequately accounted for when quantifying the landscape-scale C budget (Deirmendjian and Abril, 2018; Aho and Raymond, 2019). The geomorphological characteristics of headwater streams, such as stream bed roughness and slope, are also subject to spatial heterogeneities that result in localized zones with strong turbulence and hence evasion (Duvert et al., 2018), and our results emphatically showed that the physical and biochemical processes controlling pCO_2 may differ in headwater streams fed by groundwater and its downstream section. Therefore, a more intensive study of the variations of these processes and mechanisms with respect to changes in location within a headwater stream is a promising direction for future research on the C dynamics.

CONCLUSION

Our sampling on a high-gradient headwater stream fed by groundwater in Hong Kong indicated that headwater streams are prominent emitters of CO_2. The pCO_2 levels of the upper reaches of the headwater stream were 19–114 times higher than the atmosphere and dropped by approximately 72% over a distance shorter than 10 m from the groundwater resurgence, indicating that a substantial share of the CO_2 derived from groundwater has been outgassed into the atmosphere within such a short distance. We also found that the groundwater signature and the effect of elevated CO_2 from groundwater could be completely dissipated at a distance of up to 520 m based on the pCO_2, DO, and radon-222 measurements at the lower reach of the headwater stream. Meanwhile, other water quality parameters, such as DO, DOC, EC, and pH, also exhibited longitudinal changes within the headwater stream, and pCO_2 was found to be significantly associated with several water quality parameters including pH and DO. Although other environmental drivers, for example, the ambient temperature and the availability of DOC for metabolic activities may also modulate the pCO_2 pattern, the intense gas exchange triggered by turbulence remains the overriding factor controlling the C dynamics in this headwater stream. The existence of waterfalls and cascades within a stream network may also influence the C dynamics since they could exert an accelerating effect in CO_2 outgassing. Despite the generally small water surface area covered by a single headwater stream, this study suggests that high-gradient headwater streams are hotspots of CO_2 emissions. The omission of these systems may introduce significant biases in estimating catchment-scale and regional CO_2 flux from aquatic ecosystems, thus illustrating the importance of sampling in the immediate vicinity of groundwater emergence. We hope this work offers new knowledge that will lead to more accurate and comprehensive assessments of CO_2 emissions from headwater streams in the humid subtropical region and render the potential of upscaling the estimates to broader regions with similar climatic and land cover features.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

CC, FL, and LR contributed to conceptualization and design of the study. CC, CT, and BL performed the fieldworks and experiments. CC performed the statistical analysis and wrote the manuscript with inputs from all authors. LR supervised the project. All authors contributed to manuscript revision.

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