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Carbon Dioxide Availability in Inlands Rivers Is Driven by Dissolved Organic Carbon, Not Warming: A Case Study of Tigris River

Batool Kadhim , ***Mohammed Hamdan****

Department of Biology, College of Science for Women, University of Baghdad, Baghdad, Iraq.
*Corresponding Author

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Abstract

Rivers became supersaturated with carbon dioxide (CO_2), so they play an essential role in the global carbon budgets. To increase our understanding of the source of CO_2 availability in rivers, we studied the role of climate-changed drivers of CO_2 availability, which are ‘‘dissolved organic carbon (DOC), and warming’’. We sampled 45 locations of 3 parts within the Tigris River in Baghdad during autumn and winter. The results showed that all the studied variables (water temperature, pH, DOC, CO_2) changed over time. The variations in CO_2 availability are associated with changes in DOC concentration, not with water temperature. Overall, our results suggest that elevated CO_2 in rivers could result from increased DOC inputs. Therefore, we can conclude that increased DOC concentration in rivers was required for microbial respiration and photo-mineralization, which are the primary sources of CO_2 in river ecosystems.

Keywords: DOC, CO_2, Climate change, Warming, Carbon mineralization, Brownification.

Introduction

Dissolved organic matters are complicated and diverse organic components in nature that can pass through a 0.45 µm filter. They range from molecules with low molecular weight like; organic acid, amino acid, and sugar to high molecular weight molecules named hemic substances[1]. Allochthonous organic matter (OM) is found in the soil of the surrounding terrestrial landscape as a result of the degradation of dead organisms [2] and as a product of plant photosynthesis, it can reach aquatic ecosystems due to ongoing climate change via increasing runoff due to high precipitation, on other hand autochthonous organic matter produced by aquatic algae [3]. Organic matters are different in their continent; for instance, organic matter formed from higher plants has a comparatively high proportion of aromatic carbon, a high phenolic content, and a low nitrogen concentration, while microbially derived organic matter (from bacteria and algae) has a lower level of phenolics and an increased nitrogen concentration[4-6].

Organic Matter is an essential source of carbon in aquatic ecosystems, e.g. dissolved organic carbon (DOC)[7]. High increasing inputs of dissolved organic matter (DOM) can cause a significant change in the physical and chemical properties of aquatic ecosystems like increasing carbon concentration concentrations[8-10] via the brownification phenomenon.

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Dissolved organic carbon has an essential role in regulating the carbon cycle[11], and is regarded as a significant contributor to increasing carbon concentration by bacterial and photo-mineralization of DOC to DIC (CO_2). Recently, aquatic ecosystems have received a high amount of CO_2 due to huge entrance of DOC[12]. Rising DOC concentrations in water bodies lead to an increase in carbon continent[13] and a decrease in oxygen level that causes hypoxia[14, 15]. More DOC concentration can lead to anoxia condition which in turn causes adverse effects on all aquatic life[16]. DOC effect on nutrient and light availability, with the gradient in concentration of DOC, high DOC concentration leads to increase associated nutrients that cause high biomass of algae which in turn causes shading and decreased light availability[17, 18].

Tigris River, a significant water source and one of Iraq's major rivers, it had been observed for a long time, and several studies had been conducted on it. Several researchers have examined changes in the chemical and physical characteristics monthly and seasonally and others studied alterations in nutrient concentrations and some investigated water quality of Tigris river[19-28] .The analyses of carbon and its organic and inorganic sources are nonexistent in the Iraqi environment in general and on the Tigris River in particular. Based on a notable rise in carbon concentrations in aquatic ecosystems in last years[29], our study was concerned with studying organic carbon as a primary source of inorganic carbon, especially carbon dioxide in The Tigris River.

Material and Methods

Study Site Description

This study was conducted at some locations in the Tigris River in Baghdad (Fig. 1). The Tigris River, the second-largest river in western Asia, is surrounded by four nations: Iran, Iraq, Turkey, and Syria. The Tigris has a long history of the earliest known civilizations because of its significance to a primarily dry region and its value as a source of irrigation and transportation. Tigris River enters Baghdad city around 5 km from the tourist island in Baghdad; the town is split into two halves by the river, which runs from north to south: the right (Karkh) and the left (Risafa). Its breadth varies from 160 meters in straight sections to more than 400 meters in twisted branches, with a slope of 6.9 cm per kilometer. Numerous factors, including temperature variation and rainfall frequency, impact the Tigris River. Some of these factors are influenced by climatic change. Other human-caused variables can cause a wide range effecting on the Tigris River, e.g., irrigation, drainage work, and dams like the Samarra Dam, dams are significant to exploit the river as hydroelectric energy where they control the water level and maximize the flow potential of the river, in the same time dams cause increases in salinity concentration after the water return from these dams to the river. For our study, we sampled 45 locations in three parts on the Tigris River within Baghdad.

The estimated distance of the Tigris River between the sites is more than 10 km, where it is about 20-km from the first station to the third station, which are: Al-Gherai'at is a permanent island that is part of Rusafa and is northeast of Baghdad. It is distinguished for being covered with wild plants. Tigris River in this region occurs under direct sewage discharge from Al-Gherai'at's inhabited residential areas.

The second area is the Al-Shuhda'a Bridge, one of Baghdad's main bridges connecting the Karkh and Rusafa sides. Due to its high population and restaurants' spills of liquid pollutants into the river, it is classified as an active site.

The third area is Al-Jadriyah, a region on the side of Rusafa where the Tigris River makes a significant northeast turn. AL-Jadriyah has rapid urbanization and residential growth compared to the previously described sites, which produce a large volume and variety of liquid wastes.

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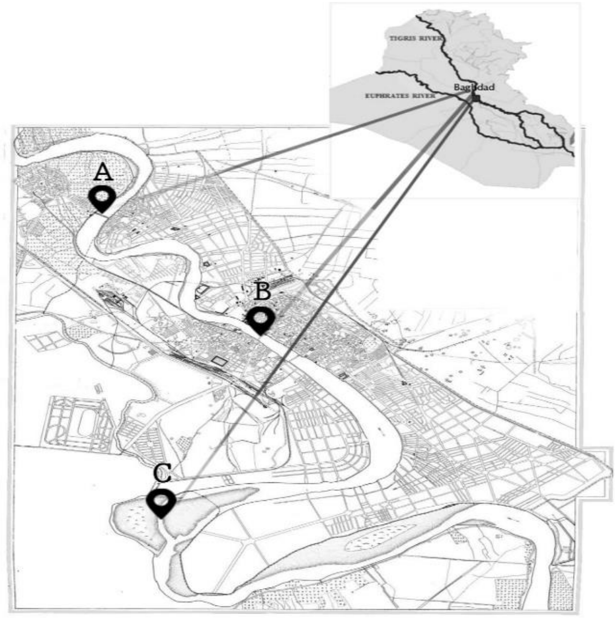

Figure 1. Map of the studied sites (A-C) on the Tigris River in Baghdad. A) AL-Gherai'at (44°20ˈ11.2"E,33°23ˈ11.1"N) B) AL-Shuhda'a Bridge (44°23ˈ10.0"E, 33°20ˈ18.9"N), and C) AL-Jadriyah (44°23ˈ07.4 E, 33°17ˈ26.5 N)

Field Measurements

Field measurements were performed using the standard methods in[30]. Water temperature(°C) was measured by AL-Hana portable pocket thermometer. pH was determined with an HQ40 multimeter manufactured by HACH company. First, the device is calibrated using a buffer solution with pH values 9, 7, and 4. Then submerge the prop in water, the result is recorded once the reading is steady.
To estimate CO_2 availability, the method adopted by Hadi[31)] and approved by Golterman[32] was used for estimating CO_2 concentration in water. This method is based on the titration of 100 ml of water sample with a solution of sodium carbonate 0.2 N until pH equals 8.4. Then titration another 100 ml with Hydrochloric acid 0.1N until pH equals 4.2. After that, we calculate the total CO_2 in 100ml of the water sample by using this Eq.1:
$X = ((A + B) * 4.4)$………………………. 1

Where A= Volume of titration with 0.2N Na2CO3, and B= Volume of titration with 0.1N HCl.
Then we calculated CO_2 by multiplying the value of X by 10, and the result was expressed by mg/L.

Laboratory Measurements

We collected the water sample and added H_2SO_4 until pH equaled 2.0 to remove DIC, then filtered the sample with a 0.45 Millipore filter in the field. The sample was transferred to the laboratory to calculate chemical oxygen demined (COD). In the lab, we used two solutions. The first was the digestion solution, which consists of 500 ml distilled water 10.216 ml of potassium dichromate, 167 ml of sulfuric acid, and 33.3 ml of mercuric sulfate. Then we completed the volume to liter. The second solution is an acid reagent consisting of 540 ml of H_2SO_4 and 5.5g of silver sulfate. After that we put the two solutions in the tube and added 2ml of samples to it. Then we put the tube in the digester for 120 minutes at 150 °C, then in the color meter, we read the result, and the result expressed as mg/l; later, we put the COD result in plutocalc water program then chose total organic carbon (TOC) which is the same represented DOC, because we filtered it firstly, as it is described in[33].

Statistics analyses

For statistical analyses (in SPSS 20) all variables were analyzed. T-tests estimated the differences variables between specific locations. A one-way ANOVA test was used to show if the variables differed significantly between the locations. Person´s correlation coefficient (r) was used to show the correlation between water temperature and nutrient concentrations. Linear regression was used to indicate if the correlations were significant or not. We also found the mean and the standard divisions for all measured parameters.

Results and Discussion

Water temperature (mean ± SD) changed significantly during the study (Table 1) when it ranged between 19.7 ± 0.04 C in October and 7.3 ± 0.12 C in January (Fig. 2 a). pH (mean ± SD) also changed during the study time (Table 1) when it ranged between 7.3 ± 0.16 in December and 8.4 ± 0.04 in January (Fig. 2d). Dissolved organic carbon (mean ± SD) changed significantly during the study

(Table 1) and ranged between 20.3 ±9.3 mg/l, in January and 1.2 ± 1.2 mg/l in December (Fig. 2 b). Carbon dioxide concentration (mean ± SD) changed significantly during the study (Table 1) and ranged between 204.1±36.1 µM in December and 110.2 ± 12.9 μM in February (Fig. 2 c).

Carbon dioxide concentration was affected by dissolved organic carbon concentration during the study (r=0.72 and p-value <0.001) (Fig. 3 a) and not by water temperature during the study (r=-0.24 and p-value = 0.10) (Fig. 3 b).

Table 1. Two-way ANOVA analysis showing the effects of time, locations, and the interaction between them on the studied environmental variables.

	Time		Location		Time x Location	
Variable	***F*-value$_{(df)}$**	***p*-value**	***F*-value$_{(df)}$**	***p*-value**	***F*-value$_{(df)}$**	***p*-value**
WT	3909.61$_{(4, 44)}$	<0.0001	7.73$_{(2,44)}$	0.001	2.55$_{(8, 44)}$	0.02
pH	14.94$_{(4, 44)}$	<0.0001	13.08$_{(2, 44)}$	<0.0001	22.31$_{(8, 44)}$	<0.0001
DOC	5.93$_{(4, 44)}$	0.001	0.42$_{(2, 44)}$	0.65	1.82$_{(8, 44)}$	0.11
CO_2	13.64$_{(4, 44)}$	<0.0001	5.03$_{(2, 44)}$	0.01	4.28$_{(8, 44)}$	0.001

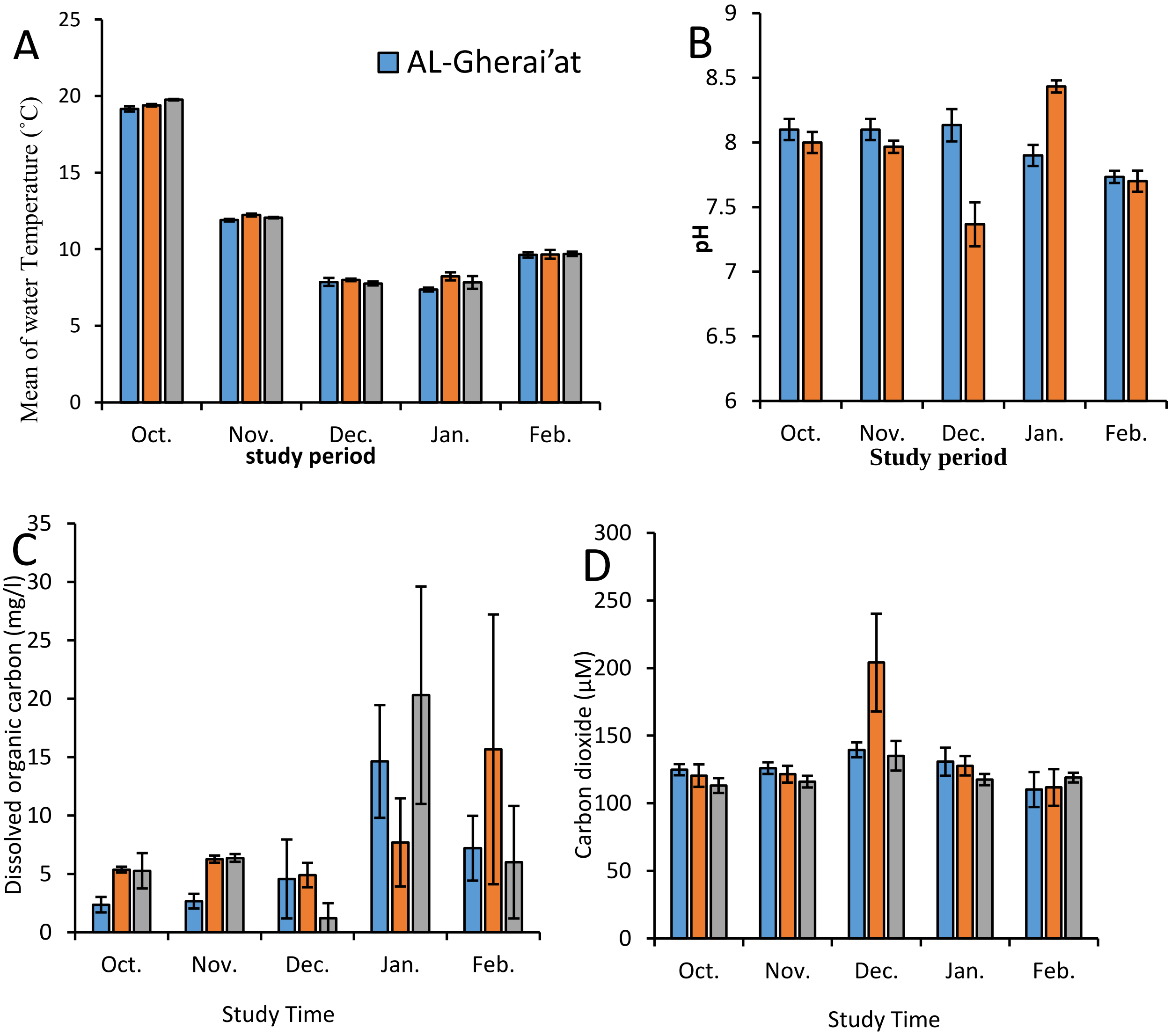

Figure 2. The studied environmental variables during the study time.

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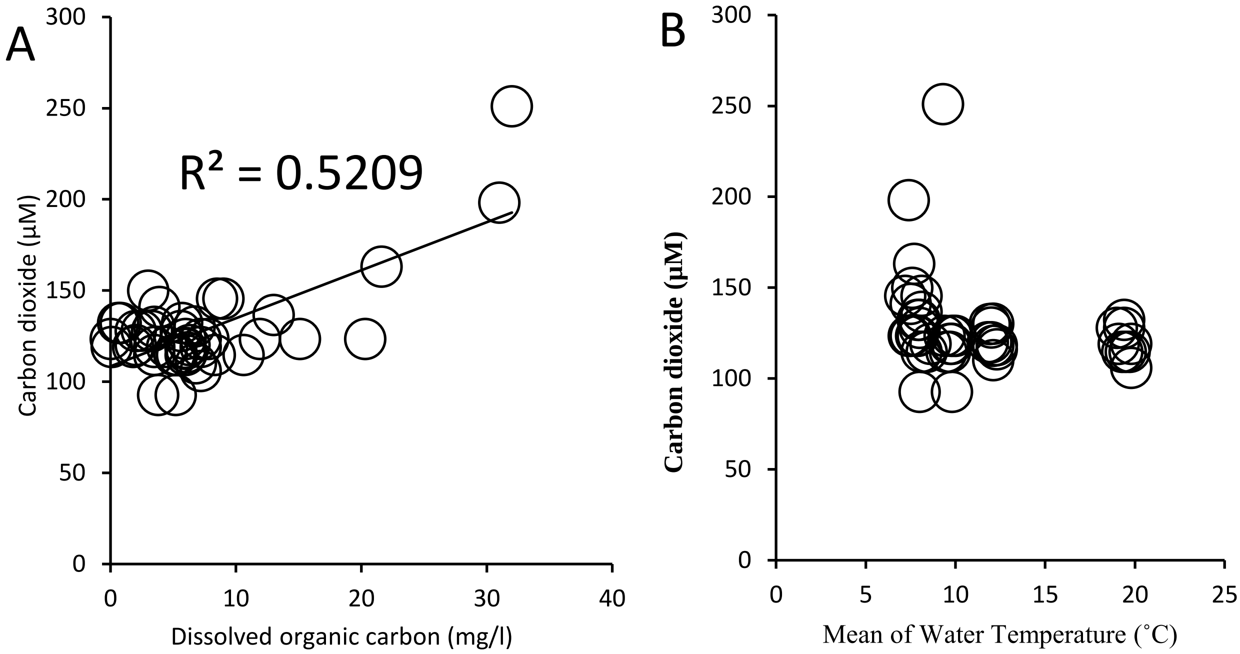

Figure 3. Carbon dioxide availability drivers during the study.

The results showed that water temperature, pH, DOC, and CO_2 concentration changed significantly during the study. It has been revealed statistically that CO_2 concentration was affected by DOC concentration and not by water temperature during the study. Carbon sources found in the aquatic environment either as dissolved organic carbon (DOC), which is created by photosynthesis and can come from the catchment adjacent to the water body or as dissolved inorganic carbon (DIC), especially CO_2, which is produced by the respiration of aquatic organisms and diffuses into water as atmospheric gas.

Carbon dioxide is an important substrate for an essential enzyme in the photosynthesis process[34, 35]. Recently, CO_2 levels started to rise in the aquatic environment[29].

We noticed that DOC changed significantly during the study period. The high observed increase was in December and January because of high rainfall, which causes high surface runoff [36], as a result, carbon dioxide concentrations increased significantly due to the photolysis and biodegradation process of dissolved organic carbon[37, 38]. On the other hand, the noticeable carbon dioxide levels during the study period were in AL-Gherai'at and AL-Shuhda'a bridge, and the reason is due to anthropogenic activities such as the waste coming from the Baghdad Medical City hospital towards the AL-Shuhda'a bridge area, as well as different type of human activities like a discharge of sewage to the Tigris River without treatment near Al-Wazir Mosque, and the construction process of a bridge in AL-Gherai'at region that led to an increase in nutrients concentration e.g., phosphorus[39], which in turn causes the bacterial stimulation DOC-mineralization to CO_2[40].

Our results showed that the pH changes significantly following the change in carbon dioxide, where CO2 is significant in controlling pH; pH falls as CO_2 rises and vice versa[41-43]. Water temperature is an essential abiotic factor that drives a variety of characteristics of an organism's life, including respiration, fertility, growth, and nutrition, as well as its behavior and eventual survival. Heat plays an essential role in regulating respiration[44]; when respiration processes noticeably increase due to rising temperatures, more CO_2 is produced. According to a different opinion, the heat had no apparent significant impact on metabolic activities[45], and the findings of our investigation agreed with this, where our results showed that temperature had no effect on CO_2 levels and the main drive of CO_2 concentrations was

dissolved organic carbon[36] that regulate the carbon budgets.
Recently, because of climate change, which has a significant role in increasing the concentration of CO_2, it has been revealed that the increase in carbon dioxide is primarily related to increases in dissolved organic carbon concentration and not due to temperature variation.

Conclusion

Overall, our results revealed that warming does not influence carbon dioxide concentration clearly, whereas CO_2 availability is affected by allochthonous DOC inputs after the microbial and photo-mineralization processes of allochthonous and autochthonous dissolved organic carbon, which caused high levels of CO_2. We can conclude that climate change can control carbon dioxide concentration in aquatic ecosystems by increasing allochthonous DOC inputs from the lands surrounding rivers due to high surface runoff processes brought on by precipitation due to the drought via increased global warming. This, in turn, raises the proportion of CO_2 availability in the river ecosystems. We recommend taking the different sources of carbon dioxide into account in the studies caring about human activities on the land surrounding the water bodies and their effects on the trophic status classification of aquatic ecosystems.

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Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

Authors' Contributions Statement

The two authors designed the study; B.K. carried out the field and lab work;.The data were analyzed statistically by M.H.; B.K wrote the first draft of the manuscript.; M.H revised the final version of the manuscript.

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الكربون العضوي المذاب، ليس الاحترار، يقود توافر ثاني أكسيد الكربون في الأنهار الداخلية: حالة دراسية لنهر دجلة

بتول كاظم، محمد حمدان

قسم علوم الحياة، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

الخلاصة

الانهار اصبحت مشبعة بثاني اوكسيد الكربون بشكل عالي وبذلك فهي تلعب دور مهم في كميات الكربون العالمية. لزيادة فهمنا حول مصادر الكربون المتوفرة في النظم البيئية النهرية، تم اجراء هذه الدراسة حول تأثير الكربون العضوي المذاب والحرارة (العوامل الرئيسية لتغير المناخ) كمحركات رئيسية لوفرة ثاني اوكسيد الكربون في الانهار. تم جمع العينات من خمسة واربعون موقع في ثلاثة اجزاء رئيسية لنهر دجلة داخل مدينة بغداد خلال فصلي الخريف والشتاء. اظهرت الدراسة ان جميع المتغيرات المدروسة (الحرارة، الأس الهيدروجيني، الكربون العضوي المذاب، وثاني اوكسيد الكربون) تتغير مع الوقت. كانت التغيرات في تركيز ثاني اوكسيد الكربون مرتبطة ايجابيا بالتغيرات في تركيز الكربون العضوي المذاب وليست بتغير درجات الحرارة. نتائجنا بشكل عام تشير الى ان الزيادة بتراكيز ثاني اوكسيد الكربون في الانهار هو نتيجة لزيادة المدخلات من الكربون العضوي المذاب. وبذلك نستنتج ان الزيادة في تراكيز الكربون العضوي المذاب في الأنهار مطلوبة كمصدر لثاني اوكسيد الكربون من خلال عمليات التنفس الميكروبي والتحلل الكيميائي.

الكلمات المفتاحية: DOC، CO_2، تغير المناخ، الاحترار، تمعدن الكربون، تحول اللون البني.