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Estimation of Rivers and Coastal Carbon Fluxes in the Lebanese Waters

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Abstract: Rivers and coastal waters transport carbon from continents to deep oceanic systems and act as important links in the carbon cycle. To the best of our knowledge, no studies have quantified the riverine and coastal carbon fluxes in the Lebanese waters, and hence this study aims to assess for the first time the carbon inputs in three major Lebanese rivers: Nahr Ibrahim, Nahr Damour and Nahr el Litani; and the coastal waters affected by their discharges. A monthly and seasonal sampling of key bio-physico-chemical parameters was conducted for Temperature, Salinity, pH, Dissolved Oxygen, Nitrates, Phosphates, Total Alkalinity (AT) and Dissolved inorganic Carbon (DIC), and subsequently the partial pressure of CO_2 (pCO_2) was derived according to the DOE handbook. The results show a clear seasonal variation of the physical parameters. The Alkalinity yield increased in all monitoring stations mostly in the river areas ranging from 0.24 to 1.8 mmol/L. DIC contribution to alkalinity is significant in rivers with relatively low alkalinity concentrations, and the DIC had a general opposite trend compared to AT; ranging from 57 and 39 mmol/L respectively. When computing the pCO_2, the results show that the a range from 817 to 3283 µatm, higher than the atmospheric CO_2 concentration showing that the studied rivers acted as a source for atmospheric CO_2. This study can be considered as benchmark to understand the mechanisms of riverine-coastal ecosystem change and help the Lebanese community manage their coastal resources.

Keywords: Lebanon, Rivers, Coastal Zone, Carbon Fluxes

1. Introduction

Rivers have a critical role in connecting terrestrial, oceanic and atmospheric carbon reservoirs, and the riverine carbon flux constitutes a significant component of the carbon cycle. Globally, rivers deliver 0.3 to 0.6 Pg C yr^{-1} to oceans, and 75% of carbon export occurs as inorganic carbon [10]. The Lebanese coast is a region that receives a flow of 3900 Mm^3/year from river discharge. Lebanon has 16 perennial and 23 seasonal rivers, and two rivers do not discharge into the Mediterranean Sea [5]. Despite their national importance, all Lebanese rivers are adversely impacted by sewages, residues from fertilizers and pesticides, heavy metals and hydrocarbons [3]. The absence of regulations in human-land practices along with the chemical weathering and atmospheric deposition can strongly influence the carbonate chemistry of riverine waters with consequent effects on the coastal ocean [10]. For instance, nitrogen pollution from intensive agriculture, industrial effluents and municipal wastewater, is a cause of eutrophication in the Lebanese coastal waters [5, 15]. Eutrophication ultimately lowers pH and causes surface water acidification in rivers and coastal waters [7, 11]. Acidification changes the carbonate buffering characteristics of rivers which affect coastal calcium carbonate equilibrium, with acute effects on marine organisms, ecosystem services and human societies [12]. In Lebanon, the scarcity of measurements causes large uncertainties regarding the quantification of riverine and coastal carbon fluxes. Also, the chemical composition of the Lebanese riverine-coastal waters, thus their resistance to changes in pH remains unknown. A better knowledge of these processes will serve as a benchmark to understand the mechanisms of riverine-coastal ecosystem change and help the Lebanese community manage their coastal resources.

2. Physical Parameters

2.1. Temperature

Temperature was measured directly on site using a regular mercury thermometer. The seasonal cycle was noticeable with the lowest temperatures of 9.6°C recorded in autumn and the highest temperatures of 14°C recorded in summer. Moreover, there was a clear increasing gradient between the coastal and river zones of all the rivers (Figure 1).

2.2. Salinity

Salinity was measured by the conductivity method using a Beckman salinometer RS7 Model-C in reference to the *Practical Salinity Scale* [6]. Similar to temperature, the salinity variations were also affected by the seasonal cycle. The highest salinity of 0.34 were recorded in summer, reaching a minimum of 0.24 in winter.

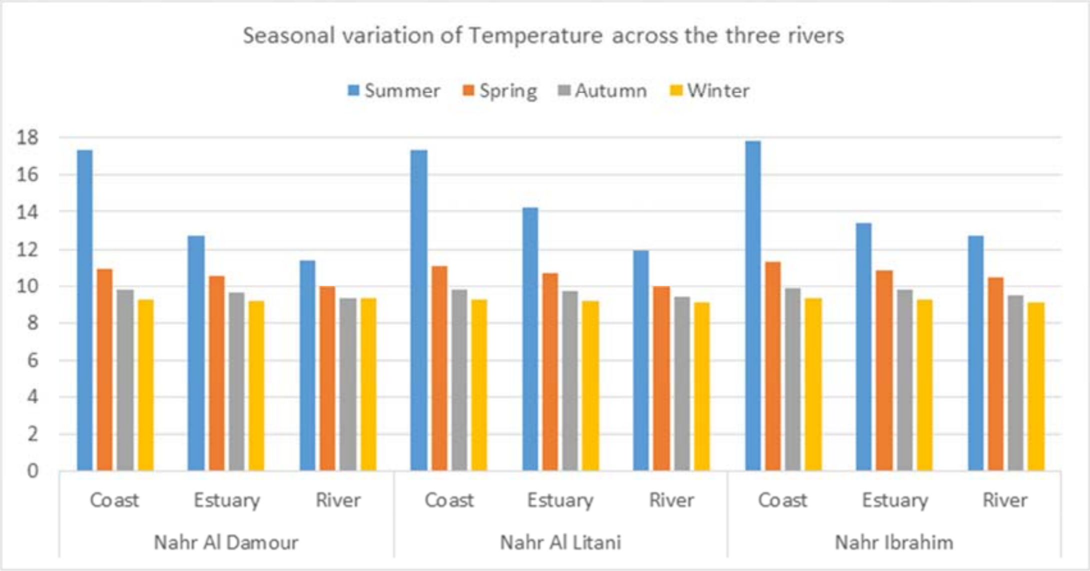

Figure 1. *Temperature variations.*

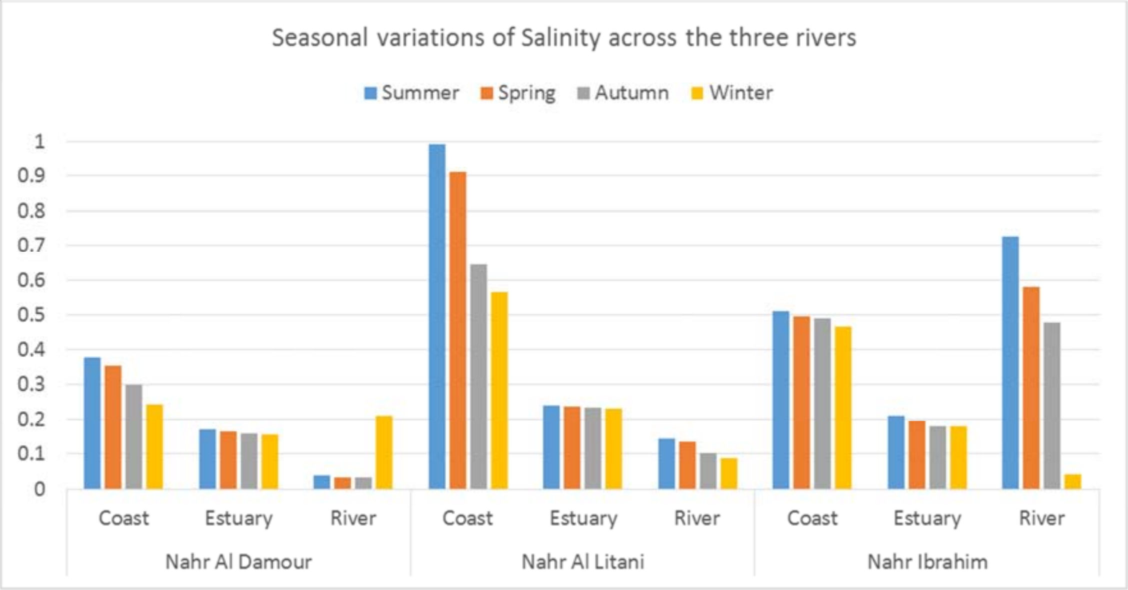

Figure 2. *Salinity variations.*

The gradient between the coastal areas and the river areas was also noticeable with high evaporation reaching its maximum in the former and causing a peak in salinity. Also, the river of Nahr Al Litani is marked by a peak of salinity in its coastal water. This can be explained by the high level of pollution and subsequently nutrients enriching the area (Figure 2).

2.3. pH

The pH was measured directly on site using a pH meter. Unlike salinity and temperature, the pH was not greatly affected by the seasonal variations. It varied throughout the year from 7.65 to 7.85 units. However, a slight increasing gradient was noticed between the coastal and river zones.

The coastal zones being affected by anthropogenic factors can cause the decrease in pH showing a tendency and vulnerability to acidification (Figure 3).

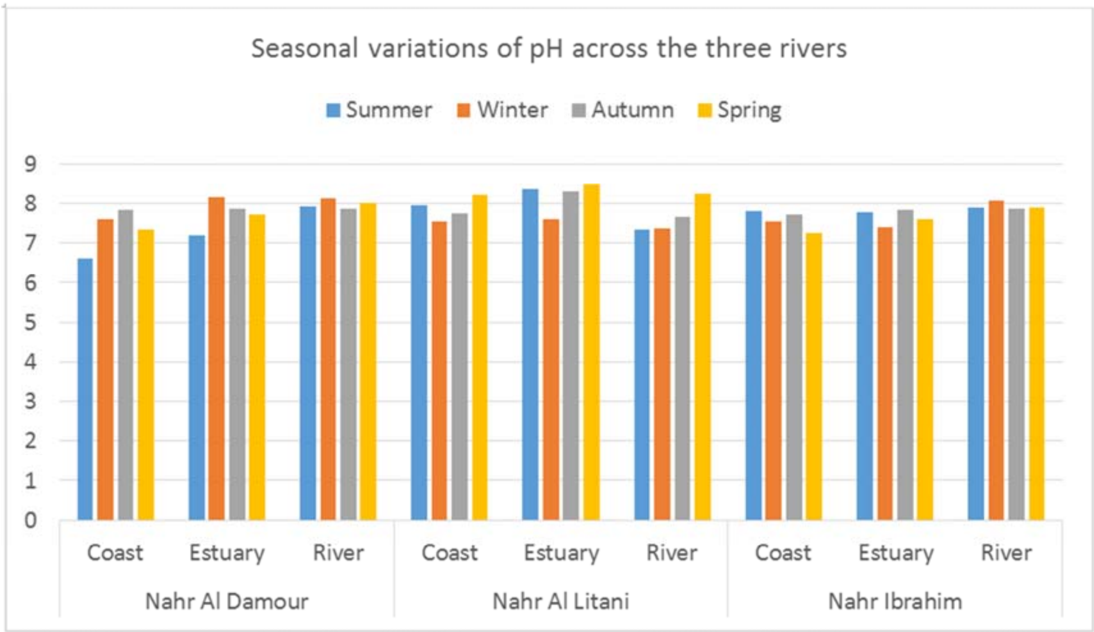

Figure 3. *pH variations.*

2.4. Dissolved Oxygen

Dissolved oxygen (DO) concentrations were measured using the Winkler Iodimetric titration ([1], [4]). The seasonal cycle was noticeable with the lowest DO concentrations of 277 µmol/L recorded in autumn and the highest DO concentrations of 303 µmol/L recorded in summer. A disparity is observed between Nahr Al Litani and Nahr Al Damour. The latter is characterized by the highest DO concentrations of 303 µmol/L. Nahr Al Damour designated by the ministry as a natural site, favors the presence of fauna and flora affecting positively the concentrations of DO (Figure 4).

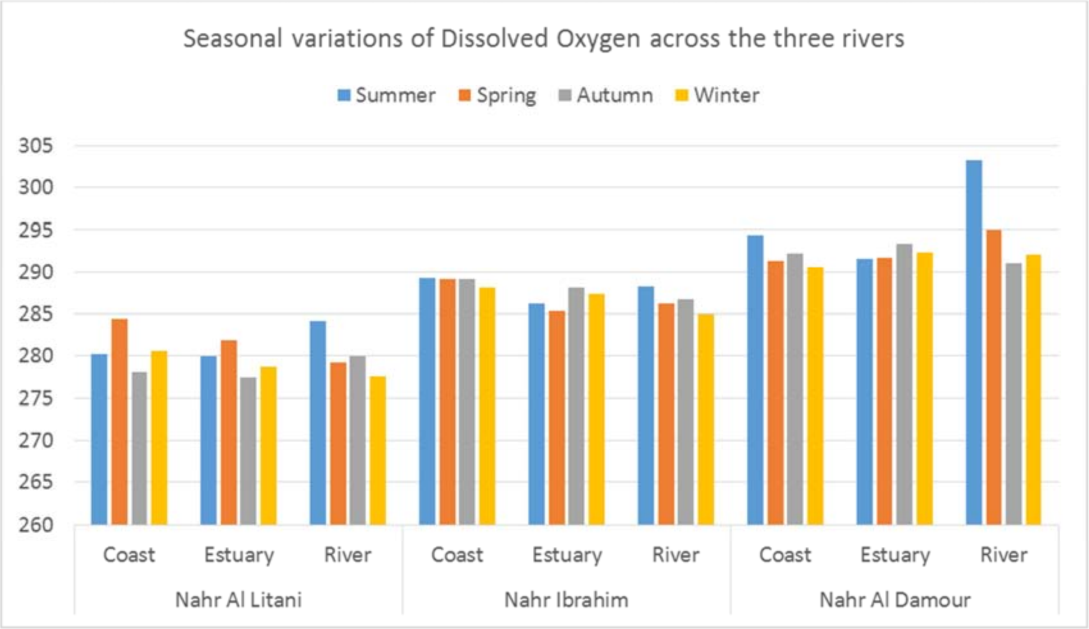

Figure 1. *Variations of Dissolved Oxygen.*

3. Nutrients

Nitrates and phosphates were analyzed respectively according to the standard titration methods ([9, 14]). Episodic discharges were observed both for Nitrates and Phosphates mainly in the Estuary zone of Nahr Al Litani, where concentrations reached respectively 0.13 and 0.002 mmol/L. In fact, Nahr AL Litani is heavily affected by pollution, such as sewage contamination, fertilizers and pesticides. The leachate form nearby municipal solid waste and the dissolution of fertilizers can explain the dominant presence of Nitrates and Phosphates.

Unexpected discharges of Nitrates were observed in the coastal zones of Nahr Ibrahim and Nahr AL Damour reaching up to 0.08 mmol/L (Figure 5). Moreover, peaks of 0.015 mmol/L Phosphates were observed in the estuary zones of Nahr Ibrahim and coastal zones of Nahr Al Damour (Figure 6).

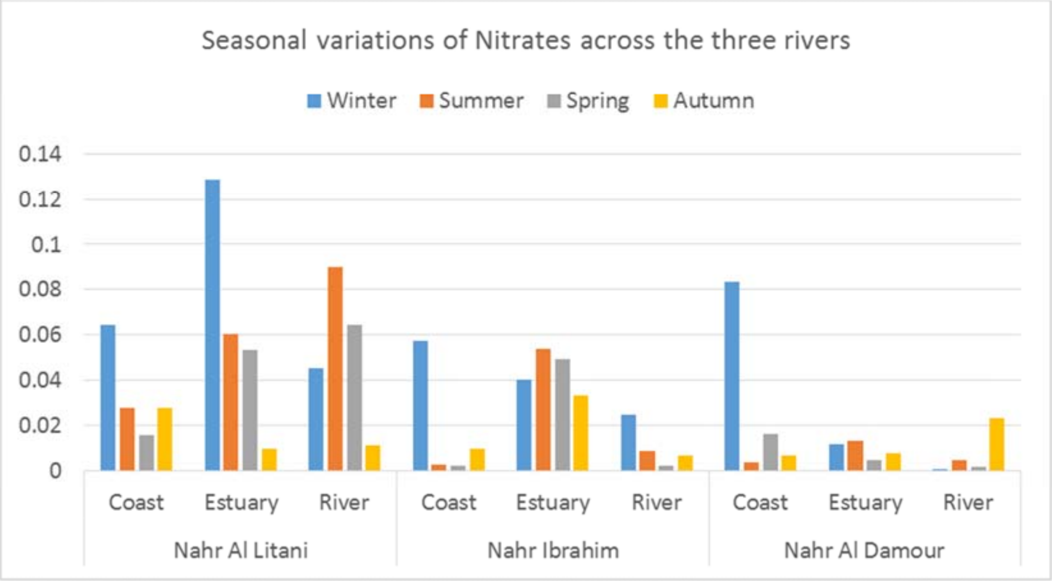

Figure 5. *Variation of Nitrates.*

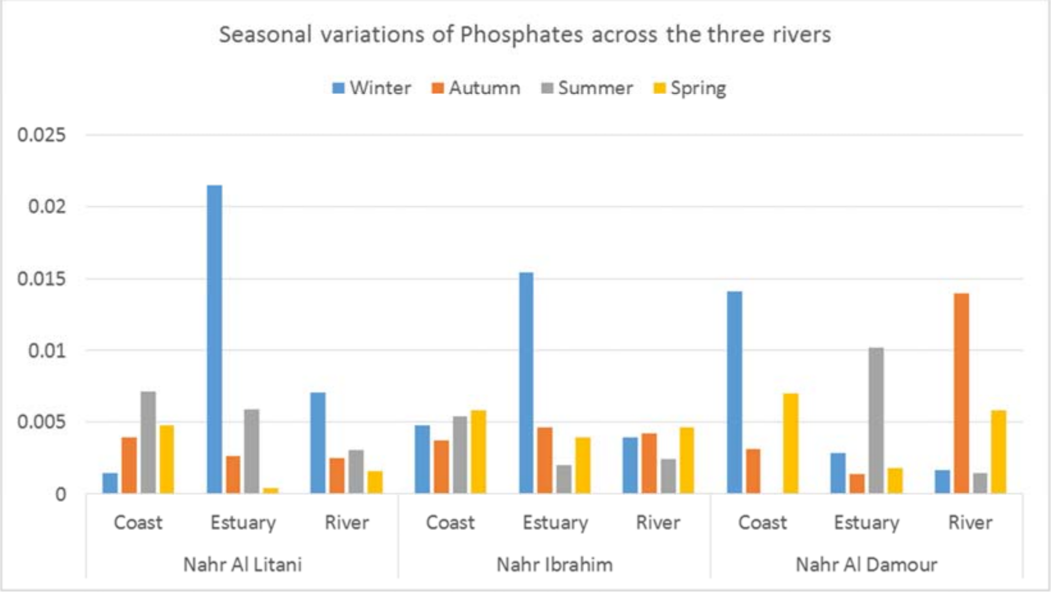

Figure 6. *Variation of Phosphates.*

Nahr Al Damour and Nahr Ibrahim are both designated by the ministry as a natural site and by principle should not be subjected to anthropogenic disturbances. This shows that the human influence is starting to affect these sites as a result of anarchic development and the absence of proper infrastructure.

4. Carbon Content

For Total Alkalinity (AT) and total Dissolved Inorganic Carbon (DIC), the principle and procedure of measurements, as well as a complete description of the system used to perform accurate analysis can be found in the DOE handbook of methods for CO_2 analysis [2].

The partial pressure of CO_2 (pCO_2) will be calculated from the data of AT and DIC, along with the equilibrium constants, in-situ temperature and salinity [13].

4.1. Alkalinity (AT)

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Waters with low alkalinity are very susceptible to changes in pH. Waters with high alkalinity are able to resist major shifts in pH. As increasing amounts of acid are added to a water body, the pH of the water decreases, and the buffering capacity of the water is consumed. Large rivers tend to have greater buffering capacity than small headwater catchments and so they are less susceptible to direct ecological effects of acidification [14].

Alkalinity yield ranged from 0.24 to 1.8 mmol/L in Nahr Al Damour and Nahr Al Litani, respectively (Figure 7). Alkalinity yield increased all monitoring stations mostly in the river areas. The increases were greatest in spring and summer. Trends in alkalinity yield can result either from changing chemical condition of the rivers or from increased runoff which enhances riverine flux of weathering products even in the absence of changes in weathering rates. This also can be explained by agricultural production including cropland area, fertilizer usage, and lime application. Agricultural production could increase weathering rates through soil disturbance and other means of increasing soil respiration ([8, 15], which increase soil CO_2 concentration.

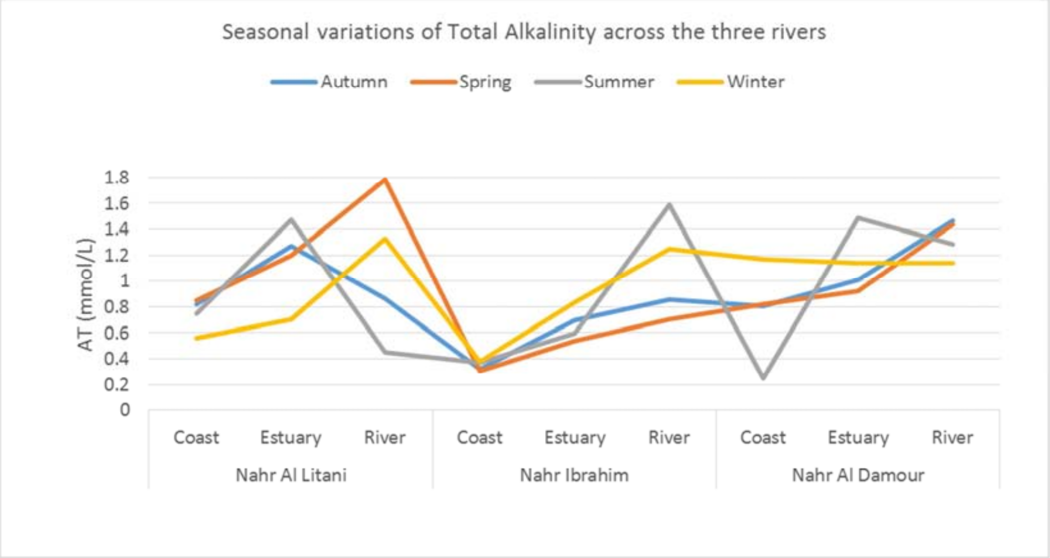

Figure 7. *Variations of Alkalinity.*

4.2. Total Dissolved Inorganic Carbon (DIC)

Typically, the supply of inorganic carbon by rivers to the coastal ocean is governed by river discharge, weathering intensity, and the geology of the drainage basin. The DIC had a general opposite direction compared to AT; with peaks in the coastal zones of the rivers of Nahr Ibrahim and Nahr Al Damour reaching 57 and 39 mmol/L respectively. DIC also shifted with the seasons. DIC trends are likely to play a role in the observed alkalinity trends in this study. DIC contribution to alkalinity is significant in rivers with relatively low alkalinity concentrations (Figure 8).

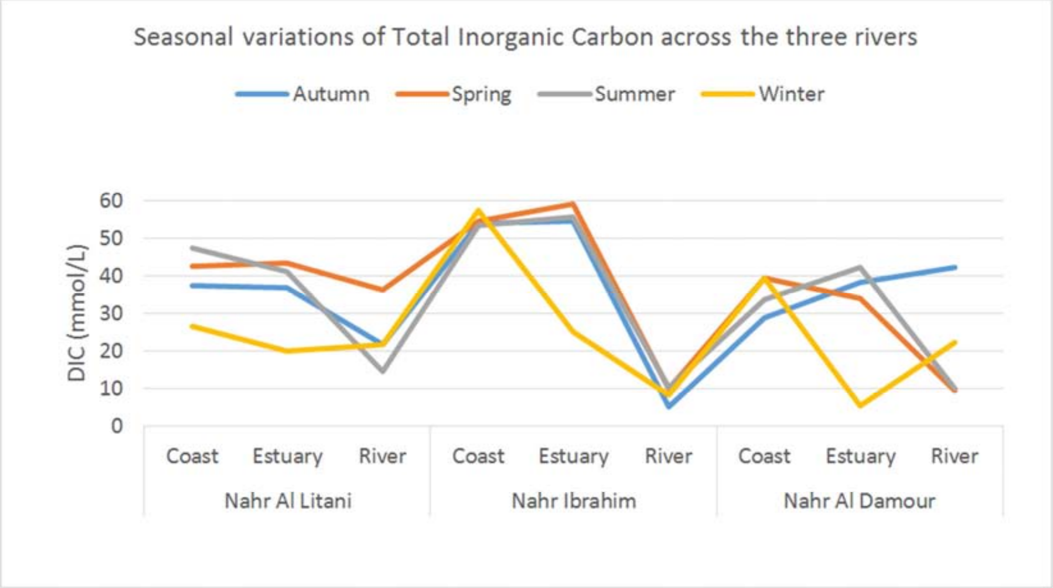

Figure 8. *Variations of DIC.*

4.3. Partial Pressure of Riverine Carbon Dioxide (pCO_2)

The weathering of carbonate and silicate minerals consumes atmospheric CO_2 and transports HCO_3^- ions and subsequent cation and anion products into oceanic systems. Eventually, CO_2 is released back into the atmosphere via oceanic carbonate sedimentation and volcanic activity. The pCO_2 was positively correlated ($P < 0.01$) with AT and could be calculated in case of missing data (Figure 9).

The partial pressure of riverine carbon dioxide (pCO_2), an important parameter in estimating CO_2 evasion, represents the direction and intensity of gas exchange at the water - to - air interface and reflects whether a river is a sink or source of atmospheric CO_2. Our results indicated that pCO_2 ranged from 817 to 3283 µatm, which was much higher than the atmospheric CO_2 concentration. Therefore, the studied rivers acted as an atmospheric CO_2 source.

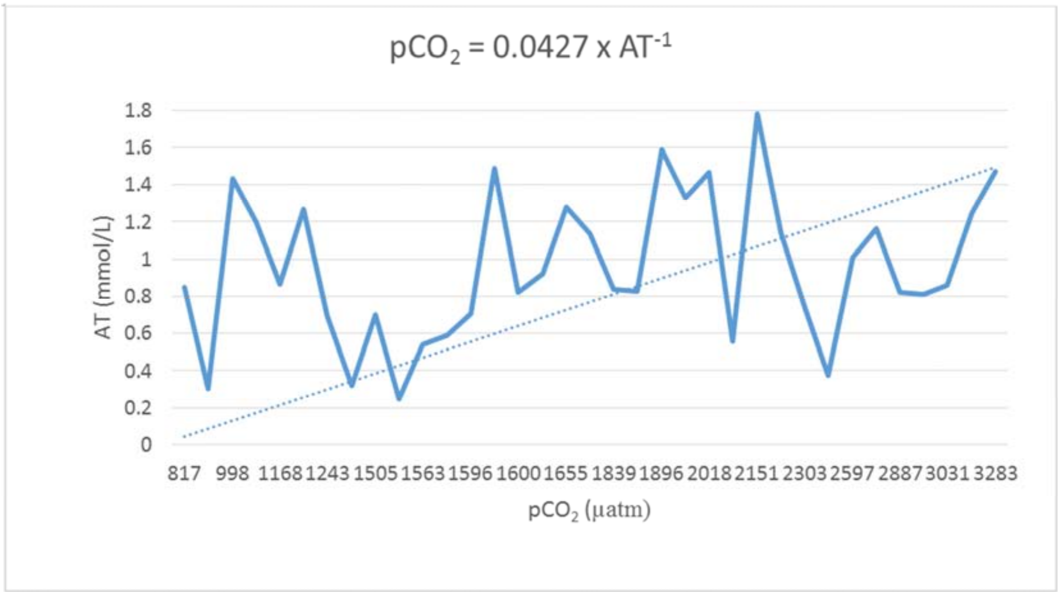

Figure 9. *Relation of pCO_2 with Alkalinity.*

5. Conclusion

In Lebanon, the scarcity of measurements causes large uncertainties regarding the quantification of riverine and coastal carbon fluxes. Also, the chemical composition of the Lebanese riverine-coastal waters, thus their resistance to changes in pH remains unknown.

This study presented the quantification of the carbon fluxes in three major Lebanese rivers characterized by a specific average flow and a different exposure to anthropogenic disturbance: Nahr Ibrahim, Nahr Damour and Nahr el Litani. The gradient between the coastal areas and the river areas was noticeable for all the parameters except pH. Episodic discharges were observed both for Nitrates and Phosphates in Nahr Al Litani, confirming that this river continues to be heavily affected by pollution. Alkalinity yield was mostly noticed in the river areas, and the increases were greatest in spring and summer. Also, the DIC contribution to alkalinity were significant in rivers with relatively low alkalinity concentrations. The pCO_2 was derived from AT and DIC measurements, with a clear trend that the concentrations of CO_2 in the rivers were much higher than in the atmosphere, indicating that the latter are actively releasing carbon dioxide to the atmosphere.

This study provides insight into the riverine CO_2 outgassing in the coastal region of Lebanon, which will improve our current understanding of CO_2 emissions from Mediterranean rivers in the world.

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