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Relationship of dissolved inorganic carbon (DIC) concentrations with some environmental variables in the Red River water in the period 2008 - 2015

Mối quan hệ giữa hàm lượng cacbon vô cơ dạng hòa tan (DIC) với một số yếu tố môi trường trong nước sông Hồng trong giai đoạn 2008 – 2015

Research article

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Dissolved Inorganic Carbon (DIC) is one of the main chemical components in water and very sensitive with environmental changes. DIC content in river water closely relates with natural weathering process and human activities in the whole basin. Therefore, DIC concentration reflects the impact of natural conditions and human activities in the basin to river water quality. This paper presents the survey results of the DIC concentrations at 4 sites in the Red River system during the period from January 2008 to December 2015 and simultaneously considers the relationship between some environmental variables and the DIC concentrations in the river water. The survey results showed that the DIC concentrations in the Red River water varied from 9.1 to 29.9 mgC.L^{-1}, averaging 19.6 mgC.L^{-1} during the study period. The DIC concentrations are positively correlated with pH values and some major ions concentrations in river water, such as K^+, Na^+, Ca^{2+}, SO_4^{2-} but negatively correlated with water temperature. These relationships also indicate that the DIC concentrations in the Red River water are influenced by natural conditions, rather than by human activities in the river basin.

Cacbon vô cơ hòa tan (DIC) là thành phần hóa học cơ bản trong nước và rất nhạy cảm với những thay đổi của các yếu tố môi trường. DIC có mối liên hệ chặt chẽ với sự phong hóa tự nhiên và các hoạt động của con người trên quy mô toàn lưu vực. Do đó, DIC phản ánh mức độ tác động của các điều kiện tự nhiên và con người trong lưu vực tới chất lượng nước sông. Bài báo trình bày kết quả quan trắc hàm lượng DIC trong nước sông Hồng, đồng thời xem xét mối quan hệ giữa một số yếu tố môi trường với hàm lượng DIC trong nước sông trong giai đoạn 1/2008 – 4/2015. Kết quả cho thấy hàm lượng DIC trong nước sông Hồng dao động trong khoảng 9,1 to 29,9 mgC.L^{-1}, trung bình đạt 19,6 mgC.L^{-1} trong giai đoạn tháng 1 năm 2008 – tháng 12 năm 2015. Hàm lượng DIC có mối tương quan theo tỷ lệ nghịch với nhiệt độ nước sông; đồng thời có mối tương quan tỷ lệ thuận với giá trị pH và hàm lượng một số ion như K^+, Na^+, Ca^{2+}, SO_4^{2-}... tại 4 vị trí quan trắc trên sông Hồng. Các mối quan hệ này thể hiện rằng hàm lượng DIC trong nước sông Hồng chịu ảnh hưởng chính của các đặc điểm tự nhiên hơn là các tác động của con người trong lưu vực.

Keywords: dissolved inorganic carbon (DIC), weathering, Red River

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1. Introduction

Dissolved inorganic carbon (DIC) is basic component of water and very sensitive with environmental factors, strongly influenced by rock weathering and human activities in the whole basin. The previous studies showed that DIC is the major component of the total carbon load of many rivers in the World such as the Mississippi, the St Lawence, the Nile River and the most of rivers in China. Some previous studies reported that the World rivers transport about 500 - 700 x 10^6 tonC.yr^{-1}, of which about 45% is DIC [11]. Recently, the DIC load from the global river systems is estimated at 33 – 400 x 10^6 tonC.yr^{-1} [3], [7], [9], [10].

The Red River is one of the largest river in Vietnam and is a good example of the South-East Asian river which is strongly impacted by both natural conditions and human activities in its basin. Like many other rivers in the world, the water quality of this river including inorganic carbon is influenced by both natural conditions and human activities. However, the researches about the carbon concentrations, especially DIC concentration of the Red River are still limited. This paper presents the observation results of the DIC concentration of the Red River during the period from January 2008 to December 2015. The relationship between some environmental variables and DIC concentrations in the Red River water are also considered in this paper.

2. Methodology

2.1 Site study

The Red River consists of three major tributaries, which are the Da, Lo and Thao Rivers, with a total area of about 156.450 km^2. Throughout the whole river catchment, the average air temperature is 14 - 27^{o}C; the average humidity is 60-82% and the average annual rainfall is 1590 mm. There are some big reservoirs in the Red River basin, which are utilized for multi-purposes such as flood control, agricultural irrigation, hydropower, water supply and flow management. The major reservoirs include: the Hoa Binh (water surface area of 218 km^2, water volume: 9.5 km^3) and the Son La (surface area is 440 km^2, water volume: 25.5 km^3) located on the Da River; and the Thac Ba (water surface area: 234 km^2, water volume: 3.6 km^3) located on the Chay river, the Tuyen Quang (surface area of 42 km^2, water volume: 3 km^3) on the Lo - Gam - Chay system [6].

The population density is not evenly distributed, the lowest is in the Da sub-basin and the highest is in the Delta region. In the whole basin area, the forest land and pastureland mainly dominate 34% and 24% respectively in the upstream part; the industrial crops accounted for 13%, accounting for 8% of paddy land; and urban land represents only a very small part (<1%).

2.2 Method

Sampling campaigns: Water samples were monthly taken during the period from January 2008 to April 2015 at four hydrological stations located in the Red River system, which are Yen Bai station (outlet of the Thao river), Hoa Binh station (outlet of the Da river), Vu Quang station (outlet of the Lo river) and Hanoi station (downstream main axe of the Red River) (Figure 1).

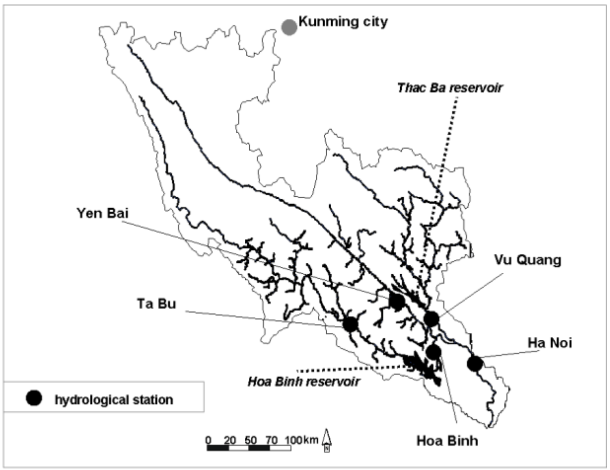

Figure 1: The Red River basin and hydrological stations

Analytical measurements: pH value was measured in-situ by a water quality checker WQC-22A (TOA, Japan). HCO_3^- content was determined by titration method with 0.01M HCl within 12 hours after sampling (APHA, 1995). For each sample, three duplicates were titrated and the analytical error was below 3%. Ions (K^+ and Na^+) were determined by the atomic absorption spectroscopy method on the AAS 240FS (Varian, Australia). SO_4^{2-} was spectrophotometrically measured by the APHA method (1995) on the UV-VIS V-630 (JASCO, Japan).

3. Results and discussion

3.1 DIC concentrations of the Red River

The pH values at all sampling sites were within 6.5 and 8.5. As known, if pH value of river water is lower than 6.3, almost carbonate ions in river water are converted to dissolved CO_2; if pH is higher than 10.3, almost carbonate ions are dominated by the CO_3^{2-} ion; and if 6.3 < pH < 10.3, almost carbonate ions are mainly under HCO_3^- ion. Thus, with pH values of the Red River from 6.5 to 8.5, DIC in Red River water over the years at all monitoring station will exist primarily in form of HCO_3^-.

During the period from 2008 – 2015, the DIC concentrations at four gauging stations were in the range of 9.1 – 29.9 mgC.L^{-1}, with an average value of 19.6 mgC.L^{-1} for the whole river system. It was observed that the mean value of the DIC concentration at Vu Quang station was the highest (22.1 mgC.L^{-1}), followed by Hanoi station (20.0 mgC.L^{-1}), Yen Bai station (18.7 mgC.L^{-1}) and Hoa Binh station (17.7 mgC.L^{-1}). There was no clear difference for the mean DIC concentrations within four stations during the monitoring years (Figure 2).

Table 1: Mean DIC concentrations at monitoring stations during the period 2008-2015

Year	Yen Bai	Hoa Binh	Vu Quang	Ha Noi
2008	19.8	18.7	21.8	20.5
2009	18.5	15.3	19.7	19.3
2010	18.5	15.2	20.9	19.1
2011	15.5	18.7	20.9	18.9
2012	17.0	14.9	21.8	19.7
2013	17.3	16.9	22.9	19.3
2014	19.2	19.7	22.6	19.5
2015	23.6	22.0	26.2	24.0
Average	**18.7**	**17.7**	**22.1**	**20.0**

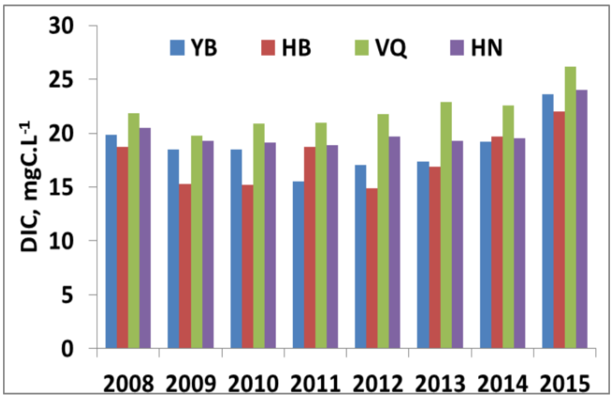

Figure 2: Mean DIC concentrations at four monitoring stations during the period 2008-2015

The mean value of the DIC concentration of the Red River was closed with the ones from some rivers in tropical regions such as the the Yangtze River (in Asia) (28mgC.L^{-1}) [3], the Ganga/Bramaputra River (23mgC.L^{-1}) [15], the Irrawaddy River (24 mgC.L^{-1}) [2], the Zhujiang River: 20 mgC.L^{-1} [19], the Jinshajiang River: 27.6 mgC.L^{-1} [4], the Han River: 29.6 mgC.L^{-1} [8], but much lower than the ones of the Tuotuo River: 55.4 mgC.L^{-1}, the Tongtian River: 58.8 mgC.L^{-1} [12] However, this value was higher than the ones of some other World Rivers such as the Amazon: 4 mgC.L^{-1} [13], the Zaire: 3 mC.L^{-1} [5], the Susquehanna/Hudson River: 3.8 mgC.L^{-1}, the York River 6.7 mgC.L^{-1}; the Parker River: 9.9 mgC.L^{-1} [14] and especially, higher than the mean value of the world rivers: 9.6 mgC.L^{-1} [17]. According to Cai et al (2008) [3], the different DIC concentrations in rivers may not depend only on the percentage of carbonate rocks distributing in their drainage basins and that the very high DIC concentrations in rivers due to the fact that they have a much higher evaporation water loss over precipitation rate in a large part of their river basins (i.e., low water river discharge).

3.2 Relationship between DIC concentrations and some environmental variables in the Red River water

Relationship with water temperature

The increase of river water temperature may provide favourable conditions for the ion dissociation in water, and accelerate chemical reactions in water. When the water temperature rises, the solubility of CO_2 in water decreases, then the ability of H_2CO_3 forming in water decreases, thus H^+ will be less, and pH increases, and DIC concentration decreases. Figure 3 shows an inversely proportional correlation between the river water temperature and DIC concentration at all monitoring stations of the Red River system.

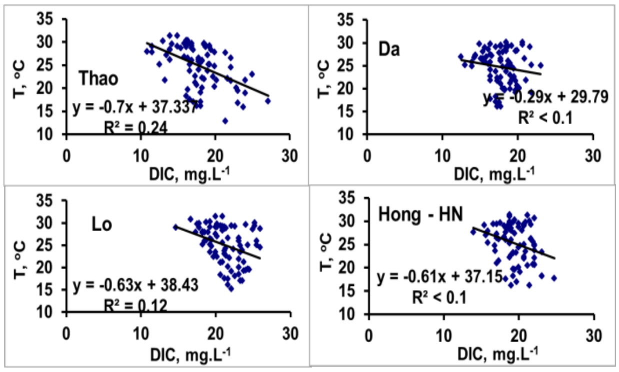

Figure 3: Relationship between DIC and water temperature of the Red River water at four stations

Relationship with pH

The concentration of ion H^+ is not only dependent on the dissociation of water but also on the separation of ions CO_3^{2-}, HCO_3^-, CO_2. Typically, ion H^+ concentration depends mainly on the concentration of bicarbonate ions [HCO_3-] basing on an inversely proportional relationship. That means, when HCO_3^-concentration increases H^+ concentration is reduced, thus, pH of the water will increase, and vice versa. The same trend between pH and bicarbonate ions [HCO_3^-] (i.e. DIC) was observed for the Red River water (Figure 4).

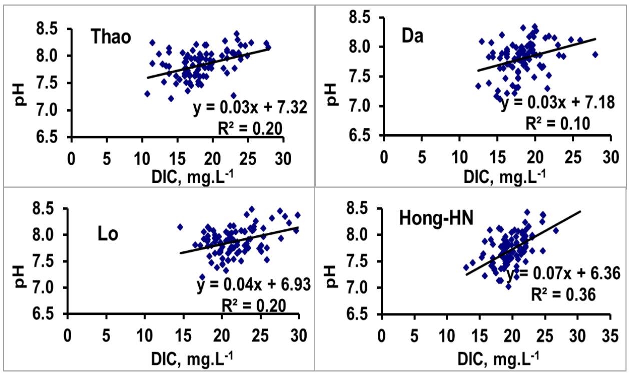

Figure 4: Relationship between DIC and pH in the Red River water at four sites

Relationship with other ions

a) Relationship with K^+ and Na^+: K and Na are two elements which are supplied by natural rocks or by fertilizer applications in agriculture which is the main economic activity in the Red river drainage basin [12]. A positive correlation between K^+ and DIC concentration was observed for the Red River although it was not significant (Figure 5).

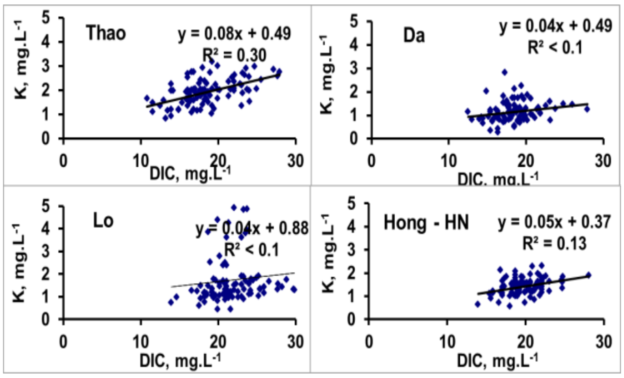

Figure 5: Relationship between DIC and K^+ in river water at four monitoring stations

A positive correlation between Na^+ concentration and DIC was also observed for all monitoring sites. (Figure 6).

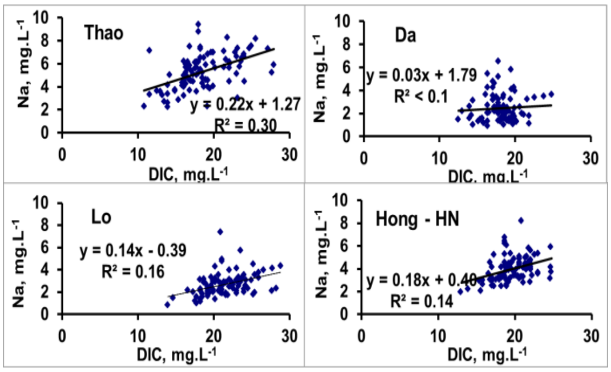

Figure 6: Relationship between DIC and Na^+ in river water at four monitoring stations

b) Relationship with Ca^{2+}:

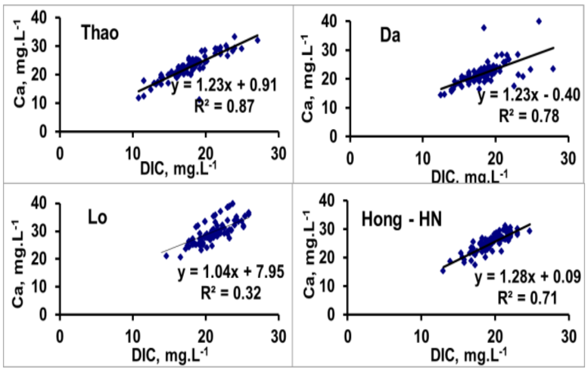

Figure 7: Relationship between DIC and Ca^{2+}in riverwater at four monitoring stations

Ca^{2+} concentrations showed a clear positive correlation with DIC concentrations at all four sites. This can be explained by chemical weathering of carbonate rocks in the basin, leading to the formation of $Ca(HCO_3)_2$ in river water and then $Ca(HCO_3)_2$ easily decompose into Ca^{2+} and HCO_3^-. Thus, the concentrations of Ca^{2+} and HCO_3^- will increase together.

d) Relationship with SO_4^{2-}:

As known, SO_4^{2-} concentration in the river water is supplied by natural conditions (dissolution of gypsum, oxidation of pyrite, volcanism, etc.) or by human activities in the river basin. In river water, the process of sulfate reduction were performed by microorganisms in anoxic environments and rich in organic matters. This process creates H_2S gas and simultaneously releases HCO_3^-, CO_2 according to the following equation:

$$2SO_4^{2-} + 4C + 3H_2O \rightarrow H_2S + HS^- + CO_2 + 3HCO_3^-$$

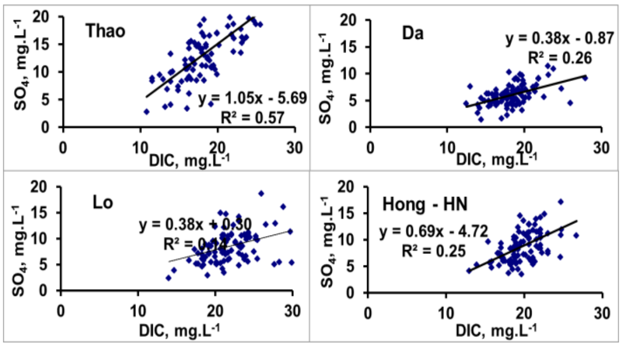

Figure 7: Relationship between DIC and SO_4^{2-} in the Red River water

This proves that if more SO_4^{2-} supplied in the river water, HCO_3^- (DIC) concentration in the water will be also increased. SO_4^{2-} concentrations tend to increase with DIC in the Red River water at all monitoring sites (Figure 7). This relationship is clearly observed at the Yen Bai station (Thao River) (R^2 = 0.57). Previous study [12] suggested that pyrite oxidation was the dominant source of sulfate in the upstream of the Red River basin as the distribution of coal-bearing and sulfide bearing deposits in this area.

4. Conclusions

The monitoring results at four sites in the Red River system during the period from 2008 – 2015 showed that the DIC concentrations were in the range of 9.1 – 29.9 $mgC.L^{-1}$ with an average value of 19.6 $mgC.L^{-1}$ for the whole river system. There was no clear different for the mean DIC concentrations within four stations during the monitoring years.

The DIC concentrations in the Red River water have a positive correlation with the pH and some ions like K^+, Na^+, Ca^{2+} and SO_4^{2-} but it showed a negative correlation with river water temperature. These relationships also indicate that the DIC concentrations in the Red River water are influenced by natural conditions, rather than by human activities in the river basin.

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