

The dynamic of major ions and dissolved inorganic carbon in urban rivers in Tianjin, North China

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Abstract The distribution of diverse lithology and human activities impacts the water chemistry and carbon biogeochemistry of river systems. Major ion chemistry and dissolved inorganic carbon (DIC) in the urban rivers at Tianjin City, China, were examined based on a temporal and spatial sampling scheme in 2021. The concentrations of major ions exhibited significant spatial variations, showing agricultural input in the upstream and urban pollution in the downstream. The isotopic composition ($\delta^{13}\text{C}$) of DIC in the rivers ranges from -12.39‰ to -0.45‰ , indicating partial equilibrium between the water and the atmosphere in some waters due to long residence time, where $\delta^{13}\text{C}$ is typically 0‰ . The waters with more negative $\delta^{13}\text{C}$ values showed that biological CO_2 was a major contributor to DIC in most rivers. It experienced slightly more depletion during the wet season than in the dry season, reflecting strong degradation of organic matter in summer. The seasonal variations likely reflected changes in metabolic processes in the river in addition to alterations in the hydrological regime, highlighting the implications of freshwater given geoscientific, ecological, and environmental aspects.

Essential aspects of human activities, including agriculture, urban development, and dam construction, significantly influence the dynamics of water chemistry and DIC. The study highlighted that variations in lithology and hydrology significantly affect the spatial and temporal changes in water chemistry and carbon geochemistry within river systems.

Keywords DIC · Lithology · Human activity · Biological CO_2 · Hydrological variabilities

1 Introduction

Rivers are crucial in connecting land and ocean cycles by transporting dissolved and solid materials from the land to the sea. Data on inorganic and organic constituents, as well as ionic fluxes in the river, have been supplemented with stable carbon isotope tracers in recent decades (Karim et al. 2011; Raymond et al. 2013; Yi et al. 2021). The transport of carbon from the land to the ocean via rivers is crucial due to its strong link with the global climate system. In many rivers around the world, dissolved inorganic carbon (DIC) fluxes constitute the majority of total carbon fluxes. It is estimated that approximately 60% of the total global carbon fluxes (10^{15} g C/yr) transported by river systems are in the form of inorganic carbon, with 0.43×10^{15} g C/yr being in the form of DIC (Meybeck 1987).

Complex processes in the riverine DIC system include chemical weathering of carbonates and silicates, bacterial oxidation of organic matter, CO_2 exchange with the atmosphere, photosynthesis, precipitation, and carbonate dissolution (Aucour et al. 1999; Raymond et al. 2013; Brighenti et al. 2024). DIC's primary component is bicarbonate, mainly from the chemical weathering of carbonates and silicates in the drainage basin. Analysis of major ion chemistry and DIC

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cycling in river systems reveals the key processes influencing water chemistry and carbon transport (Barth et al. 2003; Yi et al. 2021). The stable carbon isotope signature of DIC ($\delta^{13}\text{C}$ -DIC) serves as a valuable tool for understanding the biogeochemical dynamics of river systems. It is widely used to trace sources and processes within the riverine carbon cycle (Lee et al. 2007). The chemistry of major ions and inorganic carbon geochemistry are influenced by a range of natural and human activities. Natural factors, especially variations in lithology, have significant impacts on water chemistry (Brighenti et al. 2024; Zhao et al. 2024). Human activities, including agriculture, industrial wastewater discharge, and damming, significantly affect river chemistry (Raymond et al. 2008; Yi et al. 2021). Studies have previously been conducted at the basin scale, focusing on organic pollutants in rivers and their transmigration activity (Rao et al. 2013; Zhong et al. 2018; Li et al. 2022). However, the factors controlling riverine carbon have not been clearly understood, especially in urban rivers.

Few studies have examined the riverine carbon cycle in a densely populated catchment area that drains a low carbonate terrain and discharges directly into the sea (Barth et al. 2003; Raymond et al. 2008; Yi et al. 2021). Carbon dissolution from carbonate rocks often dominates watersheds, even in areas with trace carbonate presence and high sulfate loads (Das et al. 2011). The initial $\delta^{13}\text{C}_{\text{DIC}}$ for groundwater from globally dominant C4 plant ecosystems is approximately -23‰ , assuming no carbonate weathering is involved (Schulte et al. 2011). Carbon derived from organic materials exhibits more negative $\delta^{13}\text{C}_{\text{DIC}}$ values, reaching down to -26‰ , which is characteristic of ecosystems dominated by C3 plant metabolism (Brunet et al. 2009). This study provides a comprehensive analysis of major ions and DIC across five urban rivers in North China. The river basin features diverse lithological settings and varying anthropogenic impacts across different river reaches, facilitating the study of how various natural and human factors influence river water chemistry. This study has two primary objectives: (1) to probe seasonal and spatial variations in the concentrations of major ions, DIC, and carbon isotopes, and (2) to explore how lithology and other factors, including human activities, influence water chemistry and the DIC system. To assess the sources and cycling of solutes in river waters, our primary objective was to evaluate the influence of both anthropogenic and natural factors on the carbon cycle in the urban rivers.

2 Materials and methods

2.1 Study area

The Haihe River Basin is a key area in the western part of the Bohai Gulf. The Bohai Gulf lies to its east, while to

the west it is bordered by the Taihang Mountains. In the south, it approaches the Yellow River, and in the north, it borders the Mongolian Plateau. The total area of the basin is $32.06 \times 10^4 \text{ km}^2$, which accounts for 3.3% of the country's total area. The basin's topography is elevated in the northwest and lower in the southeast, and it can be roughly divided into three distinct landforms: plateau, mountain, and plain. The region is classified as belonging to the temperate East Asian monsoon climate zone. The distribution of rainfall in the Haihe River basin is irregular. During the summer it is affected by oceanic air masses, resulting in high temperatures and significant rainfall, predominantly from rainstorms. This heavy rainfall can lead to limited dilution and weak scouring of pollutants in the smaller rivers.

Tianjin is a major city located in northern China, with a population of 15.6 million people. It is situated between $38^{\circ}34'$ and $40^{\circ}15'$ N latitude and between $116^{\circ}43'$ and $118^{\circ}04'$ E longitude, featuring a temperate monsoon climate. The annual average precipitation in Tianjin is between 500 and 700 mm, evaporation is 1029 mm, and the temperature is 12.0°C (Wang et al. 2015). Tianjin, located in the lower reaches of the Haihe River, features a well-developed water system with numerous small rivers. Tianjin is a significant industrial city in China, known for its various industries including chemicals, plastics, and textiles. These rivers flow through industrial areas densely populated with paint factories, building materials factories, and automobile repair shops. There are shopping malls and residential areas in these densely populated locations. The rivers then become well-known receiving bodies for industrial and domestic wastewater, as well as surface runoff from agriculture and aquaculture within the city. A water quality assessment identified the main pollutants in the lower reaches of the Haihe River Basin, which included total nitrogen, chemical oxygen demand (COD), biochemical oxygen demand over 5 days (BOD₅), the permanganate index, and fluoride. The pollution levels are primarily characterized by organic matter and high nutrient concentrations. Overall, the water pollution in all evaluated rivers is severe, with 81.8% of the rivers classified as inferior class V (Liu et al. 2010).

Sites at the confluence of tributaries were key sampling locations. Treated and untreated wastewater was discharged into small urban rivers. The details of the sampling sites are shown in Fig. 1. Up to December 2021, a total of 320 water samples were collected from the rivers of Jiyun ($n=9$ localities, JY1–JY9), Chaobai ($n=4$ localities, CB10–CB13), Yongding ($n=4$ localities, YD14–YD17), Haihe ($n=12$ localities, HH18–HH29), and Duliujian River ($n=3$ localities, DJ30–DJ32) during the 10-month sampling period.

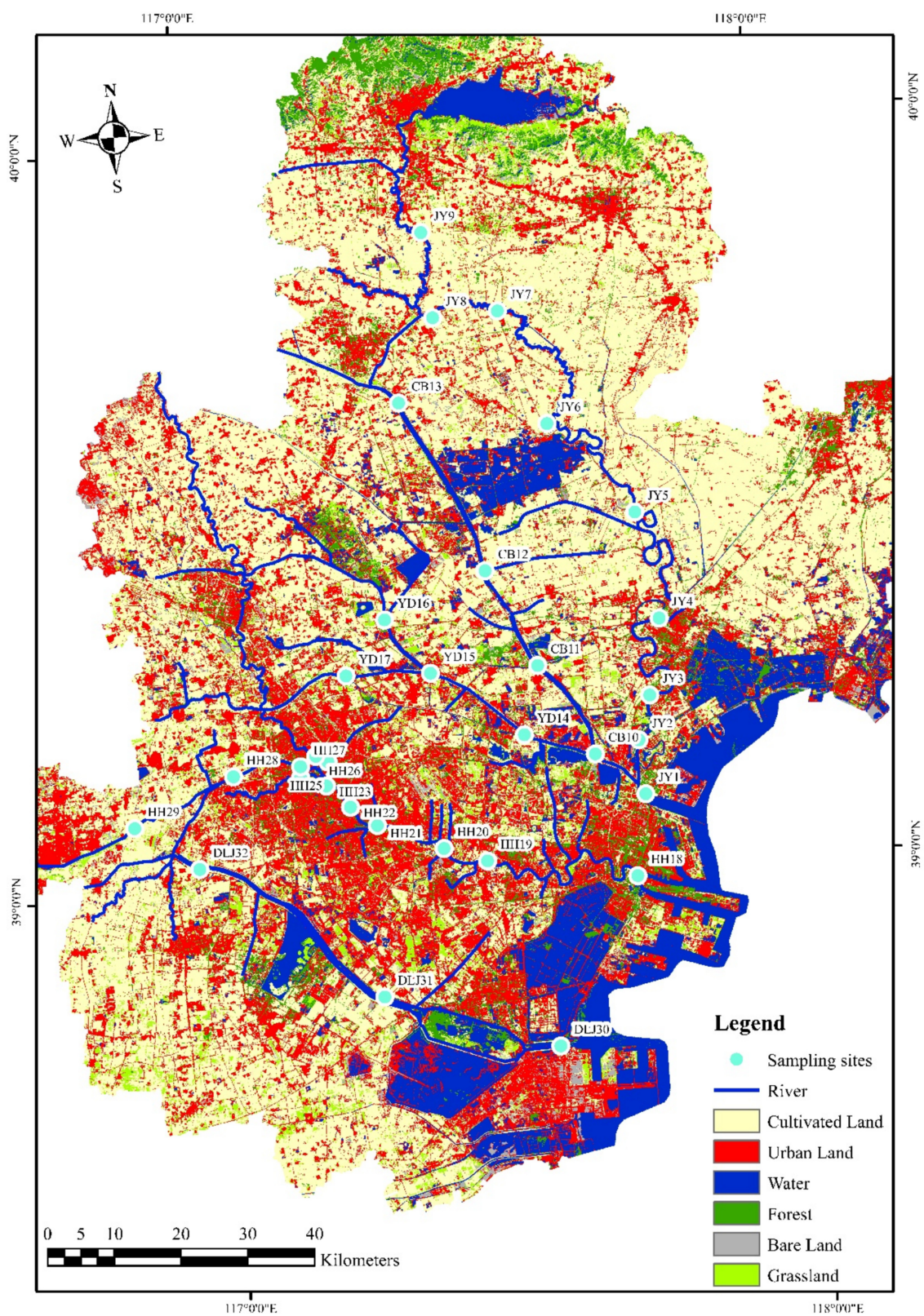


Fig. 1 The Jiyun, Chaobai, Yongding, Haihe, and Duliujian Rivers within Tianjin City of northern China and sample station numbers

2.2 Sampling and analyses

The sampling sites were located in the centers of the five rivers (Jiyun River, Chaobai River, Yongding River, Haihe River, and Duliujian River) in Tianjin City. We collected water samples each month during 1 year, from March 2021 to December 2021, and additionally sampled in the high-flow season (June 2021–August 2021) according to the runoff changes. Water samples were stored in pre-cleaned low-density polyethylene bottles and then filtered through 0.7- μm glass fiber filters. All the water samples were stored at 4 °C before analyses. Alkalinity was titrated with 0.02 mol/L hydrochloric acid within 24 h after sampling, and the DIC concentration was calculated based on mass–balance relationships (Clark and Fritz 1997). Dissolved organic carbon (DOC) concentrations were determined by a total organic carbon (TOC) analyzer (OI Analytical Aurora 1030, College Station, TX). Cation samples were acidified with 2% concentrated HNO_3 and stored in 60-mL high-density polyethylene (HDPE) bottles. Samples were kept refrigerated at ~4 °C.

Major anions were measured on a Unicam ultraviolet–visible (UV/Vis) spectrophotometer following standard laboratory procedures (Hach 1997). The standard deviations of repeat measurements were 0.009 and 0.007 mmol/L for Cl^- and SO_4^{2-} , respectively. Ca^{2+} and Mg^{2+} were determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES), while Na^+ was measured by atomic adsorption spectroscopy. Their standard deviations were 0.0125, 0.0093, and 0.0090 mmol/L for Ca^{2+} , Mg^{2+} , and Na^+ , respectively. A total of 15 mL of river water samples for $\delta\delta^{13}\text{C}_{\text{DIC}}$ analysis was first injected into sealed vacuum glass bottles that were prefilled with 2 mL 85% phosphoric acid and a magnetic stirrer bar to convert all DIC species to gaseous CO_2 . Then the produced CO_2 was purified cryogenically in a vacuum system and transferred for carbon isotopic measurements (Zhong et al. 2018). Finally, the value of $\delta^{13}\text{C}_{\text{DIC}}$ was measured using a conventional isotope ratio mass spectrometer (Finnigan MAT 252, Thermo Finnigan, USA) at the Institute of Surface-Earth System Science, Tianjin University. The $\delta^{13}\text{C}$ value was reported in terms of deviation from the standard Vienna Pee Dee belemnite (VPDB), with a standard deviation of 0.1‰.

3 Results and discussion

3.1 Spatiotemporal variations in the water chemistry of the river water

On the temporal and spatial scale, the drainage mean elevation varied from 0.92 to 8.56 m for the studied

catchments. The water temperature ranged between 1.7 °C and 32.9 °C, with an average of 16.7 °C for the collected samples. The water temperature in the wet season (June to August, 28.35 °C) is twice that in the dry season (March to May, September to December, 14.17 °C). All the river water samples were from near neutral to alkaline, with pH ranging from 7.65 to 9.55.

High concentrations of Na^+ and Cl^- were observed for all the samples, with ranges of 2.49–10,746.09 mg/L and 1.36–19,708.32 mg/L, respectively. The concentrations of Na^+ and Cl^- in the wet season (442.19 ± 1519.34 and 687.93 ± 2673.55 mg/L) were higher than those in the dry season (352.08 ± 1099.63 and 540.27 ± 1931.55 mg/L) by 90.11 and 147.66 mg/L. HCO_3^- concentration ranged from 0 to 186.4 g/L, with an average of 34.7 ± 17.54 g/L. The DOC concentration varied widely, ranging from 1.28 to 25.85 mg C/L and averaging 6.26 ± 3.37 mg C/L. The mean value of DOC did not vary significantly between seasons, with 6.07 ± 1.83 mg C/L in the wet season and 6.34 ± 3.86 mg C/L in the dry season. The DIC concentrations varied from 0 to 240.9 mg C/L, with a mean value of 45.21 mg C/L, for the five rivers. The DIC concentrations in the five rivers showed high values in the low-flow season (0–240.90 mg C/L, avg. 47.28 ± 19.31 mg C/L) and low values in the high-flow season (18.58–87.84 mg C/L, avg. 40.46 ± 13.45 mg C/L).

The $\delta^{13}\text{C}_{\text{DIC}}$ value of the five rivers ranged from -12.39‰ to -0.45‰ , with a mean value of $-7.39\text{‰} \pm 2.05\text{‰}$, -10.86‰ to -1.41‰ ($-7.12\text{‰} \pm 1.96\text{‰}$) and -12.39‰ to -0.45‰ ($-8.00\text{‰} \pm 2.15\text{‰}$) in low-flow and high-flow periods, respectively. In general, $\delta^{13}\text{C}_{\text{DIC}}$ in the wet season had a broader range than in the dry season, and the wet season values were lighter. Seasonal trends of $\delta^{13}\text{C}_{\text{DIC}}$ values differed significantly from spatial trends, with the lowest average of -9.34‰ observed during the high-flow period (July) across the months sampled from the same locality (analysis of variance [ANOVA] test, $p < 0.001$). During the wet season, a part of the discharge comes from the tributary basins, which display a diminished signal. During the dry season, when the water level drops, a larger percentage of discharge comes from tributaries with relatively enriched ^{13}C (Fig. 2). $\delta^{13}\text{C}_{\text{DIC}}$ values showed inverse variations with DIC in these five rivers ($r = -0.182$, $P \leq 0.01$) (Fig. 3). The DOC concentrations ranged from 1.28 to 25.85 mg C/L (avg. 6.26 ± 3.37 mg C/L). Seasonally, the DOC concentrations showed almost no variation between the high- and the low-flow seasons (6.07 ± 1.83 mg C/L and 6.34 ± 3.86 mg C/L).

3.2 Dynamics of major ion chemistry

3.2.1 Seasonal variations

The seasonal variations and dilution effect of increased water discharge for most ions were limited in this study

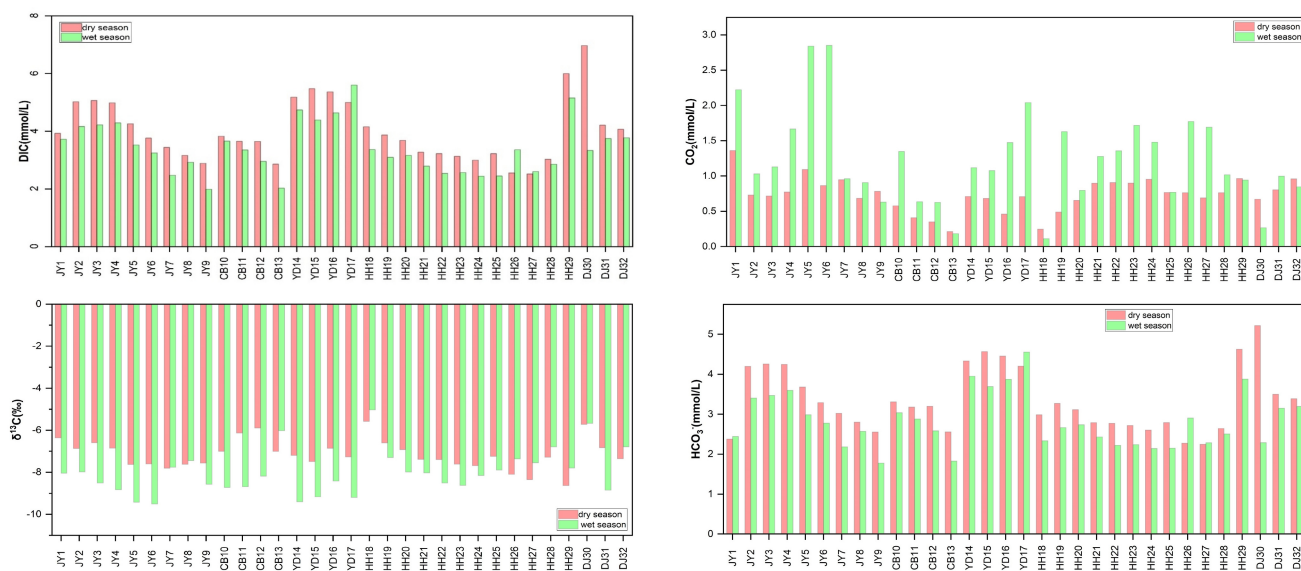


Fig. 2 The variations for carbon forms and isotope $\delta^{13}\text{C}$ during different seasons at each sampling site

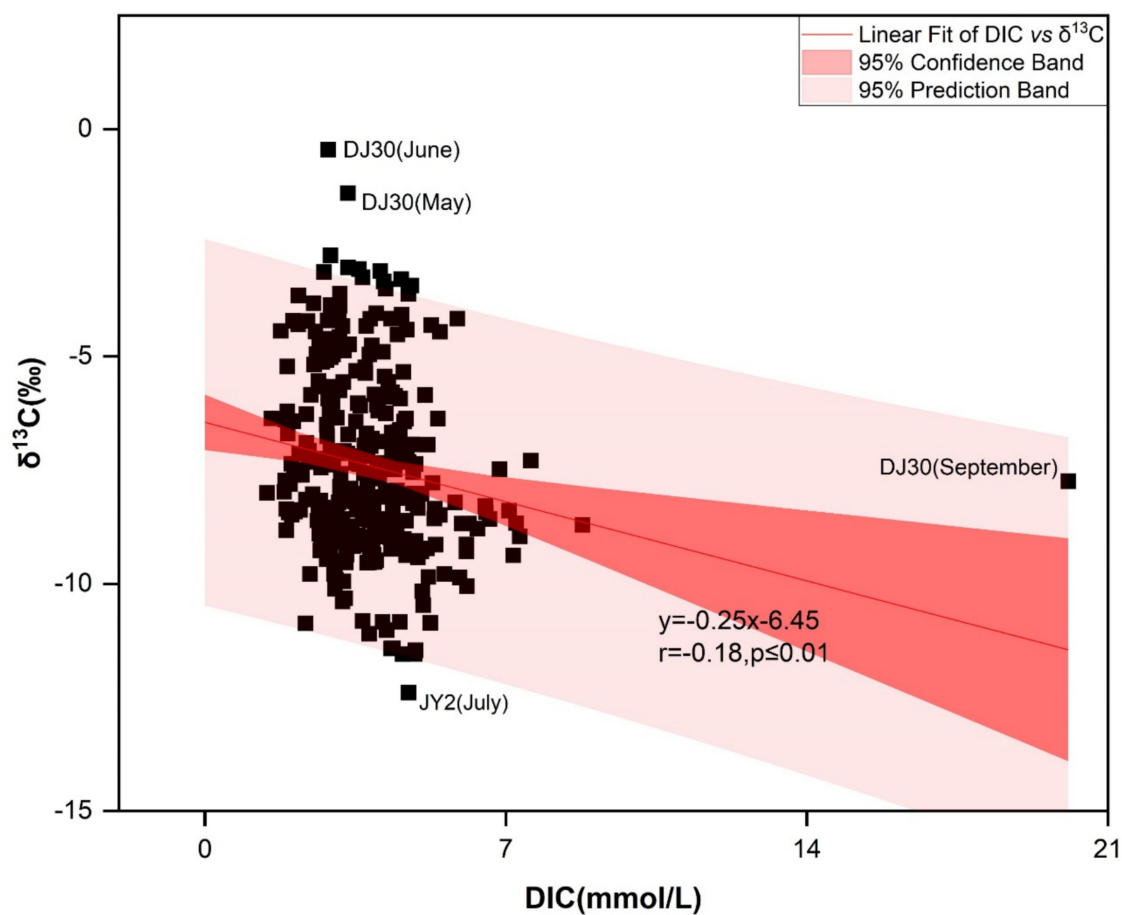


Fig. 3 The relationship between DIC and $\delta^{13}\text{C}$ values with 95% confidence and prediction band for the five rivers

(Fig. 4). River water chemistry is strongly influenced by the weathering of rocks, the dissolution and hydrolysis of minerals, and the precipitation of various substances (Meybeck 1987; Raymond et al. 2008; Brighenti et al. 2024). The processes of chemical weathering involve interactions between hydrological and biogeochemical cycles, which play significant roles in the relationship between terrestrial and aquatic environments. These interactions contribute to

the sequestration of CO_2 in both land and water systems (Schulte et al. 2011). The processes between the atmosphere and lithosphere and those between the biosphere and lithosphere both result in the release of cations (Karyotis et al. 2005). Most ions showed higher concentrations in the high-flow period; for example, Cl^- , SO_4^{2-} , Na^+ , K^+ , and Mg^{2+} were higher, at 147.68, 26.88, 90.16, 5.46, and 6.48 mg/L, than in the low-flow period (ANOVA test, $p < 0.001$). The

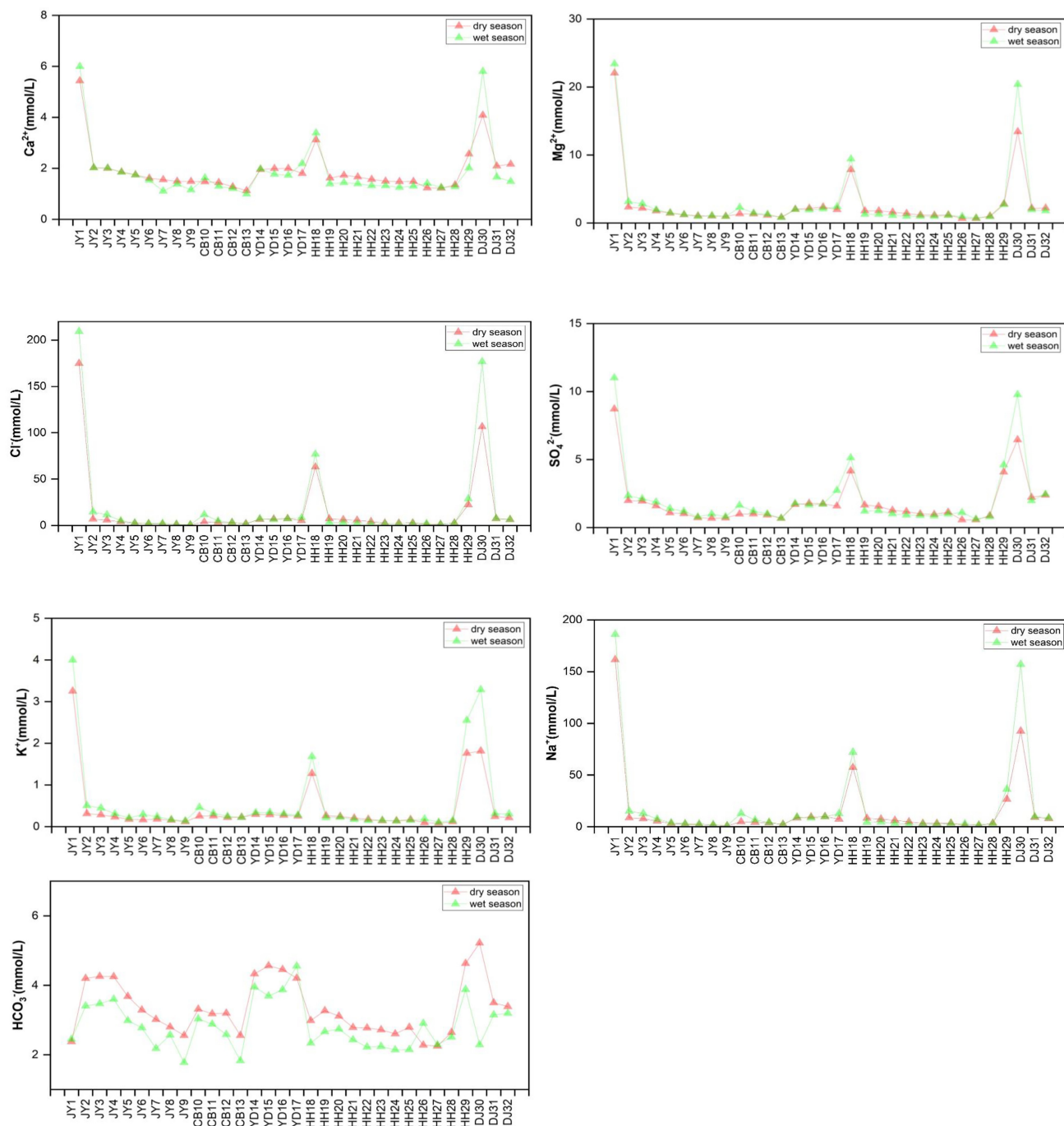


Fig. 4 The variations for anions and cations during varied seasons at each sampling site

highest concentration of Na^+ was observed during the wet season (June) at most sampling sites, particularly noticeable at the downstream points in the Haihe River. This trend was especially pronounced at the confluence of tributaries (JY1, HH18, DLJ30) that connect to the Bohai Gulf. This is likely due to large seawater intrusion at these three sampling sites. Additionally, there is a possibility of the dissolution of soluble salts from trees, leaf litter, and the topsoil, which increases with the overflow. However, HCO_3^- and Ca^{2+} were the exceptional ions and had concentrations of 26.84 and 2.8 mg/L higher in the dry period. Higher concentrations of Cl^- and SO_4^{2-} in the high-flow period reflected the enhanced contributions from diffuse pollution sources, such as fertilizers and pesticides applied in the irrigated farmland in the basin. HH29 is situated in a typical agricultural area in the southwest of Tianjin. The levels of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , and HCO_3^- demonstrate a common trend: their increases are more pronounced upstream of the Haihe River (HH29), independent of any seawater intrusion. Farmland and population are primarily concentrated along the rivers in the basin due to the influence of landforms. Most of the farmland in the basin consists of paddy and wheat fields, which have well-connected irrigation facilities that facilitate the export of chemicals, such as fertilizers and pesticides, to rivers.

The equivalent fractions of Ca^{2+} and Mg^{2+} in the JY, CB, HH, and DJ river waters showed a decreasing trend from upstream to downstream (Fig. 4), while the fraction levels of Na^+ and K^+ steadily increased. This is not applicable to the YD River, where fractions of cations and anions showed no variations. The fractions of HCO_3^- gradually decreased from upstream to downstream, of which Cl^- increased step by step; most of the sampling sites controlled the SO_4^{2-} fractions in the range of 0.2–0.34. Limestone weathering was driven and relatively stronger upstream than downstream, excluding the areas in which JY1, HH18, DJ30, and HH29 were located. Cl^- had the highest concentrations among all of the ions; chlorination of public water supplies and domestic usage can increase the amount of Cl^- in domestic sewage, in addition to brine invasion from Bohai Gulf. Even in treated sewage effluents, the concentration of Cl^- remains higher than that in natural river water (Zhang et al. 2009). This can be explained by the ternary water chemistry system in which chloride and sulfate of Na^+ , K^+ , Mg^{2+} , and Ca^{2+} predominated at JY1, HH18, HH29, and DJ30, and NaCl was prevalent at JY9 (Fig. 5). The gypsum and carbonate weathering by CO_2 was a major contributor to $\delta^{13}\text{C}$ values. JY1, HH18, and DJ30 experienced salinity enhancement due to brine invasion. The pollution from sewage discharge and non-point sources of fertilizer usage was the primary cause of the elevated salinity and pollution in HH29 (da Conceição et al. 2024). In short, the concentrations of major ions exhibited significant spatial variations, reflecting agricultural

input in the upstream and urban pollution in the downstream. In the coastal zone, seawater intrusion has a strong impact on water chemistry in the section of rivers.

3.3 Dynamics of $\delta^{13}\text{C}_{\text{DIC}}$

3.3.1 DIC, pCO_2 , and pH

The low pH and DO in the wet period show that organic matter underwent greater decomposition than in the dry period at nearly all sampling sites. Chlorophyll a (Chl-a) and DOC individually underwent different stages of photochemical and biological processes within various areas (Figs. 2, 6). pH values showed no significant differences between the dry (8.52) and wet (8.30) periods; the positive relationship between pH and alkalinity ($r=0.359$, $p\leq 0.05$) in five rivers could be explained by H^+ production by organic matter degradation (Danish and Tripathy 2024), which dehydrates HCO_3^- , causing both alkalinity and pH to $\text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2(\text{aq}) + \text{H}_2\text{O}$ decrease downstream (Figs. 2, 6). This relationship may alternatively be explained by an increase in pH and HCO_3^- resulting from the mixing of contaminated water with uncontaminated stream water or by the weathering of limestone in the streambed and channel (Fonyuy and Atekwana 2008). The relationship between alkalinity and pH in the wet season was not marked due to scouring and dilution by heavy rainwater. In the absence of excess H^+ , the loss of DIC is likely controlled by the relative partial pressure of carbon dioxide (pCO_2) of the sample in comparison to that of the atmosphere. The lack of correlation between DIC and pH levels was due to the presence of H_2CO_3 during neutralization. pCO_2 increased downstream for samples from the JY and CB Rivers, while it decreased downstream for samples from the YD, HH, and DJ Rivers, with pH varying in the downstream direction ($r=-0.827$, $p\leq 0.01$), which was induced by photosynthesis (Fig. 6).

The average DIC concentration was 3.83 mmol/L, indicating that the river water was influenced by additions from surface water. The DIC species calculations based on pH (Clark and Fritz 1997) suggested that HCO_3^- was the dominant species of DIC for all the river water samples, accounting for 83.37% of DIC on average, followed by dissolved carbon dioxide (H_2CO_3) and CO_3^{2-} , accounting for less than 1% and 1.62% of DIC, respectively. HCO_3^- accounted for majority of the alkalinity (up to 85%) for most of the river water samples. Due to the dominance of bicarbonate in the DIC and alkalinity, both followed similar seasonal and spatial patterns as HCO_3^- (Fig. 2). The DIC concentrations for samples from the JY and CB Rivers increased along the water flow direction, while those from the YD, HH, and DJ Rivers decreased from upstream to downstream. Limestone weathering and dissolution

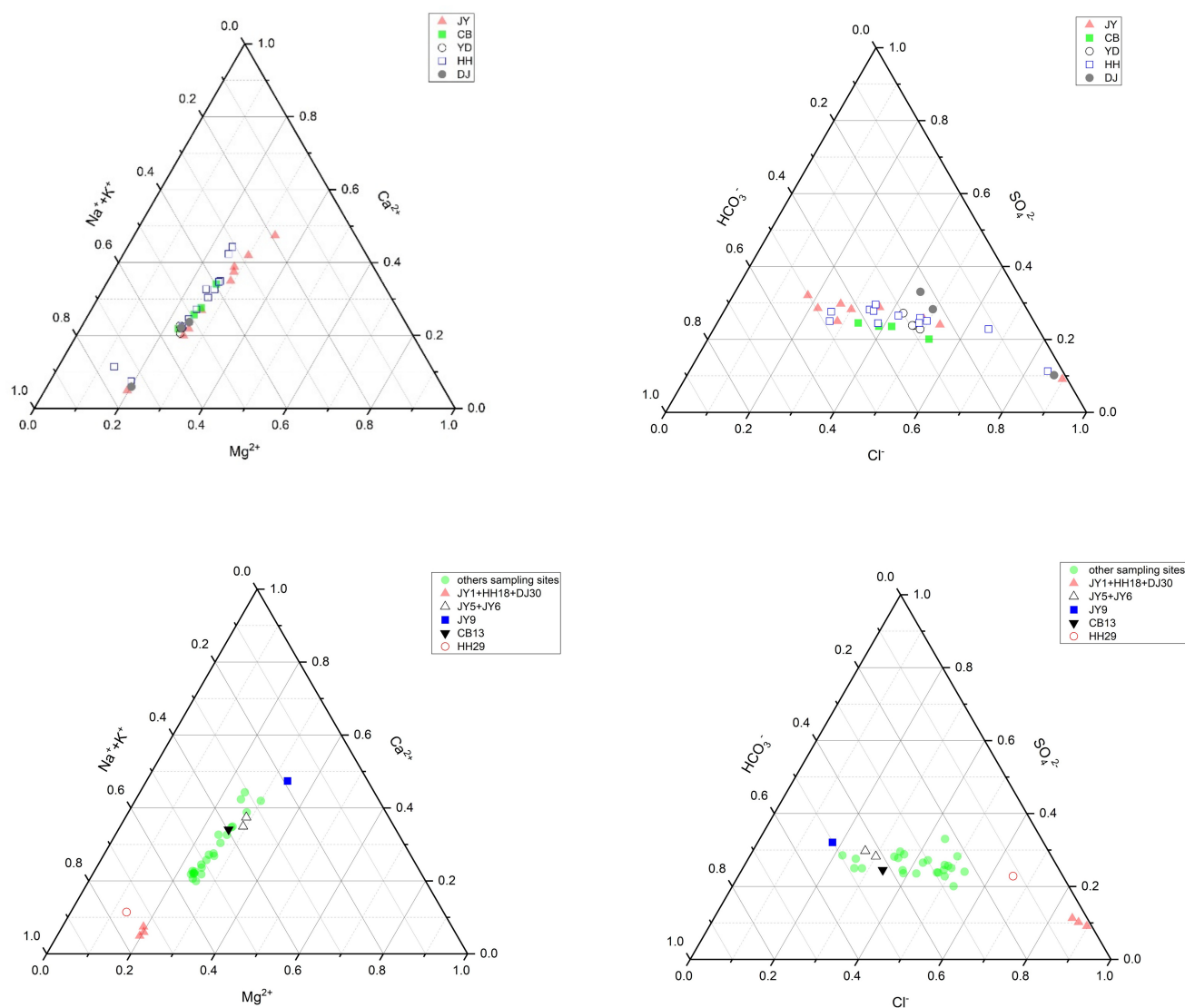


Fig. 5 Piper diagrams showing (a) the relative importance (in equivalents) of major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and (b) the relative dominance of HCO₃⁻, SO₄²⁻, and Cl⁻

from river bedrock and channels were responsible for the depletion and enrichment of DIC for samples in regions characteristic of geological background. Additionally, the protons generated during the chemical evolution of acidic effluent led to seasonal losses of DIC in stream water. This reduction in DIC in streams affected by acidic effluent has significant implications for CO₂ transfer to the atmosphere and the export of DIC from the watershed (Fonyuy and Atekwana 2008).

In the wet season, pCO₂ values varied from 1.64 to 262.4 ppm, with an average of 39.08 ± 36.28 ppm. In April (the beginning of the wet season), lower values of pCO₂ were observed at all sampling sites, ranging from 1.99 to 31.56 ppm, with a mean value of 11.82 ± 6.03 ppm. All pCO₂ concentrations were below the atmospheric

concentration (360 ppm) and undersaturated. The lowest pCO₂ was found in the Haihe River (HH18, 9.06 ppm). The spatiotemporal variation in pCO₂ was largely negative to the spatiotemporal variations in DOC ($r = -0.136$, $p \leq 0.05$). For example, the highest DOC concentration was found in the urban area (accounting for 26.78% of the area) where the population was concentrated (JY4, YD14, and DLJ30), while the highest pCO₂ occurred in the agricultural region (JY5 and JY6) in summer. CO₂ content was always higher during summer, indicating more relative decomposition of organic materials from effluents.

The levels of pCO₂ in river systems are controlled by four main processes: the influx of soil CO₂ through baseflow and interflow, the in situ respiration of organic carbon, photosynthesis by river plants, and the evasion of CO₂ from

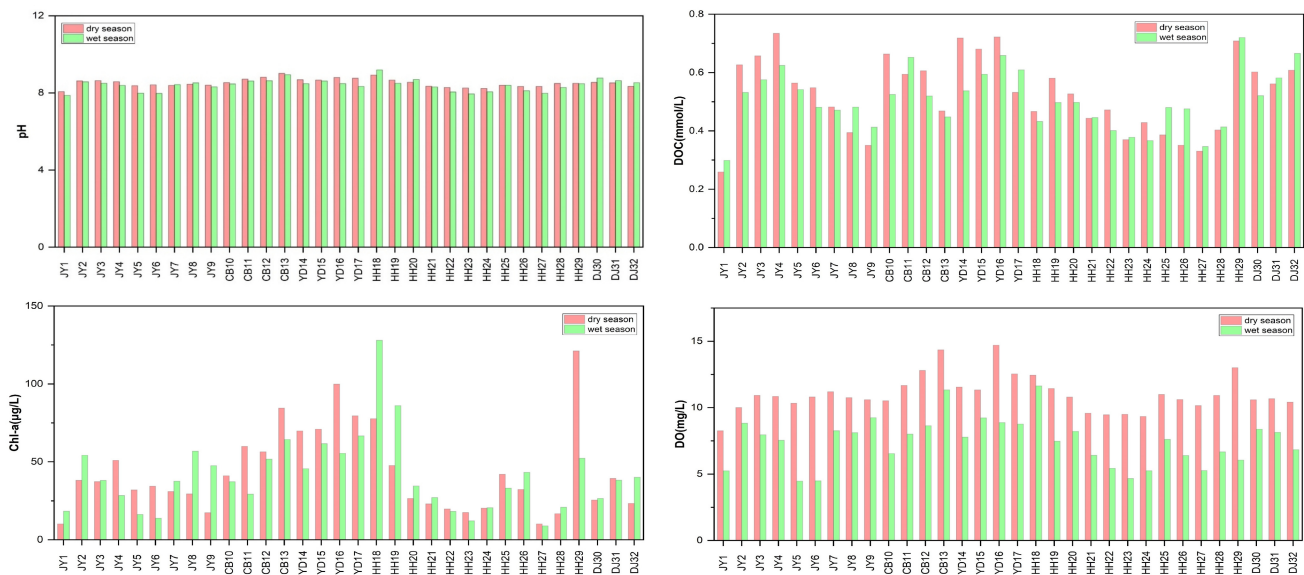


Fig. 6 Fluctuations of pH, DOC, Chl-a, and DO over all sampling sites during the dry and wet seasons

water to air (Danish and Tripathy 2024). The observation revealed a consistent seasonal pattern of $p\text{CO}_2$ levels across the entire basin, i.e., wet period (54.22 ppm) > dry period (32.44 ppm), suggesting that the increased baseflow and interflow CO_2 contributions occur in the wet season following heightened precipitation. Another contributing factor to the higher $p\text{CO}_2$ levels observed during the wet season is the in situ oxidation of both labile and pollution-derived organic matter. According to Zhang et al. (2009), the combination of elevated temperatures and increased organic carbon concentration leads to the degradation of particulate organic carbon (POC) during periods of high flow (Zhang et al. 2009).

The pattern of increasing $p\text{CO}_2$ levels correlates with higher population density, land tillage, and influx. This suggests that microbial respiration, driven by the oxidation of organic carbon and soil CO_2 influx through interflow, predominantly controls dissolved CO_2 concentrations. A notable correlation between pH and alkalinity ($r=0.118$, $p\leq 0.05$) was observed (Fig. 7), suggesting that lithology and atmospheric dissolution influenced the alkalinity distribution of riverine water and shaped $\delta^{13}\text{C}$ patterns. The CO_2 loss associated with the neutralization trend relates to wastewater contamination and the evolution of carbonates. The microbial metabolites of organic matter contribute to acidity and the transformation of bicarbonate (HCO_3^-) to CO_2 . CO_2 degassing takes place along the rivers, leading to higher $\delta^{13}\text{C}$ and lower DIC concentrations (Raymond et al. 2013). The impact of CO_2 degassing on temporal variations in carbon is not as significant as the influences of mineral weathering and biological CO_2 influx. Overall, mineral weathering, the influx of CO_2 from the soil, and the degradation of organic

matter in the rivers are the primary factors driving carbon dynamics in the five rivers of the plain tract in North China.

3.3.2 $\delta^{13}\text{C}_{\text{DIC}}$ pattern and influencing factors in rivers

In this study, the $\delta^{13}\text{C}$ values of DIC ranged from -12.39‰ to -0.45‰ , with an average of -8.00‰ during the wet period. In the dry period, the values ranged from -10.86‰ to -1.41‰ , averaging -7.12‰ . The most $\delta^{13}\text{C}$ -depleted values (avg. -8.00‰) occur during the wet season (summer), which contrasts with what would be expected if in situ photosynthesis influenced the signal. This phenomenon can be understood through hydrological factors. During the dry season, when the water level drops, a larger percentage of discharge comes from tributaries with a relatively positive $\delta^{13}\text{C}$ value (Fig. 2). This behavior also indicates that the sources of DIC in the basin are relatively stable. The observation that $\delta^{13}\text{C}_{\text{DIC}}$ values show slight enrichment in ^{13}C during the dry season at most localities indicates that in-river photosynthesis, along with high DOC concentrations and pH levels, may influence the carbon cycling in a secondary manner. The $\delta^{13}\text{C}$ values are influenced by carbon sources as well as physical processes like CO_2 degassing and source mixing and biochemical processes such as microbial respiration and aquatic photosynthesis occurring in streams. Isotopic fractionation effects related to these processes were observed (Wang et al. 2022). Potential sources of riverine DIC include atmospheric CO_2 , soil CO_2 from respiration, the breakdown of carbonate rocks, and the decay of organic carbon (dissolved and particulate organic carbon) in rivers. Stream samples generally displayed a progressive enrichment of $\delta^{13}\text{C}_{\text{DIC}}$,

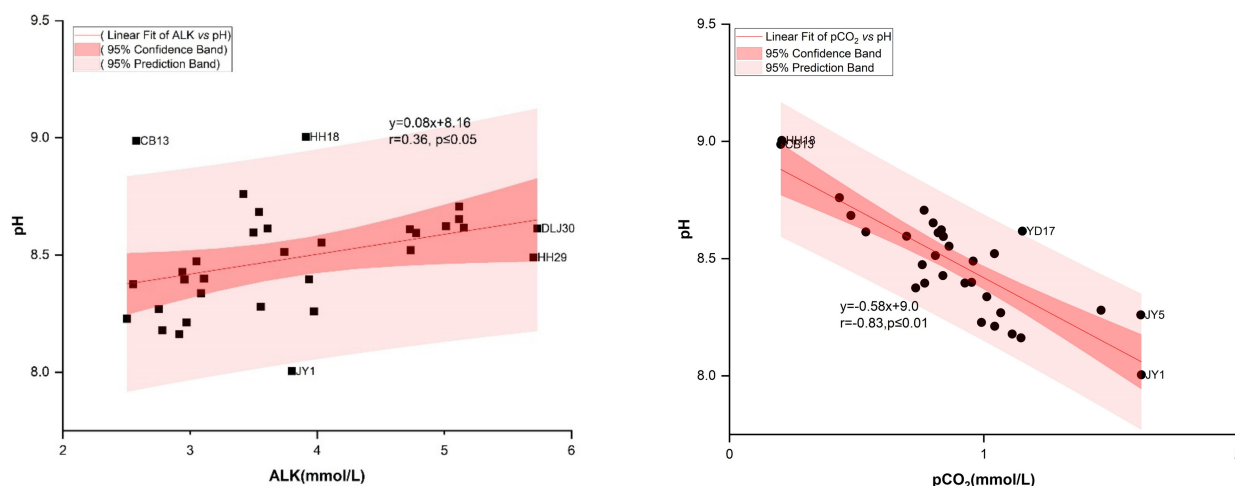


Fig. 7 Cross-plot of ALK vs. $\delta^{13}\text{C}$ and pCO_2 vs. $\delta^{13}\text{C}$ for samples from the five rivers

which is consistent with the preferential loss of ^{12}C during the evasion of CO_2 (Fig. 2).

There are positive and negative excursions for $\delta^{13}\text{C}$ values with DIC in dry and wet seasons, respectively (Fig. 2). Notably, there was significant variation in the data points for DIC concentrations exceeding 17.76 mg C/L during the wet period and exceeding 18.72 mg C/L during the dry period. The $\delta^{13}\text{C}$ values for the five rivers and their tributaries are comparable to or slightly heavier than those of the headwaters of the Ottawa River (-17.4‰ to -8.4‰ in fall and -17.3‰ to -7.3‰ in spring) (Telmer and Veizer 1999), both originating from biological sources in city rivers. Most samples show pCO_2 values lower than atmospheric CO_2 , suggesting that the samples are in nonequilibrium with atmospheric CO_2 . Thus, the enrichment of $\delta^{13}\text{C}_{\text{DIC}}$ for the river samples is not attributed to equilibrium fractionation (Clark and Fritz 1997). The wide range of $\delta^{13}\text{C}_{\text{DIC}}$, which is more enriched than -13‰ , highlights the significant influence of carbonate dissolution on the river carbon cycle. Generally, $\delta^{13}\text{C}$ values were more depleted during the wet season than the dry season at almost all sampling sites (Fig. 2). One reason for the lower $\delta^{13}\text{C}_{\text{DIC}}$ levels during the wet season is the increased decomposition of riverine organic materials, which occurs due to higher temperatures and greater concentrations of organic matter as water discharge rises. This is further supported by the observation that pCO_2 levels in river waters were about tenfold higher during the wet period than the dry period (Fig. 2). The pCO_2 in the river was measured at 39.08 ppm, which is significantly lower than the equilibrium value of atmospheric CO_2 at 360 ppm. This pattern was consistent at all sampling sites and during both seasons. As a result, the riverine DIC pool is in a state of nonequilibrium with

isotopically depleted atmospheric CO_2 . Consequently, the contribution from the atmosphere is expected to lower the riverine $\delta^{13}\text{C}_{\text{DIC}}$ due to ^{12}C dissolution. This relationship can be quantified by the correlation between pCO_2 and $\delta^{13}\text{C}_{\text{DIC}}$, which has a correlation coefficient (r) of -0.57 and is statistically significant ($p \leq 0.01$) (Fig. 2).

Lower $\delta^{13}\text{C}_{\text{DIC}}$ values in water stored in soil matrix pores could be flushed into the river during summer high discharge. The main factor affecting $\delta^{13}\text{C}_{\text{DIC}}$ in the river is the dissolution of soil CO_2 , which has negative $\delta^{13}\text{C}$ values, during the high-flow season (Li et al. 2010). After several days of incubation at the ambient temperature of the river, significant amounts of organic materials were converted to DIC (Ward et al. 2013). In this study, CO_2 dissolution in the soil might contribute to an increase in the alkalinity in river water (CO_2 vs. ALK, $r = 0.12$, $p \leq 0.05$). The dominant control of lithology and CO_2 dissolution on stable carbon isotopic composition of DIC can be illustrated from the negative relationships of $\delta^{13}\text{C}_{\text{DIC}}$ vs. alkalinity ($r = -0.16$, $p \leq 0.01$) and $\delta^{13}\text{C}_{\text{DIC}}$ vs. pCO_2 ($r = -0.57$, $p \leq 0.01$) according to statistics from 10 months of data. The highest $\delta^{13}\text{C}$ value of -0.45‰ was recorded at DLJ30 in June, where downstream in-channel weirs transformed the river into an artificial lake. Atmospheric CO_2 has an isotopic composition of approximately 8‰ , which suggests that $\delta^{13}\text{C}_{\text{DIC}}$ values around 0‰ are expected in waters that have equilibrated with the atmosphere (Ahad et al. 2008). However, the nonequilibrium of pCO_2 between the atmosphere and river water indicates that the increase in $\delta^{13}\text{C}$ values was attributable to photosynthesis in summer, which is a contrasting process to decomposition, or CO_2 evasion. The $\delta^{13}\text{C}$ values at HH18, JY1, and DJ30 were among the highest when compared to other sites. This can be

attributed to the influx of stagnant seawater, which induced poor mixing of water bodies and a reduction in dissolved oxygen. This was caused by anaerobic activity, resulting in the generation of methane. The decrease in $p\text{CO}_2$ and the ^{13}C -enriched DIC values suggest that installing similar weirs in rivers could lead to comparable anoxic effects and associated biogeochemical changes (Schulte et al. 2011).

The $\delta^{13}\text{C}$ enrichment increases by over 3.0‰ due to combined fractionation effects from diffusive loss and partial equilibrium of carbon in DIC with atmospheric CO_2 (Telmer and Veizer 1999; Schulte et al. 2011). The $\delta^{13}\text{C}$ enrichment observed at HH18 and CB13 during both the dry and wet periods may be a result of increased CO_2 evasion from the river system. On the other hand, phytoplankton productivity likely intensified due to heightened photosynthesis resulting from the longer water residence time, during which lighter $^{12}\text{CO}_2$ took part. A large amount of carbamide fertilizer, which contained nitrogen and carbon compounds, was used at JY9 in plantations and tillage on agricultural land. Metabolites from microbial respiration on organic matter, such as plant detritus and organic fertilizer, were partly reintroduced into the river through surface runoff (Telmer and Veizer 1999; Das et al. 2005). The CO_2 from this process was consumed during the weathering of limestone, contributing to the enriched $\delta^{13}\text{C}$ values of -7.56‰ during the dry period and -8.57‰ during the wet period. DIC levels decreased to minimums of 2.89 and 1.99 mmol/L, respectively. The lowest $\delta^{13}\text{C}$ values during the dry period were recorded at HH29, JY5, and JY6 in the wet period. The DOC concentration at HH29 was elevated, indicating that particulate organic matter decomposition occurred in the tilled land's water during photosynthesis. The HCO_3^- equivalent fraction was approximately 10%, while Cl^- was close to 90%. The $\delta^{13}\text{C}$ value of -8.63‰ resulted primarily from the degradation of vegetation detritus and organic fertilizers in agricultural and grassland areas, with minimal contribution from carbonate weathering. During the wet period, the $\delta^{13}\text{C}$ values at JY5 and JY6 dropped to their lowest points, reaching -9.42‰ and -9.51‰ , respectively. This decrease is attributed to the mineralization of organic matter in agricultural areas, which occurred alongside an increase in CO_2 levels, reaching a maximum of 2.84 and 2.85 mmol/L.

The clustering of data points at most sampling sites, with the exception of a few significant outliers at JY2 in July and DJ30 in May, June, and September, can be utilized to evaluate the changes in $\delta^{13}\text{C}_{\text{DIC}}$ in relation to DIC concentrations. The results indicated that as the concentration of DIC increased, the $\delta^{13}\text{C}_{\text{DIC}}$ values decreased (Fig. 3). The minimum and maximum $\delta^{13}\text{C}$ values were observed at JY2 in July (57.6 mg C/L for DIC) and DJ30 in June (34.44 mg C/L for DIC), respectively. The other $\delta^{13}\text{C}$ values fell between these two end members. The

highest DIC concentration occurred at DJ30 in September, at 241.2 mg C/L, while the $\delta^{13}\text{C}$ value of -7.74‰ was situated between the end members (-12.39‰ at JY2 in July and -0.45‰ at DJ30 in June). During the dry season, the sampling site DJ30 exhibited the highest concentration of bicarbonate (HCO_3^-) at 62.64 mg C/L, which was up to 2.3 times that of the other values recorded. This increase suggests that limestone dissolution increased both the pH and DIC levels. This process primarily influenced the $\delta^{13}\text{C}$ value, enriching it by a significant range of 4‰ to 8‰ due to the enhancing alkalinity from limestone dissolution (Fonyuy and Atekwana 2008; Yi et al. 2021). The dissolution of limestone by soil CO_2 produces a medium $\delta^{13}\text{C}_{\text{DIC}}$ value of around -12‰ , and the derived respired CO_2 produced due to the mixture of C3 and C4 plants with a $\delta^{13}\text{C}_{\text{DIC}}$ value of -10.6 (da Conceição et al. 2024). The results indicate that various processes contribute to differing extents to the depletion and enrichment of DIC. These processes include microbial respiration, photochemical reactions such as photosynthesis and photodegradation, and physical effects like CO_2 dissolution and degassing. Chemical effects involving neutralization and carbonate dissolution also play a role in influencing the carbon isotope values present in water DIC, leading to enrichment of either light or heavy carbon.

4 Conclusion

This study investigated the seasonal and spatial variations in major ions and DIC in the five rivers across Tianjin City, North China. The pattern of water chemistry showed that water quality was heavily impacted by anthropogenic inputs from farmland upstream and urban pollution along the rivers. The isotopic composition of DIC suggested that biological CO_2 from the soil and the degradation of organic matter is a major source of DIC in most rivers. DIC dynamics constrained by $\delta^{13}\text{C}$ from polluted rivers may significantly impact carbon cycling due to the degradation of organic pollutants. $\delta^{13}\text{C}$ values were found to be lower during the wet season than the dry season, ascribed to the biological source of ^{12}C at higher temperatures, except for the dissolution of atmospheric CO_2 . The evasion of CO_2 and carbonate dissolution contributed to the ^{13}C enrichment in water. These results indicate that climate, chemical weathering rates, and nutrient levels are independent variables that influence the depletion and enrichment of ^{13}C . Hydrological processes likely played an equally important role in elevating DIC as microbial metabolization of organic matter. Further studies are needed to explore the biogeochemical processes of carbon in urban rivers, the export of CO_2 to the atmosphere, and the discharge of DIC from anthropogenically altered watersheds.

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Data availability The data analyzed and/or generated during the study will be made available upon reasonable request from the corresponding author.

Declarations

Conflicts of interest The authors declare that there is no conflict of interest.

Consent for publication All authors have approved the final version of the manuscript for publication.

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