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Title:

Carbon dioxide, methane, and dissolved carbon dynamics in an urbanized river system.

Running title:

Carbon dynamics in an urban river

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Abstract

Estimates of greenhouse gas (GHG) evasion from rivers have been refined over the past decades to constrain their role in global carbon cycle processes. However, despite 55% of the human population living in urban areas, urban rivers have had limited attention. We monitored carbon dynamics in an urbanized river (River Kelvin, 331 km², UK) to explore the drivers of dissolved carbon lateral and vertical export. Over a 2-year sampling period, riverine methane (CH₄) and carbon dioxide (CO₂) concentrations were consistently oversaturated with respect to atmospheric equilibria, leading to continual degassing to the atmosphere. Carbon stable isotopic compositions ($\delta^{13}\text{C}$) indicated that terrestrially derived carbon comprised most of the riverine CH₄ and dissolved CO₂ (CO₂^{*}) load while dissolved inorganic carbon (DIC) from groundwater was the main form of riverine DIC. The dynamics of CH₄, CO₂^{*}, and DIC in the river were primarily hydrology-controlled, *i.e.*, [CH₄] and [CO₂^{*}] both increased with elevated discharge, total [DIC] decreased with elevated discharge while the proportion of biologically-derived DIC increased with increasing discharge. The concentration of dissolved organic carbon (DOC) showed a weak relationship with river hydrology in summer and autumn and was likely influenced by the combined sewer overflows. Carbon emission to the atmosphere is estimated to be 3.10 ± 0.61 kg C·m⁻²·yr⁻¹ normalized to water surface area, with more than 99% emitted as CO₂. Annual carbon loss to the coastal estuary is approximately 4.69 ± 0.70 Gg C·yr⁻¹, with annual DIC export approximately double that of DOC. Per unit area, the River Kelvin

was a smaller carbon source to the atmosphere than natural rivers / streams but shows elevated fluxes of DIC and DOC under comparable conditions. This research illustrates the role urban systems may have on riverine carbon dynamics and demonstrates the potential tight link between urbanization and riverine carbon export.

Keywords

urbanized river; dissolved carbon; carbon stable isotopes; hydrology; carbon exports

1 Introduction

Quantifying and characterising global carbon (C) cycle pathways are critical to accurately modelling future climate change and understanding land management processes that can potentially mitigate atmospheric C-accumulation. Specifically, elucidating patterns of CH₄ and CO₂ emissions from ecosystems underexplored to date is essential to constrain current estimates. Inland aquatic ecosystems play a significant role in CH₄ and CO₂ exchange between surface waters and the atmosphere (Raymond et al., 2013; Nisbet, Dlugokencky, & Bousquet, 2014). Rivers have been found to generally be oversaturated with respect to atmospheric equilibria in both CH₄ and CO₂ (Billett & Moore, 2008; Campeau & del Giorgio, 2014; Yu et al., 2017), and consequently function as net carbon sources to the atmosphere. Approximately 26.8 Tg C·yr⁻¹ as CH₄ (Stanley et al., 2016) and 1.8 ± 0.25 Pg C·yr⁻¹ as CO₂ (Raymond et al., 2013) are emitted to the atmosphere annually from fluvial ecosystems, comparable in magnitude to both the annual land (ca. 2.1 Pg C·yr⁻¹) and ocean (ca. 2.6 Pg C·yr⁻¹) sinks (Le Quéré et al., 2016). Laterally, rivers also transfer carbon in the forms of DIC and DOC, connecting terrestrial and marine systems (Cole et al., 2007). The dissolved carbon export is estimated to be approximately 0.65 Pg C·yr⁻¹, with about 0.24 Pg C·yr⁻¹ as DOC, and 0.41 Pg C·yr⁻¹ in the form of DIC (Li et al., 2017).

Urbanized and anthropogenically altered catchments are often significant sources of dissolved carbon (McGinnis et al., 2016; Yu et al., 2017; Ni, Li, Luo, & Lu, 2019; Ho et al., 2020; Wang et al., 2020). Estimated global urban cover may reach 1.7 × 10⁶ km² by 2050 (Zhou, Varquez, & Kanda, 2019), and will be home to 70% of the human population, up from 55% in 2018 (World Bank, 2020). Anthropogenic activities during urban expansion can accelerate greenhouse gas increases in the atmosphere and

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dissolved carbon loading to aquatic systems. For example, the dissolution of cement and concrete, by acid precipitation and natural organic acids, releases CO₂ to the atmosphere, and increases river alkalization (Baker, Cumberland, & Hudson, 2008; Kaushal et al., 2013). Urbanization may also enhance DOC production through contributions from higher primary production rates in urban streams, a consequence of localised nutrient additions (Kaushal et al., 2014), which may increase fluvial respiration, dissolved oxygen demand and CO₂ production. However, despite their potential significance, gaps remain in our understanding of carbon dynamics in urbanized river catchments. It is crucial to understand the role and significance of urban rivers play in the carbon cycle and to identify how this may change with increasing urbanization, particularly the potential differences / similarities with natural river networks.

To investigate the dynamics of riverine carbon fluxes in an urban river system, over a 2-year period, we examined temporal variability in fluvial carbon dynamics close to the mouth of the River Kelvin, a temperate latitude, partially urbanized (20%) UK catchment. We measured the concentrations of dissolved CH₄, CO₂^{*}, DIC and DOC to understand carbon source and recycling based on their stable carbon isotopic compositions. This profiling was undertaken to i) identify the main sources of riverine carbon, ii) elucidate the major hydrological and physiochemical drivers of carbon variation, and iii) build carbon-discharge models to characterize urbanized river carbon export and inform projections of change under future climate scenarios.

2 Study site and methods

2.1 Study site

The River Kelvin (Figure 1) is a semi-urban catchment, located in west-central Scotland, UK, with a main channel length of 35 km from its source at an area of marshy ground 55 m above sea level to its confluence with the (River) Clyde Estuary, and draining an area of approximately 331 km². The sampling site (55°52'05"N, 4°17'15"W) is approximately 0.5 km downstream of the nearest urban combined sewer overflow (CSO) pipe and approximately 1.2 km upstream of the mouth of the River Kelvin, the confluence with the Clyde Estuary.

2.2 Field sampling and data collection

Weekly sampling was conducted over a 26-month period (February 2018 to March 2020). Water physiochemical properties (pH, temperature, conductivity, and dissolved oxygen (DO) concentration) were measured *in-situ* at the time of manual water sample collection (Supporting Information). The river discharge (Q) data was obtained from the Scottish Environmental Protection Agency (SEPA) from the Kelvin@Killermnont station (55°54'25" N, 4°18'37" W) approximately 7 km upstream of the sampling point. There are no further significant confluences after the station to the sampling point but CSO pipes.

Concentration and $\delta^{13}\text{C}$ of dissolved CH₄ ([CH₄] and $\delta^{13}\text{C-CH}_4$) and CO₂* ([CO₂*] and $\delta^{13}\text{C-CO}_2$) were determined by an adapted bottle-calibration static headspace method (Johnson, Hughes, Donaghay, & Sieburth, 1990; Looman, Maher, Pendall, Bass, & Santos, 2017). Bottles (250 mL) for sampling were all rinsed three times by river water and samples were collected underwater to ensure no headspace. On return to the

laboratory, approximately 30 minutes later, 50 mL zero-air gas (CH_4 : < 0.02 ppm, CO_2 : < 2 ppm) was introduced into each bottle. After equilibrating over ca. 24 hours in cold room (6 – 8 °C), 40 mL subsample gas was extracted from the headspace and the partial pressure (p_{CH_4} and p_{CO_2}) and $\delta^{13}\text{C}$ values of CH_4 and CO_2 of the subsample were measured using a Wavelength Scanned-Cavity Ring-down spectrometer (WS-CRDS, Picarro G2201-*i* Analyser). All samples were analysed less than 28 hours after collection. Full headspace equilibration was reached after 8-hours, with no significant change in concentration or isotopic composition recorded after, indicating no significant effects of respiration or oxidation on CO_2 and CH_4 concentrations respectively (Figure S1, SuppInfo). To account for potential handler error during the headspace addition / sample extraction process, five replicate samples were analysed allowing removal of any clear outliers from the average values. Stable isotope calibration standard gases (ALPHAGAZ, Air Liquide) were used as primary standards to check the status of the Picarro Analyser. Details of the concentrations and $\delta^{13}\text{C}$ values of the primary can be found in Table S1 (SuppInfo). A secondary standard gas (CH_4 : 2.5 ppm, CO_2 : 500 ppm) was measured at the start, end, and the intervals of the sample measurements for the detecting and correction of the possible data drift during the measuring process.

The concentration of CH_4 in the liquid phase after equilibration according to the Henry's Law:

$$[\text{CH}_4] = K_{\text{CH}_4} \cdot p_{\text{CH}_4} \quad (1)$$

where K_{CH_4} (unitless) is the partition or distribution coefficient of CH_4 . p_{CH_4} is the partial pressure of CH_4 in the headspace (Johnson et al., 1990).

The concentration of CO₂* in the liquid phase after equilibration according to the Henry's Law:

$$[\text{CO}_2^*] = K_{\text{CO}_2} \cdot f_{\text{CO}_2} \quad (2)$$

where K_{CO_2} (mol·L⁻¹·atm⁻¹) is the solubility constant of CO₂ at the given temperature and salinity (Weiss, 1974). f_{CO_2} is the fugacity of CO₂ converted from p_{CO_2} :

$$f_{\text{CO}_2} = p_{\text{CO}_2} \cdot f(g) \quad (3)$$

where $f(g)$ is the fugacity coefficient (unitless) (Millero, 2007).

The influence of temperature on [CO₂*] between collection and equilibration, and the changing buffering capacity before and after equilibration was corrected (Johnson et al., 1990; Dickson, Sabine, & Christian, 2007; Looman et al., 2017; Koschorreck, Prairie, Kim, & Marcé, 2021).

The concentration of CH₄ and CO₂* in the liquid phase before equilibration can be computed according to

$$[C] \cdot V_l = [C]_l \cdot V_l + [C]_g \cdot V_g \quad (4)$$

where [C] is the concentration of CH₄ and CO₂* in the liquid phase before equilibration, [C]_l is the concentration of CH₄ and CO₂* in the liquid phase after equilibration, [C]_g is the concentration of CH₄ and CO₂ in the gas phase after equilibration, V_l and V_g are the volumes of the liquid phase and the gas phase, respectively (Johnson et al., 1990).

Dissolved inorganic carbon concentration ([DIC]) and δ¹³C (δ¹³C-DIC) were measured in triplicate samples using the Isotopic Continuous Dissolved Inorganic Carbon Analyser (ISO-CADICA) (Bass, Bird, Munksgaard, & Wurster, 2012). Briefly, water

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samples were acidified by an automated acidification interface to convert DIC to free CO₂. Acidified samples were introduced in a gas-permeable Teflon tubing for 15 min, allowing CO₂ to equilibrate with a headspace in closed loop circulation with a WS-CRDS. Sodium bicarbonate (NaHCO₃) was used for concentration calibration, and three carbonates with different δ¹³C-DIC values (CaCO₃: +2.48 ‰ vs PDB, NaHCO₃: -4.67 ‰ vs PDB, and CaCO₃: -24.23 ‰ vs PDB) were used for δ¹³C-DIC calibration (Waldron, Scott, & Soulsby, 2007).

Dissolved organic carbon concentration ([DOC]) was measured using a Thermalox TOC analyser. Organic carbon was combusted to CO₂ at 680 °C and measured by a non-dispersive infra-red sensor. The concentration of DOC was measured from the samples used for measuring alkalinity, thus particulate material and DIC had been removed by filtration and acidification. Before combustion, the samples were put in an ultrasonic bath for 15 minutes for degassing (Zheng, Waldron, & Flowers, 2018). Triplicate measurements were made of each sample.

Carbon dioxide efflux (F_{CO₂}, normalized to water surface area) was calculated from the accumulation rate of CO₂ in a floating chamber of known volume. CO₂ concentration was measured *in-situ* using a Licor (LI-840) infrared CO₂ / H₂O gas analyzer (Liu, Dreybrodt, & Wang, 2010; Bass et al., 2014). Degassed CO₂ from air-water interface accumulated in the chamber for 4 minutes and repeat three times. Carbon dioxide efflux was calculated using the following equation (Frankignoulle, 1988):

$$F_{CO_2} = \left(\frac{dpCO_2}{dt} \right) \cdot \left(\frac{V}{RTS} \right) \quad (5)$$

where F_{CO_2} is the CO_2 efflux ($\mu\text{M}\cdot\text{CO}_2\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), dp_{CO_2}/dt accumulation rate of CO_2 in the chamber ($\mu\text{atm}\cdot\text{s}^{-1}$), V is the volume of the chamber (m^3), R is the gas constant ($0.082 \text{ m}^3\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), T is the air temperature (K), and S is the surface area of the chamber at the air-water surface (m^2).

Methane efflux (F_{CH_4} , normalized to water surface area) was calculated based on the relationship between gas flux and the concentration gradient in water ($[\text{CH}_4]_{\text{water}}$) and air ($[\text{CH}_4]_{\text{air}}$) and gas transfer velocity (k) (Raymond et al., 2012):

$$F_{\text{CH}_4} = k_{\text{CH}_4} \cdot ([\text{CH}_4]_{\text{water}} - [\text{CH}_4]_{\text{air}}) \quad (6)$$

where F_{CH_4} is the CH_4 efflux ($\mu\text{M}\cdot\text{CO}_2\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), k is the gas transfer velocity, and k_{CH_4} can be calculated by the relationship between k_{CH_4} and k_{CO_2} (SuppInfo).

2.3 Two end-member mixing models

Stable isotope ratios were determined via CRDS and reported as delta values in parts per thousand (‰). The ratio of ^{12}C to ^{13}C is indicative of a combination of source and subsequent processing (be in biological or physical). In this study we utilised observed isotopic variability, coupled to constrained source end-member values to produce a series of mixing models determining proportional C source. To elucidate the role of hydrology in riverine carbon dynamics, two end-member mixing models were established, which are power-law relationships between the concentrations / $\delta^{13}\text{C}$ values of dissolved carbon and discharge (Figure 5):

$$y = a \cdot Q^b \quad (7)$$

$$y = a \cdot Q^b + c \quad (8)$$

where y is the concentration and $\delta^{13}\text{C}$ of dissolved carbon in sampling water, Q is the river discharge, a , b , and c are constants. The concentration- Q relationships were plotted on logarithmic axes for easier visualization where $(\lg(y) = b \cdot \lg(Q) + \lg(a))$. In equation 7, the concentration of allochthonous C is greater than the background concentration in the river if $b > 0$. Inversely, the concentration of allochthonous C is lower than the background concentration in the river if $b < 0$ and the dilution controls the concentration varying. When $b = 0$, the fluvial systems behave chemostatically, indicating the concentrations do not vary with the changing discharge. In equation 8, the constant b reflects the influence of allochthonous carbon on the $\delta^{13}\text{C}$ value and the absolute value of b represents the contribution of allochthonous carbon to riverine dissolved carbon. Constant c is introduced into the power-law relationship of $\delta^{13}\text{C}$ - Q (equation 8) and represents $\delta^{13}\text{C}$ values of the allochthonous carbon source.

2.4 Statistical analysis

Statistical analysis was carried out using R statistical package version 3.6.1 [R Core Group 2019]. Data distribution was checked before the analysis of seasonal and climate difference. Pearson correlation analysis was used to explore the relationship between the concentration and $\delta^{13}\text{C}$ of dissolved carbon, water properties, and river hydrological dynamics. Linear and nonlinear regression were performed to test the possible relationships of dissolved carbon and other environmental parameters. For all tests, p values < 0.05 were considered statistically significant.

3 Results

3.1 River Hydrology and physicochemical properties

The highest and most variable river discharge was measured from September to March. Discharge peaks were also observed during the dry periods (April to August), but of a lesser magnitude. At the time of sampling (Feb 2018 – Mar 2020), the summer of 2018 was the fourth driest summer on record in Scotland. The river discharge was exceptionally low in July 2018, and this period is defined here as an extremely dry period (ED period). Significant rainfall events occurred during February and March 2020 in Scotland, and the highest discharge peaks were recorded concurrently. This period is defined as rainfall storm period (RS period). The remaining time through the 2-year monitoring period is defined as normal climate conditions (NC periods), many individual flow peaks were recorded in the normal climate periods, corresponding to the occurrence of rainfall events (Figure 2 A).

River pH ranged from approximately 6.4 to 8.4 (mean \pm SD = 7.6 ± 0.4 , from this point, unless otherwise stated, values are presented as means \pm SD), and alkalinity ranged from 36.9 to 147.1 mg·L⁻¹ (84.5 ± 27.0 mg·L⁻¹). Specific conductivity (EC) ranged from 140 to 1357 μ S·cm⁻¹ (319 ± 132 μ S·cm⁻¹), with a median value of 292 μ S·cm⁻¹. There was a significant EC peak in February 2018, attributed to prolonged salting of the roads to facilitate snow melting after heavy snow events (Figure S2 E, SupplInfo). Water physicochemical properties, pH, EC, and alkalinity, all showed dilution with the increasing discharge (Figure S3, SupplInfo), The relationship between DO and discharge is significant but weak ($r = -0.28$, $p < 0.01$, Figure S3 D and Figure S4, SupplInfo), suggesting DO was not strongly hydrologically influenced.

3.2 Temporal variation of [CH₄], [CO₂*], [DIC], and [DOC]

Temporal variation in CH₄ and CO₂* — The concentration of dissolved CH₄ ranged from 75 to 241 nM (135 ± 34 nM), and CO₂* concentration ranged from 25.9 to 112.7 μM (70.2 ± 20.3 μM) (Table 1). The river was consistently oversaturated in CH₄ and CO₂ relative to the atmospheric equilibria (CH₄: ~4 nM, CO₂: ~23.9 μM, Figure 2). Spring-[CH₄] was lower than winter-[CH₄] ($p < 0.05$, Table 2) while spring-[CH₄] had no significant difference from summer-[CH₄] and autumn-[CH₄]. Mean [CO₂*] in winter was significantly greater than in spring ($p < 0.01$, Table 2) and summer ($p < 0.01$), and summer had the lowest mean [CO₂*]. The values of δ¹³C-CH₄ and δ¹³C-CO₂ ranged from -60.2 to -47.0 ‰ (-53.1 ± 2.7 ‰) and from -24.0 to -13.5 ‰ (-20.6 ± 1.9 ‰), respectively. The values of δ¹³C-CH₄ and δ¹³C-CO₂ varied throughout, but both showed a reduced range in 2019 compared to 2018. Sharply increasing [CH₄] and [CO₂] were observed in June 2018, coinciding with a significant rainfall event after very dry antecedent conditions. Several rainfall events happened after this initial flushing event in June, but did not generally lead to concentration and δ¹³C changes of similar magnitude, illustrating the importance of preceding catchment conditions.

During the normal and storm flow, δ¹³C-CH₄ decreased with increasing [CH₄] ($R^2 = 0.35$, $p < 0.01$, Figure 4 A). However, during the extremely dry period in 2018, δ¹³C-CH₄ was more ¹³C-enriched (Figure 3 B, Figure 4 A). Although no statistically significant relationship between [CH₄] and δ¹³C-CH₄ was recorded in extremely dry period (may be a function of a small dataset, Figure 4 A), a weak decreasing trend of δ¹³C-CH₄ with increasing [CH₄] seems apparent.

Temporal variation in DIC and DOC — The concentration of DIC ranged from 0.47 to 2.77 mM (1.42 ± 0.56 mM), while δ¹³C-DIC ranged from -19.7 to -8.9 ‰ ($-15.6 \pm$

2.0 ‰). The concentration of DOC ranged from 0.27 to 1.11 mM (0.53 ± 0.17 mM, Table 1). Seasonal control on DIC was limited (Table 2), with discharge being the primary control of [DIC] (Figure 5 C). The concentration of DIC and $\delta^{13}\text{C-DIC}$ both showed significantly negative correlations with increasing discharge ($r = -0.66$, $p < 0.001$ for [DIC] and $r = -0.36$, $p < 0.001$ for $\delta^{13}\text{C-DIC}$, respectively). The greatest [DIC] (2.77 ± 0.02 mM) was measured in the extremely dry period and relatively low [DIC] (< 0.50 mM) occurred several times during high discharge periods. The concentration of DOC in summer and autumn were similar but significantly greater than in spring and winter ($p < 0.05$).

The relationships between [DIC] and $\delta^{13}\text{C-DIC}$ were consistent during the whole sampling period (Figure 4 B), with $\delta^{13}\text{C-DIC}$ increasing with the increasing [DIC] ($R^2 = 0.22$, $p < 0.01$). Dissolved inorganic carbon in the extremely dry period had greater concentration than in the storm period and $\delta^{13}\text{C-DIC}$ in storm period was more ^{13}C -depleted than in the dry period ($p < 0.05$, Figure 3 D). In contrast, $\delta^{13}\text{C-CO}_2$ decreased with increasing $[\text{CO}_2^*]$ during the whole study period ($R^2 = 0.23$, $p < 0.01$, Figure 4 C).

4 Discussion

4.1 Riverine CH₄ magnitude, sources, and dynamics

Riverine CH₄ is sensitive to regional environment differences (Hutchins, Prairie, & del Giorgio, 2019), a consequence of the generally low levels of CH₄ production, land-use heterogeneity, and the insolubility of CH₄ in water. The difference in riverine [CH₄] can cover several orders of magnitude (Guérin et al., 2006; Sawakuchi et al., 2014; Teodoru et al., 2015; Natchimuthu, Wallin, Klemedtsson, & Bastviken, 2017; Wang et al., 2018). The range of [CH₄] in the River Kelvin (75 – 241 nM, 5.8 – 18.1 μatm, Table 1) was within the range of [CH₄] in the urbanized Chongqing River network in China (50 – 12790 nM: Wang et al. (2018)), the human-managed Skogaryd Catchment in southwest Sweden (10 – 46100 nM: Natchimuthu et al. (2017)), and the human-influenced Amazon River system (20 – 500 nM: Sawakuchi et al. (2014)). The highest [CH₄] in the River Kelvin was comparatively low compared to these human-disturbed rivers. All samples in this study were collected from the mouth of the river, restricting the concentration range, especially the maximum value, which may be highly dependent on point source proximity. Methane concentration in the lower reach of the River Kelvin might still be greater than in the lower reach of natural streams, however. For example, in the stream Brocky Burn in Scotland, [CH₄] in upper and middle stream (1800 nM and 300 nM, respectively) were both greater than in lower reach of the River Kelvin, but [CH₄] was too low to detected (< 50 nM) in the lower reach in Brocky Burn (Hope, Palmer, Billett, & Dawson, 2001).

The dynamics of [CH₄] and δ¹³C-CH₄ observed for the River Kelvin is typical of a two end-member mixing dynamic: a low-[CH₄], more ¹³C-enriched δ¹³C-CH₄ (δ¹³C-CH₄: -

50 – -20 ‰) of thermogenic origin (Figure 4 A, dashed arrow); and a high-[CH₄], more ¹³C-depleted CH₄ (δ¹³C-CH₄: -110 – -50 ‰) of biogenic origin (Figure 4 A, two-dash arrow). In the extremely dry period, [CH₄] was greater compared with the low discharge-[CH₄] in the normal periods and δ¹³C-CH₄ was more ¹³C-enriched compared with the similar [CH₄] range in the normal periods (Figure 4 A, Figure 5 A). The increased concentration gradient resulted from the greater [CH₄] in the extremely dry period than in the normal periods suggests the River Kelvin could potentially be a larger CH₄ source to the atmosphere. Thermogenic CH₄ dominated the extremely dry period with little dilution by surface runoff.

In fluvial systems, biogenic CH₄ could originate from 1) water bodies that could provide anaerobic conditions, e.g., wetlands (Teodoru et al., 2015), 2) methanogenesis in the anaerobic zone of subsurface soil (Lai, 2009), and 3) landfill (Van Breukelen, Röling, Groen, Griffioen, & van Verseveld, 2003) and wastewater treatments (Alshboul, Encinas-Fernández, Hofmann, & Lorke, 2016). The wetland regions are in the upper reaches of the River Kelvin (Figure 1) and given the low solubility of methane gas and subsequent tendency to rapidly degas, their influence downstream is likely low. Organic carbon (OC)-rich soil, e.g., agricultural land (Mingxing & Jing, 2002; Humphreys, Brye, Rector, & Gbur, 2019), grassland (Soussana et al., 2007; Kammann, Hepp, Lenhart, & Müller, 2009), and peatland (Lai, 2009), generally acts as a significant CH₄ source. More than 75 % area of the River Kelvin catchment is OC-rich soil (Figure 1), including woodland, grassland, arable and horticulture, and so could be a source of CH₄ to the river channel. Methane export from landfills has previously been observed to result in greater [CH₄] and more depleted δ¹³C-CH₄ in the connected river systems (Van Breukelen et al., 2003; Hu et al., 2018; Zhang, Guo, Wang, & Chen, 2019). Landfill leakage in the catchment likely supplies more CH₄ when the river flows

through urban, as opposed to headwater soils (Van Breukelen et al., 2003). In the urban area component of the River Kelvin catchment, there are multiple landfills (29 closed and one active) close to the river. Due to fractionation during degassing, landfill $\delta^{13}\text{C-CH}_4$ generally ranges from -60 to -50 ‰ (Bergamaschi et al., 1998; Liptay, Chanton, Czepiel, & Mosher, 1998; Börjesson, Chanton, & Svensson, 2001), similar to the $\delta^{13}\text{C-CH}_4$ of the high concentration CH_4 in the River Kelvin (Figure 4 A). Consequently, the dominant biogenic sources of dissolved CH_4 in the River Kelvin are likely OC-rich soil and landfills. As we were unable to source CH_4 directly from the adjacent landfills in this study, instead relying on the existing reported range of values, conclusions should be necessarily cautious.

Methane concentration and $\delta^{13}\text{C-CH}_4$ were primarily controlled by the river hydrology. Methane concentration increased with river discharge ($r = 0.49$, $p < 0.01$, Figure 5 A) in the normal and rainstorm periods, corresponding to a more ^{13}C -depleted signature ($r = -0.41$, $p < 0.01$, Figure 5 B). This phenomenon indicated significant exogenous CH_4 with lower $\delta^{13}\text{C}$ was transferred into the river during high flow, an amount substantial enough to offset any dilution effect due to increased runoff input. A significant $[\text{CH}_4]$ peak was observed in the rainstorm period (Figure 2 B). The high-frequency and heavy rain events increased the amount of water in the soil and enhanced the movement of dissolved CH_4 from soil layers to the river.

Consequently, dissolved CH_4 presented two different patterns in the extremely dry period and in the other two weather conditions (normal climate periods and the rainstorm period). In the extremely dry period, riverine water in the River Kelvin was mainly from deep groundwater, suggesting during the extremely dry period, dissolved CH_4 was mainly from the thermogenic source (background- CH_4) and the concentration

of dissolved CH₄ in the extremely dry period was greater than in the low-discharge period in the normal climate (Figure 2 B, Figure 3 A). In the low-discharge period in the normal climate, the background-CH₄ was diluted by the runoff and showed a relatively lower [CH₄] compared to in the extremely dry period. With the increasing discharge in the rainstorm period, greater concentration of biogenic CH₄ than in the normal climate period was transported into the river from deep soil layers, causing the elevated [CH₄] and more ¹³C-depleted values of δ¹³C-CH₄. Therefore, riverine CH₄ in very wet and very dry conditions was likely to be greater than in the normal weather and thus higher CH₄ flux from the river to the atmosphere would have occurred.

To fully elucidate the hydrological controls on CH₄ dynamics, we can consider both [CH₄] and δ¹³C-CH₄ in the normal climate periods and rainstorm period as functions of discharge (Figure 5 A, B). Both [CH₄] and δ¹³C-CH₄ showed power-law exponent relationships with discharge, suggesting a changing contribution of exogenous biogenic CH₄ to the riverine CH₄ when discharge varies. When discharge was low, thermogenic source predominated dissolved CH₄, leading to the feature of low-[CH₄] and ¹³C-enriched δ¹³C-CH₄, corresponding to the dashed-arrow end member in Figure 4 A. With elevated discharge, the contribution of biogenic CH₄ increased, primarily due to: 1) thermogenic CH₄ was diluted by the increasing input of runoff and subsurface water, and 2) the significant input of in biogenic CH₄. The increasing contribution of biogenic CH₄ indicated by high-[CH₄] and ¹³C-depleted δ¹³C-CH₄. The contribution of biogenic CH₄ was generally under 40% of the CH₄ pool and was usually between 0 – 20%, which may partly be due to methanotrophy in the water column (de Angelis & Scranton, 1993; Sawakuchi et al., 2016; Matoušů et al., 2018). Microbial methane oxidization can consume CH₄ and enrich ¹³C in the remaining CH₄ pool, resulting in a decrease in [CH₄] and concurrent increase of δ¹³C-CH₄. Dissolved oxygen in the River

Kelvin was near saturation consistently during the sampling period (92.0 – 136.4%, Table 1) and correlated negatively with [CH₄] ($r = -0.36$, $p < 0.01$, Figure S4, SupplInfo), suggesting that microbial methane oxidation consumed dissolved CH₄ and acted to decrease overall [CH₄] in the water.

4.2 Riverine DIC and CO₂* magnitudes, sources, and dynamics

The concentration of DIC in the River Kelvin (1.42 ± 0.56 mM, 0.47 – 2.77 mM, Table 1) was within the range observed in large-scale rivers (0.13 – 4.80 mM) (Guo et al., 2008; Tamooh et al., 2013; Khadka, Martin, & Jin, 2014; Cai, Guo, Wang, & Aiken, 2015). However, [DIC] in the River Kelvin was lower than in the urbanized Schwabach River in Germany (191 km², 0.68 – 1.40 mM: Lee, van Geldern, and Barth (2017)). Compared to the River Kelvin ($\delta^{13}\text{C-DIC}: -15.6 \pm 2.0$ ‰), DIC was also more ¹³C-enriched (-12.1 ± 0.8 ‰) in the Schwabach River and the trend of increasing $\delta^{13}\text{C-DIC}$ and [DIC] in Schwabach River reflects greater contribution from carbonate sources when [DIC] increases. When compared to small natural streams, [DIC] in the River Kelvin could be greater than in comparable Scottish streams (0.26 – 1.33 mM: Billett et al. (2004)) and in Sweden (0.08 – 0.39 mM: Wallin et al. (2013)), which may be from urbanization, and weathering of concrete for example. The concentration of CO₂* at the mouth of the River Kelvin (25.9 – 112.7 μM, 461 – 1702 μatm) had a relatively narrow range compared to other urbanized rivers (528 – 8943 μatm: Müller et al. (2015); Lee et al. (2017); Yu et al. (2017); Li, Luo, Wu, and Jun Xu (2020)), but with few inflows immediately before sampling and degassing to the atmosphere occurring, the narrower concentration range may be expected.

The relationship between [DIC] and $\delta^{13}\text{C-DIC}$ (Figure 4 B) reflects the mixing of two potential sources: a ¹³C-enriched, high-concentration end member and a ¹³C-depleted,

low-concentration end member. The surface water evaporation of rivers and lower runoff water input in drier periods could increase the contribution of deep groundwater DIC (Barth, Cronin, Dunlop, & Kalin, 2003; Atkins, Santos, & Maher, 2017). Maximum values of [DIC] and $\delta^{13}\text{C}$ -DIC were observed in the extremely dry period (Figure 2 C, Figure 4 B) when groundwater would have dominated flow. Consequently, groundwater DIC can be associated with the ^{13}C -enriched, high concentration end member. Similarly, the correlation between $[\text{CO}_2^*]$ and $\delta^{13}\text{C}$ - CO_2 (Figure 4 C) suggests two potential sources contribute to riverine CO_2^* : one high- $[\text{CO}_2^*]$, ^{13}C -depleted source, and one low- $[\text{CO}_2^*]$, ^{13}C -enriched source, and the groundwater DIC is associated with the low- $[\text{CO}_2^*]$, ^{13}C -enriched source.

The concentration of DIC decreased with increasing river discharge ($r = -0.66$, $p < 0.01$, Figure 5 C) as the increasing runoff after precipitation diluted the DIC pool (Cai et al., 2015; Lee et al., 2017; Zhong, Li, Tao, Yue, & Liu, 2017; Abongwa & Atekwana, 2018; Reiman & Xu, 2019). The imported DIC in high flow was characterised by low concentration and lower $\delta^{13}\text{C}$, likely from organic-derived CO_2 (Cerling, Solomon, Quade, & Bowman, 1991; Leith, Garnett, Dinsmore, Billett, & Heal, 2014; Reiman & Xu, 2019). The constant b in the power-law exponent relationship between [DIC] or $\delta^{13}\text{C}$ -DIC and discharge (Figure 5 C, D) indicate that with the dilution effect, the contribution of organic-derived DIC generally ranged from 20 to 40% and the maximum contribution could reach 80% in this system. Concurrently, this organic-derived CO_2 input with increasing discharge also increased riverine $[\text{CO}_2^*]$ ($r = 0.66$, $p < 0.01$, Figure 5 E). Negative correlations between $[\text{CO}_2^*]$ and discharge have been widely observed in both natural rivers and urbanized rivers (Battin et al., 2008; Teodoru, del Giorgio, Prairie, & Camire, 2009; Crawford, Striegl, Wickland, Dornblaser, & Stanley, 2013; Yu et al., 2017), which can be caused by $[\text{CO}_2^*]$ dilution with

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increasing water volume (Crawford et al., 2013), enhanced gas evasion from the water-air interface due to elevated turbulence in high flow (Teodoru et al., 2009), and the shortened residence time for organic carbon breakdown to CO₂ by microbial metabolism (Battin et al., 2008). However, in the River Kelvin, the impact of these factors was offset by the significant input of exogenous organic-derived CO₂, indicating the significance of high proportion organic-rich soil (Figure 1) in the catchment. When discharge was low, riverine CO₂* was under the control of geogenic DIC from deep groundwater, presenting ¹³C-enriched δ¹³C-CO₂. However, during high-flow periods, increased runoff and subsurface flows flushed high-concentration soil respiratory CO₂ in the river, leading to the elevated contribution of soil CO₂ in riverine CO₂* and driving CO₂* to be more ¹³C-depleted (Figure 5 E). The contribution of this organic-derived CO₂ ranged generally from 10% to 60% and could become even more significant (> 80%, Figure 5 E, F). Furthermore, we observed a declining trend in pH with the increased discharge (Figure S3 A, SupplInfo), which might be caused by the input of terrestrial organic acids (Laudon, Westling, & Bishop, 2000; Laudon & Buffam, 2008). Declined pH can drive the bicarbonate buffer system to the end of CO₂*, elevating [CO₂*] and thus enhancing CO₂ emission from the river (Cleaves, 2011).

Although riverine [DIC] and [CO₂*] showed different responses to hydrological variation (Figure 5 C, E), δ¹³C-DIC and δ¹³C-CO₂ both decreased with increasing discharge (Figure 5 D, F), supporting the hypothesis of a proportionally significant organic-derived CO₂ input due to increasing runoff. In C3-plant dominated river catchments, ¹³C-depleted CO₂* (-28 – -25 ‰) is generally from allochthonous origin e.g., riparian soil CO₂ input (Cerling et al., 1991), wastewater discharge (Yoon, Jin, Begum, Kang, & Park, 2017; Jin et al., 2018), and *in-situ* OC degradation (MacGilchrist

et al., 2014) (solid arrows, Figure 4 B, C). In the extremely dry period, ^{13}C -depleted CO_2^* was primarily derived from *in-situ* OC degradation and wastewater discharge. However, $[\text{CO}_2^*]$ in this period was significantly lower than in the normal periods and in the rainstorm period ($p < 0.01$, Figure 3 E), and $\delta^{13}\text{C}\text{-CO}_2$ in the extremely dry period was more ^{13}C -enriched (-19.3 – -13.5 ‰) than in the normal periods (-24.0 – -16.7 ‰) and the rainstorm period (-23.0 – -19.4 ‰) ($p < 0.01$, Figure 3 F), suggesting that *in-situ* OC degradation and wastewater input only had a very limited influence to the CO_2^* pool of the River Kelvin during base-flow conditions.

Consequently, the input of the allochthonous soil-C is the primary contribution to the depletion of $\delta^{13}\text{C}\text{-DIC}$ and $\delta^{13}\text{C}\text{-CO}_2$ in the River Kelvin. For DIC, soil carbon is associated with the low- $[\text{DIC}]$, ^{13}C -depleted end member, but for CO_2^* , soil carbon is associated with the high- $[\text{CO}_2^*]$, ^{13}C -depleted end member.

The correlation between $\delta^{13}\text{C}\text{-DIC}$ and river discharge is not strong and shows significant scatter (Figure 5 D), suggesting the contribution of the two different end members were either not constant, and / or $\delta^{13}\text{C}\text{-DIC}$ may be impacted by physical and biological processes during transport (arrows in Figure 4 B) (van Geldern, Schulte, Mader, Baier, & Barth, 2015). Furthermore, as an urbanized river, the River Kelvin has been altered extensively since the 18th century (Moore, McGillivray², Yeomans, & Murphy, 2017). The dissolution of concrete used in bridges, artificially modified riverbank properties, and drainage infrastructure in the urban watershed by natural organic acids may also increase $[\text{DIC}]$ and drive $\delta^{13}\text{C}\text{-DIC}$ to be more ^{13}C -enriched.

4.3 Riverine DOC dynamics

The concentration of DOC in the River Kelvin (0.53 ± 0.17 mM, 0.27 – 1.11 mM, Table 1) was similar to the urban rivers in the Eden (0.67 mM) and Shannonbrook (0.48 mM)

Rivers, Australia (Atkins et al., 2017). DOC concentration was greater than that in urban river Zhuxi in China (0.39 ± 0.07 mM, 0.30 – 0.45 mM: Li et al. (2020)), the Schwabach River in Germany (0.33 ± 0.08 mM, 0.21 – 0.62 mM: Lee et al. (2017)), and Neponset River in the USA (0.3 – 0.6 mM: Tian, Wang, Chen, and Huang (2012)). Organic-carbon rich land provided high level of allochthonous DOC to the fluvial system in the catchment (Huang et al., 2013; Liu et al., 2014).

Average DOC concentration in the extremely dry period (0.48 ± 0.05 mM) and the normal periods (0.55 ± 0.18 mM) was not significantly different but were both greater than in the rainstorm period (0.38 ± 0.09 mM) (Figure 6 A). During the storm period, the discharge of the River Kelvin was greatest, with many individual other events (Figure 2). Although the concentration was significantly lower than the normal and extremely dry periods (Figure 6 A), the highest outlet-export rate of DOC occurred in the storm period (Figure 6 B). While [DOC] had a weak positive relationship with river discharge in the summer ($R^2 = 0.13$, $p < 0.05$) and autumn ($R^2 = 0.29$, $p < 0.01$), no significant overall relationship was observed for the rest of the annual cycle or for the complete data set ($p > 0.05$, Figure 6 C). Sewage-derived substances can increase DOC concentration and support CO₂ production in the river water (Jin et al., 2018; Burdon et al., 2020) and the sediment (Lopes dos Santos & Vane, 2016) and the numerous CSOs in this catchment may further contribute to rapid DOC lateral export in the higher discharge periods.

4.4 Gas emissions and dissolved carbon exports to outlet

Areal *in-situ* instantaneous CO₂ fluxes ranged from 7 to 266 $\mu\text{g C}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (68 ± 64 $\mu\text{g C}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), and calculated instantaneous CH₄ fluxes ranged from 0.05 to 0.81 $\mu\text{g C}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (0.20 ± 0.18 $\mu\text{g C}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, Table 1). The CH₄ and CO₂ evasion rates from the River

Kelvin were hydrologically responsive ($r = 0.70$, $p < 0.01$ for F_{CH_4} , and $r = 0.81$, $p < 0.01$ for F_{CO_2} , respectively, Figure S5, SuppInfo), indicating that alongside the air-water concentration gradient, hydraulics act as an important control on gas efflux from rivers, also previously observed at this site (Long et al., 2015). Increased concentration gradients of CH_4 and CO_2^* at the water-air interface (Figure 5 A, E) and greater turbulence during higher discharge would have enhanced gas transfer rates from water surface to the atmosphere.

Carbon emissions (CH_4 , CO_2) and dissolved carbon exports to the outlet (dissolved CH_4 , CO_2^* , DIC, and DOC) in the River Kelvin are all primarily hydrologically controlled. Consequently, regression models for carbon evasion losses (F_{CH_4} , F_{CO_2}) and carbon exports to the outlet (CH_4 : outlet- F_{CH_4} , CO_2^* : outlet- F_{CO_2} , DIC: F_{DIC} , and DOC: F_{DOC}) can be established based on the relationships of gas emissions / carbon concentrations and discharge (Table 3).

At the mouth of the River Kelvin, annually areal gaseous carbon evasion loss was dominated by CO_2 with $3.09 \pm 0.60 \text{ kg C}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$, compared to $9.0 \pm 1.5 \text{ g C}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$ by CH_4 (Table 4). Although CH_4 emissions accounted for only approximately 0.3 % of the areal gaseous carbon emission, CH_4 could be responsible for about 8 % of gaseous carbon potential global warming from the River Kelvin as 100-year global warming potential of CH_4 is 28 times that of CO_2 (Pachauri et al., 2014). The average daily emission rate of CH_4 in the River Kelvin was greater than the CH_4 emission rates reported for other urbanized rivers of similar size in different climates (Table 4, Table 5). However, CH_4 emission from the River Kelvin was much lower than from the Adyar River (Table 5) in India (Nirmal Rajkumar, Barnes, Ramesh, Purvaja, & Upstill-Goddard, 2008), which is highly-polluted because of extensive and unregulated

domestic developments. The global warming potential of rivers increases sharply as river water quality degrades due to pollution (Ho et al., 2020). The Adyar River experienced severe hypoxia (DO: 31.4 ± 17.7 %) and eutrophication in the watershed, making the river a zone of CH₄ production. Furthermore, rivers not only emit CH₄ vertically to the atmosphere, but also laterally transport the dissolved CH₄ downstream where oxidation can consume DO in the estuary and deteriorate water quality (Valentine, Blanton, Reeburgh, & Kastner, 2001). The annual export of dissolved CH₄ from the River Kelvin to the Clyde Estuary was estimated at 434 ± 100 kg C·yr⁻¹.

The average CO₂ flux in the River Kelvin was greater than in the Cuenca urbanized river basin in Ecuador (tropical climate, 3.28 ± 0.61 g C·m⁻²·d⁻¹ from sites close to urban area (Ho et al., 2020), Table 5). In Cuenca River, DO may be the most important limitation on CO₂ concentration, as the lower DO concentration (< 5.6 mg·L⁻¹) may restrict the respiration rate. The average CO₂ flux in the River Kelvin was similar to the average fluxes in the Minhang River (subtropical climate, 6.79 ± 0.77 g C·m⁻²·d⁻¹: Yu et al. (2017)), Zhuxi River (subtropical climate, 5.39 g C·m⁻²·d⁻¹: Li et al. (2020)), and Chongqing river network (subtropical climate, 5.03 g C·m⁻²·d⁻¹: Wang et al. (2017)) in China (all urbanized rivers of similar size to the River Kelvin). As comparatively little data exists for similar-scale urbanized rivers, we compared the CO₂ flux with a large urban river, Daning River (subtropical climate, 3.96 ± 5.64 g C·m⁻²·d⁻¹: Ni et al. (2019)), and here the average daily CO₂ flux was lower than the River Kelvin, perhaps as the River Kelvin catchment has a higher urban proportion (3.02 % urban + 16.98 % suburban) than the Daning River drainage area (0.44 % urban) (Ni et al., 2019). Both CH₄ and CO₂ areal emissions from the mouth of the River Kelvin were lower than a natural stream, Skogaryd Catchment (7 km²) in Sweden (Natchimuthu et al., 2017).

Here the catchment has almost exclusively OC-rich soils, which could support significant CH₄ and CO₂ production.

The annual DIC and DOC export from the mouth the River Kelvin to the Clyde Estuary were 3.06 ± 0.39 Gg C·yr⁻¹ and 1.63 ± 0.31 Gg C·yr⁻¹, respectively (Table 4). Area-normalized DIC and DOC exports were 9.25 ± 1.19 Mg C·km⁻²·yr⁻¹ and 4.93 ± 0.93 Mg C·km⁻²·yr⁻¹ (Table 5). The normalized DIC and DOC export were both greater than from the Anacostia River, an urban river in USA (Smith & Kaushal, 2015). Although Anacostia River watershed has been developed to a higher level (46 % urbanized) and influenced by anthropogenic activities more than the River Kelvin, the background DIC concentration as lower than in the River Kelvin, may result in a smaller DIC export than the River Kelvin. Furthermore, because of greater urbanization, DOC input from OC-rich soil area (< 34 %) was lower than the River Kelvin, thus DOC export was also lower in Anacostia River. The normalized DIC export in the River Kelvin was comparable to the urbanized Schwabach River in Germany (9.53 Mg C·km⁻²·yr⁻¹), but the normalized DOC export in the River Kelvin was significantly greater than in the Schwabach River (0.94 Mg C·km⁻²·yr⁻¹) which may be due to limited soil erosion in the Schwabach catchment (Lee et al., 2017). Furthermore, the River Kelvin exports greater DIC and DOC than the Abiskojojokka stream in Sweden (DIC: 1.4 ± 0.23 Mg C·km⁻²·yr⁻¹, DOC: 0.8 ± 0.3 Mg C·km⁻²·yr⁻¹, respectively: Giesler et al. (2014)), which might be due to difference of geology and land-use types including less urbanization in the Abiskojojokka stream.

5 Conclusion

Studies of carbon systematics in both large rivers and small streams have increased in recent decades, but few studies have focused on river systems with significant urban land-use in the catchments. Our 2-year study of temporal dynamics of dissolved carbon in a temperate urbanized river showed that riverine CH_4 and CO_2^* were constantly oversaturated with respect to atmospheric equilibria and the River Kelvin is predominantly a C-source to the atmosphere. Increasing runoff after precipitation events flushed CH_4 and CO_2^* from soil biological sources into the river. DIC input from groundwater was the dominant source in low flow conditions and soil CO_2 in the catchment became proportionally more important for DIC under high flow conditions. The [DOC] was partially hydrology-controlled in summer and autumn and was likely influenced by the CSOs in higher discharge periods. Greenhouse gas emission were dominated by CO_2 , and the river emits significantly more carbon during higher discharge periods. The annual dissolved carbon export to the outlet as DIC is approximately double that of DOC.

Urbanized rivers are expanding globally, which makes it crucial when considering the role of urbanized rivers in the global carbon cycle, particularly under climate change. The key results demonstrated that urbanized rivers potentially exhibit significant differences to natural fluvial systems from a carbon dynamics perspective. While classically known hydrological links seem to be robust, *e.g.*, hydrology drives the variations of $[\text{CH}_4]$, $[\text{CO}_2^*]$, and [DIC], the magnitude of these fluxes per unit area potentially varies significantly. For example, we found elevated rates of DIC and DOC exports and reduced rates of CH_4 and CO_2 emissions in the urbanized river. This work illustrates the potential impact future urbanization may have on regional fluvial C-

dynamics and their (dis)similarities to natural systems and highlights the necessity for a comprehensive elucidation of urban river carbon cycle dynamics and the detailed quantification and inclusion in regional aquatic C-cycle.

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Authorship

We attest that all named authors contributed significantly to the creation of the manuscript, all authors have been involved in drafting the manuscript and revising it critically for important intellectual content. Each author has given final approval of the version to be published and agreed to be accountable for this work.

We confirm that the manuscript has been read and approved by all named authors and the order of authors listed in the manuscript has been approved by all authors.

Conflict of Interest Statement

All authors of this paper have no financial or relationship with other people or organizations that could inappropriately influence or bias the content of the paper. We state that there is no conflict of interest with other people or organizations that could inappropriately influence or bias the content of the paper.

Supporting Information legends

SuppInfo_1: Measurement of water physiochemical properties

SuppInfo_2: Testing Equilibration Duration

SuppInfo_3: Flux calculation

Figure S1. Standard results showing the variation of $[\text{CH}_4]$, $\delta^{13}\text{C}-\text{CH}_4$, $[\text{CO}_2^*]$, and $\delta^{13}\text{C}-\text{CO}_2$ with equilibration time.

Figure S2. Temporal variation of water properties and *in-situ* CO_2 flux

Figure S3. Correlations between water properties with the river discharge.

Figure S4. Correlations between dissolved C concentration and / or $\delta^{13}\text{C}$ and water physiochemical properties.

Figure S5. Correlations between *in-situ* CO_2 flux and calculated CH_4 flux and river discharge.

Table S1. The concentration and $\delta^{13}\text{C}$ value of CH_4 and CO_2 in the stable isotope calibration standard.

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Figure legends

Figure 1. The River Kelvin catchment (Land-use map) annotated with the sampling site and the import point of river water from the River Kelvin into the Clyde Estuary (data source: <https://digimap.edina.ac.uk/>).

Figure 2. Daily discharge (shaded area) and precipitation (bars) as recorded at Killermont Station (data source: Scottish Environment Protection Agency, SEPA) and the temporal variations of surface water [CH₄], [DIC], [CO₂*], [DOC], $\delta^{13}\text{C-CH}_4$, $\delta^{13}\text{C-DIC}$, and $\delta^{13}\text{C-CO}_2$ (Feb 2018 to Mar 2020). The dashed line in (B) and (D) represents the atmospheric equilibria of CH₄ and CO₂* to the water.

Figure 3. Box plots of concentrations and $\delta^{13}\text{C}$ of CH₄ (A, B), DIC (C, D), and CO₂* (E, F) in the extremely dry period (ED), the normal periods (NC), and the rainstorm (RS) period. Mean \pm SD are labelled (Different lowercase letters represent significant difference exists among weathers).

Figure 4. The relationships between the concentration and $\delta^{13}\text{C}$ of (A) CH₄, (B) DIC, and (C) CO₂*. Arrows indicate what influence the allochthonous input or the *in-situ* biochemical reactions could have on the concentration and $\delta^{13}\text{C}$ of dissolved carbon in the river, e.g., the ingression of soil CO₂ could increase [DIC] and [CO₂*] and concurrently drive $\delta^{13}\text{C-DIC}$ and $\delta^{13}\text{C-CO}_2$ to be more ¹³C-depleted (solid arrows in B and C).

Figure 5. Hydrological controls on riverine carbon in the River Kelvin. The concentration-Q relationships have been converted to log-log format for visualization. Black solid lines are the models of power-law exponent of dissolved carbon concentrations and $\delta^{13}\text{C}$ vs. Q. Grey lines (A, C, E) and dashed lines (B, D, F) are the

predictions of the situation of dissolved carbon when allochthonous contribution varies (the absolute value of constant b). The shaded areas represent the $\delta^{13}\text{C}$ features (B, D, F) of carbon from allochthonous sources. The $\delta^{13}\text{C}$ values used to build the models (constant c) are -64 ‰ for $\delta^{13}\text{C}\text{-CH}_4$, -21 ‰ for $\delta^{13}\text{C}\text{-DIC}$, and -26 ‰ for $\delta^{13}\text{C}\text{-CO}_2$, respectively.

Figure 6. Box plot of DOC and DOC flux in three different periods (A, B) and the relationships between DOC concentrations and fluxes (C, D) and the river discharge in different seasons.

Table Legends

Table 1. Water physiochemical properties, dissolved carbon concentration, $\delta^{13}\text{C}$, and gas fluxes during the 2-year sampling period.

Table 2. Seasonal (Spring, Summer, Autumn, and Winter[†]) differences of concentrations and $\delta^{13}\text{C}$ of dissolved carbon (mean \pm SD)

Table 3. Models of gas effluxes and outlet-export for CH_4 , CO_2^* , DIC, and DOC.

Table 4. Daily and annual data of discharge, carbon losses via gas evasions and exports to outlet at the mouth of the River Kelvin.

Table 5. The comparison of area-normalized gas evasions (A) and export of dissolved carbon (B) in worldwide urban rivers.

Table 1. Water physicochemical properties, dissolved carbon concentration, $\delta^{13}\text{C}$, and gas fluxes during the 2-year sampling period.

	Q	T _{water}	pH	DO	EC	Alkalinity	CH ₄	CO ₂ *	DIC	DOC	$\delta^{13}\text{C}$ -CH ₄	$\delta^{13}\text{C}$ -CO ₂	$\delta^{13}\text{C}$ -DIC	F _{CO2}	F _{CH4}			
	m ³ ·s ⁻¹	°C		mg·L ⁻¹	%	μS·cm ⁻¹	mg·L ⁻¹	nM	μatm	μM	μatm	mM	mM	‰	‰	‰	μg C·m ⁻² ·s ⁻¹	
Mean	8.99	9.0	7.56	12.07	102.8	319	84.5	135	11	70.2	1061	1.42	0.53	-53.1	-20.6	-15.6	68	0.20
SD	10.04	4.6	0.40	1.51	7.1	132	27.0	34	3	20.3	247	0.56	0.17	2.7	1.9	2.0	64	0.18
Max	77.95	19.6	8.40	17.10	136.4	1357	147.1	241	18	112.7	1702	2.77	1.11	-47.0	-13.5	-8.9	266	0.81
Min	0.83	1.4	6.40	9.17	92.2	140	36.9	75	6	25.9	461	0.47	0.27	-60.2	-24.0	-19.7	7	0.05
Median	5.15	8.2	7.51	12.22	101.6	293	81.1	129	10	72.4	1057	1.31	0.49	-52.8	-20.9	-15.7	47	0.14
n	790	134	134	113	113	133	134	101	101	101	101	120	133	101	101	120	34	20

Table 2. Seasonal (Spring, Summer, Autumn, and Winter) differences of concentrations and $\delta^{13}\text{C}$ of dissolved carbon (mean \pm SD).

	CH ₄ (nM)	CO ₂ * (μM)	DIC (mM)	DOC (mM)	$\delta^{13}\text{C}$ -CH ₄ (‰)	$\delta^{13}\text{C}$ -CO ₂ (‰)	$\delta^{13}\text{C}$ -DIC (‰)
Spring [†]	122 \pm 30 ^{a‡} (21 [§])	63.6 \pm 22.2 ^a (21)	1.44 \pm 0.57 ^a (27)	0.45 \pm 0.10 ^a (37)	-53.4 \pm 2.3 ^a	-21.1 \pm 1.4 ^a	-15.3 \pm 2.2 ^a
Summer	139 \pm 33 ^{ab} (25)	55.7 \pm 17.6 ^{ab} (25)	1.76 \pm 0.57 ^b (29)	0.61 \pm 0.21 ^b (29)	-50.8 \pm 2.9 ^b	-20.0 \pm 2.7 ^b	-14.9 \pm 2.4 ^{ab}
Autumn	129 \pm 18 ^{abc} (23)	74.0 \pm 15.4 ^{ac} (23)	1.34 \pm 0.55 ^{ac} (32)	0.64 \pm 0.18 ^{bc} (32)	-52.4 \pm 1.8 ^{ac}	-20.5 \pm 1.7 ^{abc}	-16.5 \pm 1.5 ^c
Winter	146 \pm 43 ^{bc} (32)	83.1 \pm 14.7 ^d (32)	1.16 \pm 0.38 ^{ac} (32)	0.46 \pm 0.10 ^a (35)	-55.2 \pm 1.7 ^d	-21.1 \pm 1.2 ^{ac}	-15.6 \pm 1.5 ^{ab}

[†]. Spring: March – May, Summer: June – August, Autumn: September – November, and Winter: December – February.

[‡]. Different lowercase letters represent significant difference exists among seasons.

[§]. Numbers in brackets are the number of each type of sample in seasons. The number of $\delta^{13}\text{C}$ samples are the same as corresponding dissolved C.

Table 3. Models of gas effluxes and outlet-export for CH₄, CO₂^{*}, DIC, and DOC.

	Equation	R ²	<i>p</i>
F _{CH₄} (nmol·m ⁻² ·s ⁻¹)	F _{CH₄} = 2.53 · Q + 3.70	0.46	< 0.01
F _{CO₂} (μmol·m ⁻² ·s ⁻¹)	F _{CO₂} = 1.01 · Q + 0.17	0.64	< 0.01
outlet-F _{CH₄} (mmol·s ⁻¹)	outlet-F _{CH₄} = 0.17 · Q - 0.17	0.91	< 0.01
outlet-F _{CO₂} (mol·s ⁻¹)	outlet-F _{CO₂} = 0.09 · Q - 0.10	0.96	< 0.01
F _{DIC} (mol·s ⁻¹)	F _{DIC} = 0.66 · Q + 3.44	0.80	< 0.01
F _{DOC} (mol·s ⁻¹)	F _{DOC} = 0.51 · Q + 0.25	0.77	< 0.01

Table 4. Daily and annual data of discharge, carbon losses via gas evasions and exports to outlet at the mouth of the River Kelvin.

	Q	F _{CH₄}	F _{CO₂}	CH ₄ export	DIC export	DOC export
Daily	0.77±0.87 M m ³ ·d ⁻¹	27.40±26.31 mg C·m ⁻² ·d ⁻¹	9.60±10.53 g C·m ⁻² ·d ⁻¹	1.37±1.74 kg C·d ⁻¹	9.13±6.87 Mg C·d ⁻¹	5.04±5.35 Mg C·d ⁻¹
Annual	0.25±0.05 G m ³ ·yr ⁻¹	9.0±1.5 g C·m ⁻² ·yr ⁻¹	3.09±0.60 kg C·m ⁻² ·yr ⁻¹	434±100 kg C·yr ⁻¹	3.06±0.39 Gg C·yr ⁻¹	1.63±0.31 Gg C·yr ⁻¹

Table 5. The comparison of area-normalized gas evasions (A) and export of dissolved carbon (B) in worldwide urban rivers.

A. Gaseous evasion	Location	Area km ²	Climate	F _{CH₄}	F _{CO₂}	References
				mg C·m ⁻² ·d ⁻¹	g C·m ⁻² ·d ⁻¹	
River Kelvin (U) †	UK	331	temperate	27.40 ± 26.31	9.60 ± 10.53	this study
Cuenca River (U)	Ecuador	223	tropical	20.6 ± 6.1	3.28 ± 0.61	Ho et al. (2020)
Shanghai River Network (U)	China	370	subtropical	13.97 ± 14.31	6.79 ± 0.77	Yu et al. (2017)
Chongqing River Network (U)	China	166.5	subtropical	/	5.03	Wang et al. (2017)
Chongqing River Network (U)	China	166.5	subtropical	16.80 ± 21.96	/	Wang et al. (2018)
Schwentine River (U)	Germany	726	temperate	22.4 ± 16	/	McGinnis et al. (2016)
Qing River (U)	China	150	temperate	2.3 – 201.0	/	Wang et al. (2020)
Adyar River (U)	India	530	tropical	276 ± 312	/	Nirmal Rajkumar et al. (2008)
Zhuxi River (U)	China	349	subtropical	/	5.53 ± 5.11	Li et al. (2020)
Daning River (U)	China	4426	subtropical	/	3.96 ± 5.64	Ni et al. (2019)
Skogaryd Catchment (N)	Sweden	7	hemiboreal	106 ± 282	19.2 ± 57.6	Natchimuthu et al. (2017)
B. Downstream export	Location	Area km ²	Climate	DIC export	DOC export	References
				Mg C·km ⁻² ·yr ⁻¹	Mg C·km ⁻² ·yr ⁻¹	
River Kelvin (U)	UK	331	temperate	9.25 ± 1.19	4.93 ± 0.93	this study
Anacostia River (U)	USA	176	temperate	0.43 ± 0.19	0.23 ± 0.11	Smith and Kaushal (2015)
Schwabach River (U)	Germany	191	temperate	9.53	0.94	Lee et al. (2017)
Neponset River (U)	USA	250	subtropical	/	5.2	Tian et al. (2012)
Santa Fe River (U)	USA	3585	subtropical	1.03	0.25	Khadka et al. (2014)
Mississippi River (U)	North America	3.1 × 10 ⁷	subtropical	0.4	0.13	Reiman and Xu (2019)
Pearl River (U)	China	4.5 × 10 ⁵	subtropical	12.7	/	Guo et al. (2008)
Abiskoajokka (mostly natural)	Sweden	565	temperate	1.4 ± 0.2	0.8 ± 0.3	Giesler et al. (2014)
Krycklan catchment (N)	Sweden	67	temperate	0.7 ± 0.1	3.9 ± 0.5	Wallin et al. (2013)

†. in the bracket, U means urbanized river / stream; N means natural river / stream.

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